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IMPACTS OF MATERIAL TYPES AND FABRICATION METHODS TO ENHANCE NEAR FIELD RADIATIVE TRANSFER FOR ENERGY HARVESTING DEVICES

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Abstract: Radiative heat transfer between surfaces separated by smaller-than wavelength distances, which is referred to as near-field radiation, has shown to be enhanced compared to those separated by larger scale gaps. When the gap between two energy exchanging surfaces is perfectly evacuated so that conduction and convection heat transfer is negligible, the near-field radiation is shown to be of orders of magnitude greater than Planck’s blackbody radiation. This enhancement has potential use for thermophotovoltaic applications, where the infrared (IR) radiation is converted into electricity. For a complete analysis of near-field thermal radiation characteristics and device behaviour of nano-TPV systems, understanding the material types and system geometry is necessary, both of which affect the device fabrication procedures and working conditions. From the materials point of view, surface waves created along the interface of energy exchanging surfaces can be surface plasmon polaritons (SPP’s), surface phonon polaritons (SPhP’s), or a combination of both. SPhP’s can be excited in the near-IR spectrum, and the use SPhP supporting materials in nano-TPV systems is a meaningful choice. Some materials supporting SPhP’s are SiC, c-BN, h-BN, and BC. In this study, effect of the material choice (plasmonic, phononic, or their combination) on near-field radiative heat transfer along with harvesting device fabrication requirements has been discussed. The literature is reviewed to outline recent advances in the field such as the effect of the presence of artificially made materials with superior electrical and optical properties (metamaterials) in nano-TPV structures.

Keywords: thermophotovoltaics, surface plasmon polaritons, surface phonon polaritons, near field thermal radiation

1. Introduction

In the book Theory of Heat Radiation by Planck [49], the wavelengths and the dimensions of bodies were strictly distinguished such that, throughout the discussion, "the linear dimensions of all parts of space considered, as well as the radii of curvature of all surfaces under consideration, are large compared with the wave lengths of the rays considered.". With this assumption, neglecting the influence of diffraction by the surrounding surfaces completely, and applying the ordinary laws of reflection and refraction of light was considered to be plausible. Application of the phenomenological laws to small scale problems result in significant differences in predictions, since they do not pretty much consider the underlying microscopic phenomena [9]. In case of thermal radiation, phase information carried by photons is usually neglected in macroscale, yet has to be accounted for in micro- and nano-scale. Wave properties of energy carriers, e.g., interference, diffraction, and tunneling become important in micro- and nanoscale thermal radiation problems [9]. In this case, Maxwell's Equations are used in describing thermal radiation as a phenomenon based on the propagation of waves, rather than a
packet of photons. Environmental consciousness and ever-increasing energy requirement has made the way for high efficiency requirement in energy conversion systems, with less pollution of environment. Potential of using the vast amount of waste heat generated even in modern fossil fuel powered combined cycle power plants make thermophotovoltaic (TPV) energy conversion devices more efficient and less complex, in comparison to central power generation [6]. On the other hand, low conversion efficiency of conventional TPV devices stand as a limitation, which has been proposed to be solved through the application of microscale thermal radiation principles [2]. In this respect, combining small scale thermal radiation with TPV’s as a prominent energy harvesting principle has attracted significant attention.

2. Near Field Thermal Radiation and its Relation to Thermophotovoltaics

Considering the electromagnetic wave based mechanism, it is possible to differentiate far- and near-field (NF) regimes in terms of the distance along which electromagnetic waves radiate. In far-field (FF), energy transfer occurs due to propagating waves spreading along a distance greater than a wavelength. For NF, evanescent waves are dominant heat carriers [21]. Near-field thermal radiation (NFR) is promising for energy conversion, thermal management, local heating or cooling, etc. [42]. TPV’s overall efficiency may be improved by placing high temperature (emitter) and low temperature (receiver) components in close proximity and creating a near-field, as shown in Fig. 1. Due to tunneling of energy carriers, improvements in device performance is expected.

![Figure 1. Schematic of a near-field TPV device [46]](image)

In Fig. 1, energy exchanging media are shown with gray. The system mimics TPV principles to harvest near-field radiation. NFR is desired to take place in vacuum to render radiation as the dominant mechanism.

3. Literature Review

NFR experiments have been mainly concerned with plane-parallel, tip to plate, and sphere to plate configurations. Most experiments other than those performed by [59-61] were conducted in vacuum. Experiments in [59-61] performed on samples fabricated in [1] enclosed vacuum to have the thermal radiation distinguishable from conduction and convection. For plane-parallel configuration, NF has been created by placing parallel surfaces in close proximity. In [27] proximity effect on radiative transfer between two Cr coated plates at high vacuum was reported. At 323 K and 306 K, proximity effect was shown. Radiative heat flux between two Cu plates at
cryogenic temperatures and ultrahigh vacuum was measured in [16]. Spacing between emitter and receiver was 2010 µm-10 µm, 440 µm -50 µm, and 170 µm for emitter temperatures of 10 K, 15.1 K, and 13.8 K, respectively. Results indicated that spacing effect that was important at smaller spacings. In [28], radiative heat flux between two glass surfaces were measured at high vacuum. The gap between the flats was maintained via polystyrene microspheres. Results showed an increase in NF heat flux for increasing emitter temperatures and it exceeded the blackbody limit by 35% in the investigated temperature range. In [35], NF heat transfer between two plane parallel W layers on Al2O3 substrates was measured under vacuum. The cold plate was held at 5 K and the hot plate's temperature varied as 10 K-40 K. As emitter plate was heated from 10 K to 40 K, heat flux became 4 orders of magnitude greater than that in the FF, and 2 orders of magnitude greater than that between blackbodies. NFR between two macroscopic sapphire plates was measured in [47] under vacuum. Improved heat transfer was observed via radiation in NF. A recent work on fabrication [1] and measurement of NFR of a test sample under ambient conditions was performed by our group [59-61]. An experimental setup for the measurement of NFR between two SiC plates was reported in [59]. The setup was placed in ambient environment, while the test sample was sealed under near-vacuum. In [60], sample and test setup design options were presented, and quantification of NFR between parallel surfaces was aimed. Experimental results for measurement of NFR between SiO2 surfaces was reported in [61]. For plane surface-sphere configuration, gap between media was mostly adjusted via a microscope cantilever. With such a configuration, conducting measurements for smaller separations, compared to plane parallel surfaces was possible. NFR between a SiO2 microsphere attached to the tip of a Si3N4/Au bimaterial AFM cantilever and a substrate (glass, arsenic doped n-type Si, and Au) was measured via a cantilever system placed in vacuum [56]. Energy transfer in NF caused the cantilever to bend as a result of the change in cantilever's temperature distribution. Energy transfer between polar dielectric surfaces was 3 orders of magnitude greater than Planck's blackbody radiation. In [34], NF measurements on radiative heat transfer between a variable-temperature scanning thermal microscope (VT-STM) tip and a planar surface under ultrahigh vacuum was reported. Energy density increased with decreasing separation, in general, down to the extreme of the NF (10 nm gap). Use of NF scanning optical microscope (NSOM) that used thermal IR evanescent waves and behaved as an optical scanning tunneling microscope was demonstrated in [11]. For sphere-sphere configuration, a numerical investigation of NFRbetween two adjacent and non overlapping SiO2 spheres of equal diameters and separations was done in [44]. Results showed spectral conductance's dependence on not only the gap but also the size of the sphere. In [55], NFR was computed for the case of two spheres of unequal radii, namely R1 and R2, satisfying the relation R2 ≤ 40·R1 for which the smallest gap between the spheres was d = 0.016·R1. NFR between SiC nanoparticle clusters was studied in [17]. NF conductance for compact clusters exceeded that for lacy ones as the nanoparticles of compact clusters were closer to each other. Nano-scale thermal radiation principles can be applied to conventional TPV systems to improve their considerably low conversion efficiency [2]. Selective emission is important in TPV systems since a PV cell can only convert the portion of thermal radiation incorporated by photons with energy greater than its bandgap. For this purpose, metamaterials are investigated specifically on manipulating the response of the material to applied electromagnetic energy or an optical wave [53]. Photonic crystals [62] are also
artificial materials with periodicity in their dielectric function, enabling control of light [32]. Metamaterial based absorbers were investigated for improved NFR at 300 K and 700 K [65]. Theoretical investigations were performed for energy conversion performance and efficiency of an \( \text{In}_{0.2}\text{Ga}_{0.8}\text{Sb} \) TPV cell paired with a hyperbolic metamaterial emitter consisted of W nanowire arrays introduced in an \( \text{Al}_2\text{O}_3 \) host [7]. In comparison with a plain W emitter, hyperbolic metamaterial emitter led to higher electrical power output. In [23], spectral NF and FF radiation due to combination of surface polaritons of thin films and nanoparticles embedded in thin films were computed. Host materials were SiC and polystyrene, while nanoparticles were BN and Au. Results showed an impact of the presence of nanoparticles on emission spectra. NFR between two semi-infinite and vertically aligned carbon nanotube (CNT) arrays covered with graphene with varying doping levels was investigated in [64]. A slight increase of NF radiative heat flux in the presence of graphene sheets was observed. A NF solar TPV device of planar and cylindrical configurations made up of a MEMS device working as a high density power generator was modeled in [20]. The system consisted of a Ta absorber whose surface was covered by photonic crystals, a W emitter, an \( \text{In}_{0.18}\text{Ga}_{0.82}\text{Sb} \) PV cell, and a microcooler. A theoretical investigation of a NF-TPV system consisting of a W thermal source and an \( \text{In}_{0.18}\text{Ga}_{0.82}\text{Sb} \) TPV cell has been presented in [48]. Results revealed diminishing conversion efficiency for gaps smaller than 10 nm. In [37], a full planar nanophotonic solar TPV device, with a 1D Si/SiO\(_2\) photonic crystal emitter, an array of vertically aligned multi-walled CNT’s absorber, and an InGaAsSb PV cell was reported. Emitter-to-absorber area ratio (AR) varied as 1-10 to obtain an optimized performance, and experiments were conducted under vacuum. Highest conversion efficiency was obtained for AR = 7. A NF thermal modulator made up of two graphene-covered SiC plates separated by a vacuum gap at 400 K and 300 K was reported in [63]. Spectral heat flux shifted to higher frequencies for higher chemical potentials of graphene. A NR-TPV energy conversion device of multilayered graphene stacked with SiO\(_2\) dielectric layer on the TPV cell was reported in [39]. Multilayered graphene was advantageous for a vacuum separation larger than 50 nm. Increased number of graphene layers was not always advantageous in terms of the spectral heat flux. NFR between two doped-Si plates was measured in [38], via a MEMS-based platform laced in a vacuum chamber, to sustain the gap between the plates, which could be down to 400 nm. Thermal management in nano-TPV devices is also a major concern. W radiator at 2000 K separated by a sub-wavelength distance from an \( \text{In}_{0.18}\text{Ga}_{0.82}\text{Sb} \) TPV cell at room temperature was studied in [19]. Enhancement in the NFR compared to the FF reached to 12 times provided that TPV cell was kept at room temperature. This enhancement decreased when TPV cell was not cooled properly. Authors concluded that nano-TPV concept could lose relevance without the use of thermal management. For appreciable energy harvesting, energy exchanging materials must be selected properly. In this and sequential studies, it is aimed to fabricate such a device with effective pair of materials for enhanced NFR and overall device performance.

4. Fabrication of a the Near-Field Energy Harvesting Device

A general flowchart for the fabrication of a NF energy harvesting device is shown in Fig. 2, where thin film coating, lithography, etching, wafer bonding and dicing processes are sorted as additive, patterning, subtractive, and mechanical steps [41]. As depicted in Fig. 2, fabrication starts with a Si wafer and structures are implemented subsequently. First phase is deposition of a
thin film. Next, desired pattern can be applied via lithography. After mechanical steps (wafer bonding and dicing) a sandwich structure with a vacuum cavity is formed. Individual dies can be produced via dicing. SiC films attracted interest due to chemical, thermal and electrical stability over Si, since SiC films showed stable behavior above 600°C while Si was stable below 175°C [36]. SiC films have been preferred due to their improved hardness, which is advantageous for the incorporation in MEMS devices for device's protection from harsh environments [52]. SiC films support SPhP's, and their NFR performance was investigated in [12-15].

Possible production steps for a structure with SiC thin films are listed in Table 1.

**Table 1.** Fabrication stages for NF energy harvesting device with SiC coatings as energy exchanging layers

<table>
<thead>
<tr>
<th>Fabrication stage</th>
<th>SiC coated sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin film deposition</td>
<td>Chemical vapor deposition (CVD), low pressure CVD, sputtering, ion beam assisted deposition, plasma enhanced CVD [54], RF magnetron sputtering, DC magnetron sputtering [36]</td>
</tr>
<tr>
<td>Lithography</td>
<td>Photolithography [50], e-beam lithography [4]</td>
</tr>
<tr>
<td>Etching</td>
<td>via chlorine trifluoride (ClF₃) gas [25], Cl₂ based inductively-coupled plasma reactive ion etching (RIE) [33], anodic etching in alkaline solutions [18], hydrogen etching [51], deep RIE [57]</td>
</tr>
<tr>
<td>Wafer bonding</td>
<td>direct wafer bonding [24]</td>
</tr>
<tr>
<td>Wafer dicing</td>
<td>dicing saw, laser cutting</td>
</tr>
</tbody>
</table>

**5. Material Selection for Initiating Plasmonic / Phononic Effects**

Material type of energy exchanging surfaces is important. Dielectric function of different type of materials is described using different models. The Drude model describes frequency-dependent conductivity of metals and semiconductors, while The Lorentz model is used for dielectrics [3].
The Drude-Lorentz model has been used for modeling of SiC [12-14]. Polariton propagation on a surface necessitates a negative dielectric constant, which may be a result of collective conduction electron oscillations (plasmon polaritons) or lattice vibrations (phonon polaritons, in polar crystals) [29]. Surface phonon polaritons (SPhPs) are a type of electromagnetic waves resulting from the coupling of light and optical phonons (or, polar atomic vibrations [10]) [29] confined between a polar material and a lossless dielectric [26]. The photon is of transverse-magnetic IR and the phonon is transverse-optic, and this mode occurs in specific spectral regions where the material has a negative dielectric function [45]. The electromagnetic field characterized by the dispersion relation is mainly located below the light-line of the dielectric material [58].

Generally, SPhP's can be excited via IR or THz radiation [29]. Mainly, while polar crystals such as SiC and GaN [29], quartz or α-SiO₂ [26,29], Ga rich InₓAlᵧGa₁₋ₓ₋ᵧN with x = 0-0.1 and y = 0.06 [45] are few of the materials supporting SPhP's, while metals support SPP's. Combination of SPP's and SPhP's could form surface plasmon-phonon polaritons [5]. SPP's appear in visible and near-UV region, while SPhP's exist in IR. In terms of the thermal excitation of the surface waves in IR, SPhP supporting materials can be used [43]. Spectral emissive power ($E_{\lambda,b}$) for a blackbody [30] is described as in (1) and plotted in Fig 3.

$$E_{\lambda,b}(\lambda, T) = \frac{3.742 \times 10^8 [W \cdot \mu m^4/m^2]}{\lambda^5 \left( \exp \frac{1.439 \times 10^4 [\mu m \cdot K]}{\lambda T} - 1 \right)}$$ (1)

where $\lambda$ and $T$ stand respectively for the wavelength and absolute temperature.

![Figure 3. Spectral blackbody emissive power for different temperatures](image)

Transmittance values of sapphire, Ge and Si are gathered from [31] and plotted in Fig. 4 to give a rough estimate on how much heat incident can be transmitted to NF energy exchanging layers. Considering a system of an emitter (at 500 K) and a receiver (at 300 K), maximum emissive powers are respectively at of 10 µm and 5.978 µm, from Wien's Displacement Law. To use the incident heat effectively, wafer should be as transparent as possible in the wavelength range, since the energy incident on the wafer is desired to be transferred to the energy exchanging layers as much as possible.
In the given wavelength range (i.e., 10 µm - 5.978 µm), Fig. 4 shows that uncoated Si has a transmissivity of maximum ~55% and minimum ~5%, while the transmissivity of uncoated Ge was approaching ~50% for its maximum and shows a comparatively stable behavior around ~45%. Selection of the material type for the pair of NF energy exchanging surfaces is important. For enhanced NFR, there should not be a mismatch in material properties causing an offset in the resonance effects [56]. This behavior was shown for SiO$_2$-SiO$_2$; SiO$_2$-Si, and SiO$_2$-Au surfaces, and the former gave the best performance among the others. NFR between dissimilar materials was also studied in [8]. Interaction of surface plasmon modes could result either in enhancement or decrement of NFR. Deciding on a proper thickness of the thin film is important, as demonstrated for SiC films in [22]. They showed that ratio of the energy exchanging layer thickness to the vacuum gap had an impact on the NF radiative heat flux.

6. Conclusions
In the literature, a large number of studies are concerned with just the NF measurement or numerical simulation. The radiation heat transfer part of solar thermal and thermochemical applications are complex, as they are transient multiscale problems [40]. To date, all the experimental studies have been performed under the idealistic vacuum condition. Hence, they are difficult to find real-life applications. The present work starts from the design and fabrication of an actual and stable NF-TPV device that would work in real operational conditions, and to end up with a prototype device whose NFR heat transfer is measurable and identifiable from conduction and convection heat transfer mechanisms. Through the literature search; SiC, SiO$_2$, and BN were determined as possible promising materials for a NR energy harvesting device considered.

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References


Modeling of Thermodynamic and Thermophysical Properties of Refrigerant Mixtures

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Abstract: In order to analyze a refrigeration system as a thermodynamic or heat transfer system, a complete thermodynamic and thermophysical property sets should be available in computer environment. Thermophysical properties such as thermal conductivity, viscosity, surface tension, and thermodynamic properties of saturated, liquid and vapor phases are needed in a complete system analysis. In recent years, properties of refrigerant mixtures gain much attention as well as pure refrigerants. Thermodynamic and thermophysical properties of refrigerant mixtures are modelled as a set of programs in java language in order to simulate and analyze refrigeration systems.

Due to recent adaptations of new refrigerants and phase out of old refrigerants, data for all new set of refrigerants should be available for utilization of researchers. International standard office (ISO) is started an afford to make a standard equation of states, and developed equations for some pure refrigerants and refrigerant mixtures as ISO 17584-2005. This standards covers the basic equation of states for pure refrigerants R744(carbon dioxide), R717(Ammonia), R12, R22, R32 ,R123, R125, R134a, R143a, R152a and refrigerant mixtures:

R404A(R125%44/R143a%52/R134a%4), R407C(R32%23/R125%25/R134a%52),
R410A(R32%50/R125%50) and R507A(R125%50/R143a%50).

The basic equations are in the form of Helmholtz free energy equations for pure gases and mixtures. This standards as is, not covers all the possible refrigerants and the thermodynamic properties of remaining refrigerants can be found from several research papers. Afford of NIST should be specially noted. Data found for the remaining gases covers a variety of equation of states such as Benedict-Webb-Rubin, Martin-Hou, Peng-Robinson-Stryjek-Vera. Properties of further set of refrigerant mixtures are developed by using Peng-Robinson-Stryjek-Vera EOS. These refrigerants are:

R402A(R22%38/R125%60/R290%2),R402B(R125%38/R290%2/R22%60)
R401A(R22%52/R124%33/R152a%15),R401B(R22%61/R152a%11/R124%28)

Details of, Peng-Robinson-Stryjek-Vera will also be given in this paper. Equation of states are usually given as a function of temperature and specific volume of Helmholtz free energy or pressure. The remaining properties derives from Legendre transforms of these equation of states called Maxwell relations. In order to use any other set of independent variables requires root finding methods. Root finding from thermodynamic processes is a challenging process due to enormous differences in properties of liquid and gaseous state such as specific volume. In order to overcome this difficulty a general form of equation of states with easier methods of root solving such as cubic equation of states can be utilized as first estimation method. For the saturation(phase change) region of the equation of state and for
thermophysical properties, it is found out that using cubic spline and B-spline interpolation methods supply minimum errors in data.

By combining all these methods, numerical models of thermophysical and thermodynamic models of refrigerants R22, R12,R124, R23, R744, R32, R123, R125, R134a, R143a, R152a, R404A, R407C, R410A, R507a, R728, R1150, R50, R702, R508B, R1270, R740, R732, R717, R718, R704, R720, R142b, R402A, R401A, R401B, R1234yf are developed as java programs, furthermore by using these thermodynamic and heat transfer simulations of refrigeration system components and complete systems are developed. Programs are freely available for all scientists requires to use such analysis. Program codes are available from address www.turhancoban.com

1. EQUATIONS USED FOR SIMULATIONS

1.1 ISO 17584-2005 EQUATION OF STATE

International Standard organization defined a standard equation of state for refrigerants. So far the standard is unfinished and does not include properties of all refrigerants but still the best resource to define their properties. The standard includes the following refrigerants: R744(Carbon dioxide), R717(Ammonia), R12(dichlorodifluoromethane), R22(chlorodifloromethane), R32(Difloromethane), R123(2,2dichloro,1,1,1trifloroethane), R125(Pentafloroethane), R134a(1,1,1,2tetrafloroethane), R143a(1,1,1,trifloroethane), R152a(1,1 diflороethane), and following refrigerant mixtures R404A-R125/142a/134a(23/25/52), R407C-R32/125/134a(23/25/52), R410A-R32/125(50/50), R507a-R125/143A(50/50) The standart based on Helmhols free enegy type equation of state for pure refrigerants:

\[
\phi = \frac{A}{RT} = \phi_d + \phi_r \quad (1.1.1)
\]

“id” in the equation indicates ideal gas and r indicates real gas part of the equation of state.

\[
\phi_r = \sum_k N_k / \tau^k \delta^d \exp[-\alpha_k(\delta - \epsilon_k)]^k \exp[-\beta_k(\tau - \gamma_k)^{m_k}] \quad (1.1.2)
\]

In this equation

- \(\tau\) Non-dimensional temperature parameter \(T^*/T\)
- \(T^*\) Normalisation factor, usually equal to critical temperature
- \(\delta\) Non-dimensional density \(\rho/\rho^*\) \((1/(v \rho^*)\)
- \(\rho^*\) Normalisation factor, usually equal to critical density
- \(N_k\) Coefficients of the equations
- \(\alpha_k, \beta_k, \epsilon_k, \gamma_k\) Coefficients of the equations
- \(t_k, d_k, l_k, m_k\) Power coefficients of the equation
Ideal gas term of the equation:

\[ \phi_{id} = \frac{h_{ref}}{RT} - \frac{s_{ref}}{R} - 1 + \ln \left( \frac{RT \rho}{P_{ref}} \right) + \frac{1}{RT} \int_{T_{ref}}^{T} C_{p, id} dT - \frac{1}{R} \int_{T_{ref}}^{T} \frac{C_{p, id}}{T} dT \]  

(1.1.3)

In this equation

- \( h_{ref} \): ideal gas enthalpy reference state (\( \text{kJ/kg K} \))
- \( s_{ref} \): ideal gas entropy reference state (Usually taken as \( 1 \text{ kJ/kg K at 0 C liquid state entropy} \))
- \( h_{ref} \) is usually selected as \( 200 \text{ kJ/kg at 0 C liquid} \). This equation also requires ideal gas specific heat values. These values can be computed as:

\[ C_{p, id} = c_0 + \sum_{\tau} c_\tau T^{\tau - 1} + \sum_{k} a_k \ln \left[ 1 - \exp \left( -\tau \delta_k \right) \right] \]  

(1.1.4)

In this term

- \( u_k = \frac{b_k}{T} \), \( c_k, a_k \) and \( t_k \) are coefficients.

For some fluids additional components for the ideal gas part of the equation of state is defined as:

\[ \phi_{id} = d_1 + d_2 \tau + \ln \delta + d_3 \ln \tau + \sum_{\tau} d_{\tau} \tau^{\lambda_{\tau}} + \sum_{k} a_k \ln \left[ 1 - \exp \left( -\tau \delta_k \right) \right] \]  

(1.1.5)

In the equation \( d_1, d_2, d_3, \lambda, a_k, t_k \) are coefficients. Equation (1.1.5) is same as equation (1.1.3).

An equivalent \( C_p \) value can also be written as:

\[ \frac{C_{p, id}}{R} = d_0 + 1 - \sum_k d_{\tau} t_k (T_k - 1) \left( \frac{T^*}{T} \right)^{\lambda_{\tau}} + \sum_k a_k \frac{u_k^2 \exp(u_k)}{[\exp(u_k) - 1]^2} \]  

(1.1.6)

For some refrigerants a third term is added to the Helmholtz equation of state as

\[ \phi = \frac{A}{RT} = \phi_{id} + \phi_r + \phi_{crit} \]  

(1.1.1a)

\[ \phi_{crit} = \sum_k N_k \delta^{^{k_h}} \Psi \]  

(1.1.7)

In here

\[ \Delta = \theta^2 + B_k \left[ (\delta - 1)^2 \right]^{h_k} \]  

(1.1.8)

\[ \theta = (1 - \tau) + A_k \left[ (\delta - 1)^2 \right]^{h/2} \]  

(1.1.9)

\[ \Psi = \exp \left[ -C_k (\delta - 1)^2 - D_k (\tau - 1)^2 \right] \]  

(1.1.10)
In equation \( N_k, A_k, B_k, C_k, D_k, \alpha_k, \beta_k \) terms are coefficients determined by curve fittings data. As an alternative, if Benedict-Webb-Rubin equation of state is given, this equation can be converted into Helmholtz free energy form as:

\[
P = \sum_{k=1}^{\infty} a_k \rho^{k} + \exp(-\rho^2 / \rho_{\text{crit}}^2) \sum_{k=10}^{15} a_k \rho^{2k-17} \tag{1.1.11}
\]

In this equation \( a_k \) are coefficients. Conversion factors are:

\[
P = \left( \frac{\partial A}{\partial V} \right)_T \tag{1.1.12}
\]

\[
\phi_r = \frac{A_r(T, \rho)}{RT} = -\int \left( \frac{P}{RT} - \rho \right) dV \tag{1.1.13}
\]

This equation can be used together with the ideal gas part of the equation to get the complete equation of state. When equation of state is obtained, the remaining thermodynamic properties can be obtained by deriving Helmholtz equation of state as:

\[
P = RT \rho \left( 1 + \delta \frac{\partial \phi}{\partial \delta} \right) \tag{1.1.14}
\]

\[
u = RT \left( \tau \frac{\partial \phi_d}{\partial \tau} + \tau \frac{\partial \phi_r}{\partial \tau} \right) \tag{1.1.15}
\]

\[
h = RT \left( 1 + \tau \frac{\partial \phi_d}{\partial \tau} + \tau \frac{\partial \phi_r}{\partial \tau} + \delta \frac{\partial \phi_r}{\partial \delta} \right) \tag{1.1.15}
\]

\[
s = R \left( - (\phi_d + \phi_r) + \tau \frac{\partial \phi_d}{\partial \tau} + \tau \frac{\partial \phi_r}{\partial \tau} \right) \tag{1.1.17}
\]

\[
g = RT \left( 1 + \phi_d + \phi_r + \delta \frac{\partial \phi_r}{\partial \delta} \right) \tag{24.18}
\]

\[
C_v = R \left( - \tau^2 \frac{\partial^2 \phi_d}{\partial \tau^2} - \tau^2 \frac{\partial^2 \phi_r}{\partial \tau^2} \right) \tag{1.1.19}
\]

\[
C_p = C_v + R \left( 1 + \delta \frac{\partial \phi_r}{\partial \delta} - \delta \frac{\partial^2 \phi_r}{\partial \delta^2} \right) \tag{24.20}
\]
In the saturation region the following equations can be used to obtain saturation thermodynamic properties.

\[
P(\tau, \delta_{\text{saturated liquid}}) = P(\tau, \delta_{\text{saturated vapor}}) \quad (1.1.21)
\]

\[
g(\tau, \delta_{\text{saturated liquid}}) = g(\tau, \delta_{\text{saturated vapor}}) \quad (1.1.22)
\]

These saturation properties can also be obtained by using cubic spline interpolation from the original data. Cubic spline interpolation details as a method to define specific heat data for ideal gas will be given in next section.

If our refrigerant is not a pure fluid, but a mixture of the fluids, by using mixing rules, mixture thermodynamic properties can be obtained from the pure fluid properties.

\[
\phi_{\text{mix}} = \frac{A}{RT} = \phi_{\text{mix, id}} + \phi_{\text{mix, r}} \quad (1.1.23)
\]

\[
\phi_{\text{mix, id}} = \sum_{i=1}^{n} \left[ x_i \phi_{i, id} + x_i \ln x_i \right] + f_3 + f_4/T \quad (1.1.24)
\]

\[
x_i \text{ component molar ratio } x_i = \frac{N_i}{\sum_{j=1}^{n} N_j} \quad (1.1.24a)
\]

\[
x_i \ln x_i \text{ mixing term coming from entropy term. } f_3 \text{ and } f_4 \text{ are used to shift the thermodynamic surface such that the reference state for enthalpy is 200 kJ/kg and entropy is 1 kJ/(kg·K) at the saturated liquid at 0 °C, similar to that done for the pure fluids. Setting the parameters } f_3 \text{ and } f_4 \text{ to zero corresponds to a reference state based solely on the constituents of the mixture.}
\]

The residual part is given by Equation

\[
\phi_{\text{mix, r}} = \sum_{i=1}^{n} x_i \phi_{i, r} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j \delta_{ij} \quad (1.1.25)
\]

\[
T^* = \sum_{i=1}^{n} x_i T_i^* + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j \xi_{ij} \quad (1.1.26)
\]

\[
\delta = \frac{\rho_{\text{mix}}}{\rho} \quad (1.1.27)
\]

\[
\frac{1}{\rho^2} = \sum_{i=1}^{n} \frac{x_i}{\rho_i^2} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j \xi_{ij} \quad (1.1.28)
\]
The parameters $\zeta_{ij}$ and $\xi_{ij}$ are interaction parameters due to coexistence of two fluids together. $T_i^*$ and $p_i^*$ are coefficients of pure fluids, and taken usually as critical values. $\phi_{ij}$ function calculated as:

$$
\phi_{ij} = F_j \sum_k N_k \delta^{d_j} \tau^i \exp(-\delta^{i_j}) \quad (1.1.29)
$$

Calculation of properties at liquid-vapor equilibrium involves an iteration to find the reduced liquid and vapor densities $\delta_{liq}$ and $\delta_{vap}$ and liquid and vapor compositions $x_{liq,i}$ and $x_{vap,i}$ which satisfy the following system of equations

$$
P(\tau, \delta_{liq}) = P(\tau, \delta_{vap}) \quad (1.1.30)
$$

$$
f_{liq,i}(x_{liq,i}, \tau, \delta_{liq}) = f_{vap,i}(x_{vap,i}, \tau, \delta_{vap}), \text{ for } i=1..n
$$

The fugacity $f$, for component $i$ is given by

$$
f_i = x_i \rho RT \exp \left[ \frac{\partial(n \phi_{mix,\tau})}{\partial n_i} \right]_{T,V,n_i} \quad (1.1.31)
$$

Where $n_i$ is the number of molecules of component $i$ in the blend, and derivative is taken holding constant the temperature, total volume and number of molecules of the other components. This calculations are established, but found that they involve quite time consuming system of non-linear equation solutions. Instead of these cubic spline curve fitting of the original data is used in actual model with same degree of accuracy. Details of cubic spline method is given in the following sections.

As an example of coefficients of the equations, coefficients R410a is given below. Since R410a is a mixture of R32 and R125 let us list the properties of these refrigerants as first and then the mixture properties. For further coefficients, please refer to ISO 17584:2005(E) standard document[11].

**Table 1.1.1 R32 coefficients of ideal gas part**

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<tr>
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<th>$a_k$</th>
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### Table 1.1.2 R32 coefficients for real gas part

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<th>t_k</th>
<th>d_k</th>
<th>l_k</th>
<th>a_k</th>
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**R32 Normalization factors:**

\[ T^* = 351.255 \text{ K}, \; \rho^* = 8.1500846 \text{ mol/l}, \; M = 52.024 \text{ g/mol}, \; R = 8.314471 \text{ J/(mol·K)} \]

**R32 Reference parameters**

\[ T_{\text{ref}} = 273.15 \text{ K}, \; p_{\text{ref}} = 1.0 \text{ kPa}, \; h_{\text{ref}} = 28204.341 \text{ J/mol}, \; s_{\text{ref}} = 171.6913 \text{ J/(mol·K)}, \; f_1 = 7.25470784, \]
\[ f_2 = 2231.55735 \]

### Table 1.1.3 R125 coefficients of ideal gas part

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Table 1.1.4 R125 coefficients of real gas part

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<th>d_k</th>
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R125 Normalization factors:

\[ T^* = 339.173 \text{ K}, \quad \rho^* = 4.779 \text{ mol/l}, \quad M = 120.0214 \text{ g/mol}, \quad R = 8.314472 \text{ J/(mol·K)} \]

R125 Reference parameters

\[ T_{\text{ref}} = 273.15 \text{ K}, \quad p_{\text{ref}} = 1.0 \text{ kPa}, \quad h_{\text{ref}} = 41266386 \text{ J/mol}, \quad s_{\text{ref}} = 236.1195 \text{ J/(mol·K)}, \quad f_1 = 29.8766745, \]

\[ f_2 = 3013.2267 \]
Table 1.1.5 Composition of R410A

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<th>i</th>
<th>Component</th>
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<th>Mole fraction</th>
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<td>2</td>
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M=72.5855 kg/kmol

R410A Range of Validity

The coefficients are valid within the following ranges:

\[ T_{\text{min}}=172.52 \text{ K} , \quad T_{\text{max}}=435 \text{ K} ; \quad P_{\text{max}}=60 \text{ MPa} ; \quad \rho_{\text{max}}=20.2 \text{ kmol/m}^3 (1496 \text{ kg/m}^3) \]

R410A Interaction parameters

For equation (1.1.26), \( \bar{T}^{*} \xi_{12}=28.95 \); For equation (1.1.28), \( 1/ \rho^{*} \xi_{12}=-0.006008 \)

Table 1.1.6 Coefficients and exponents of the excess functions of R410A

<table>
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<th>( \xi_k )</th>
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<th>l_k</th>
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<td>2</td>
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<td>3</td>
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<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>

\( F_{12}=1.0; \quad i=1; j=2 \)
R410A Reference parameters

\[ f_3 = 0.617469323, \quad f_4 = -0.596795 \]

1.2 PENG-ROBINSON-STRYJEK-VERA EQUATION OF STATE

The Peng-Robinson-Strjek-Vera equation of state was used for refrigeration mixtures that are not yet listed in ISO 17584-2005 standards. Basic equation of state has a cubic form:

\[ P = \frac{RT}{V - b} - \frac{a}{V^2 + 2bV - b^2} \]  \hspace{1cm} (1.2.1)

Where P is in kPa, T is in K, V is in m³/mol and R=0.008314 kJ/mol K. The constants a and b are calculated as follows:

\[ a = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j a_{ij} \]  \hspace{1cm} (1.2.2)

\[ b = \sum_{i=1}^{N} b_i \]  \hspace{1cm} (1.2.3)

Where

\[ x_i \] = mole fraction of component i;
\[ x_j \] = mole fraction of component j;

\[ a_{ij} = (a_i a_j)^{0.5} (1 - k_{ij}) \]  \hspace{1cm} (1.2.4)

\[ b_i = 0.077796 \frac{RT_i}{P_{ci}} \]  \hspace{1cm} (1.2.5)

\[ a_i = (0.457235 \frac{RT_i^2}{P_{ci}}) \alpha_i \]  \hspace{1cm} (1.2.6)

\[ k_{ij} = \text{binary interaction coefficient for component i and j} \]

\[ \alpha_i = \left[ 1 + \kappa_i (1 - T_i^{0.5}) \right] \]  \hspace{1cm} (1.2.7)

if \( T_i \leq 0.7 \) \hspace{1cm} \[ \kappa_i = \kappa_{0i} + \kappa_i \left[ (1 + T_i^{0.5})(0.7 - T_i) \right] \]

else (\( T_i > 0.7 \)) \hspace{1cm} \[ \kappa_i = \kappa_{0i} \]  \hspace{1cm} (1.2.8)

\[ \kappa_{0i} = 0.378893 + 1.4897153 \omega_i - 0.17131848 \omega_i^2 + 0.0196554 \omega_i^3 \]  \hspace{1cm} (1.2.9)

\[ \kappa_i = \text{adjustable parameter for component i} \]

\[ T_{ri} = T_i / T_{ci} \] reduced temperature for component i
Coefficients of equations for refrigerant mixture R401A(R22%53/R152a%13/R124%34) is as follows

**Table 1.2.1 R401A PRSV EOS constants**

<table>
<thead>
<tr>
<th>Component</th>
<th>i</th>
<th>$T_{ci}$</th>
<th>$P_{ci}$</th>
<th>$\omega_i$</th>
<th>$\kappa_{1i}$</th>
<th>$x_i$</th>
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<td>4977.0</td>
<td>0.2214</td>
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<td>R152a</td>
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<td>4519.8</td>
<td>0.2752</td>
<td>-0.04</td>
<td>0.18587</td>
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<td>R124</td>
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<td>3616.0</td>
<td>0.2859</td>
<td>0.049</td>
<td>0.23528</td>
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**Table 1.2.2 R401A PRSV EOS binary interaction parameters $k_{ij}$**

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<th>j=1</th>
<th>j=2</th>
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<tr>
<td>i=3</td>
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<td>-0.01314</td>
<td>0</td>
</tr>
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</table>

**1.3 CUBIC SPLINE CURVE FITTINGS**

If a third degree polynomial is considered with data set $[(x_0,y_0), (x_1,y_1),\ldots, (x_k,y_k), (x_{k+1},y_{k+1}),\ldots, (x_n,y_n)]$ is considered to be fitted into a cubic polynomial equation

$$r_k(x) = a_k(x - x_k)^3 + b_k(x - x_k)^2 + c_k(x - x_k) + y_k \quad 1 \leq k \leq n$$  \hspace{1cm} (1.3.1)

In the interpolation process polinoms should be passing through all data points

$$r_{k-1}(x_k) = r_k(x_k) = y_k \quad 1 \leq k \leq n$$ \hspace{1cm} (1.3.2)

In the same time the first derivative of the polynomial should also be continious while passing from one polynomial to the next one at the data point

$$r'_{k-1}(x_k) = r'_k(x_k) \quad 1 \leq k \leq n$$ \hspace{1cm} (1.3.3)

For the third degree polynomial second derivative of the polynomial should also be continious while passing from one polynomial to the next one at the data point

$$r''_{k-1}(x_k) = r''_k(x_k) \quad 1 \leq k \leq n$$ \hspace{1cm} (1.3.4)
All these conditions are not enough to solve the coefficients of the polynomials. Two more conditions are required. This two additional conditions (A and B of the following equation) can be given by user.

\[ r''_0(x_0) = A \]  \hspace{1cm} (1.3.5)

\[ r''_n(x_n) = B \]  \hspace{1cm} (1.3.6)

They are the second derivatives at the both sides of the series of polynomials. If A and B values are taken equals to 0, it is called a natural cubic spline. Other end conditions such as the ones depends one the first derivatives can also be set to solve the system of equations.

Defining \( h_k = x_k - x_{k-1} \) \( 1 \leq k \leq n \) \hspace{1cm} (1.3.7)

System of equations become:

\[ a_{k-1}h_k^3 + b_{k-1}h_k^2 + c_{k-1}h_k = y_k - y_{k-1} \] \hspace{1cm} (1.3.8)

\[ 3a_{k-1}h_k^2 + 2b_{k-1}h_k + c_{k-1} - c_k = 0 \] \hspace{1cm} (1.3.9)

\[ 6a_{k-1}h_k + 2b_{k-1} - 2b_k = 0 \] \hspace{1cm} (1.3.10)

\[ 2b_0 = 0 \] \hspace{1cm} (1.3.11)

\[ 6a_nh_k + 2b_n = 0 \] \hspace{1cm} (1.3.12)

This set contains 3n-3 equations. This could a considerable load to the system of equation solving programs. To make calculation load simpler a special third degree polynomial can be considered. If our cubic polynomial is in the form of:

\[ S_k(x) = a_k(x - x_k) + b_k(x_{k+1} - x) + [c_{k+1}(x - x_k)^3 + c_k(x_{k+1} - x)^3]/(6h_k) \] \hspace{1cm} (1.3.13)

then derivative equations becomes

\[ S'_k(x) = a_k - b_k + [c_{k+1}(x - x_k)^2 + c_k(x_{k+1} - x)^2]/(2h_k) \] \hspace{1cm} (1.3.14)

\[ S''_k(x) = [c_{k+1}(x - x_k) + c_k(x_{k+1} - x)]/h_k \] \hspace{1cm} (1.3.15)

\( a_k \) and \( b_k \) coefficients can be expressed as a function of \( c_k \)

\[ b_k = [6y_k - h_k c_k]/(6h_k) \] \hspace{1cm} (1.3.16)

\[ a_k = [6y_{k+1} - h_k^2 c_{k+1}]/(6h_k) \] \hspace{1cm} (1.3.17)

In this case only \( c_k \) terms left in the system of equations to be solved.
\[ 6h_{k-1}c_{k-1} + 2(h_k - h_{k-1})c_k + h_kc_{k+1} = \left[ \frac{y_{k+1} - y_k}{h_k} - \frac{y_k - y_{k-1}}{h_{k-1}} \right], \quad 1 \leq k \leq n \quad (1.3.18) \]

This system of equation has only n-2 terms to be solved. By making definition

\[ w_k = \frac{y_{k+1} - y_k}{h_k}, \quad 1 \leq k \leq n \quad (1.3.19) \]

System of equation becomes

\[
\begin{bmatrix}
1 & 0 & 0 & \ldots & 0 & 0 & 0 & 0 \\
h_1 & 2(h_1 + h_2) & h_2 & \ldots & 0 & 0 & 0 & 0 \\
0 & h_2 & 2(h_2 + h_3) & \ldots & 0 & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \ldots & 2(h_{n-3} + h_{n-2}) & h_{n-2} & 0 & c_{n-2} \\
0 & 0 & 0 & \ldots & h_{n-2} & 2(h_{n-2} + h_{n-1}) & h_{n-1} & c_{n-1} \\
0 & 0 & 0 & \ldots & 0 & 0 & 0 & 1
\end{bmatrix}
= \begin{bmatrix}
c_0 \\
c_1 \\
c_2 \\
\vdots \\
c_{n-2} \\
c_{n-1} \\
c_n
\end{bmatrix}
\]

Where A and B are the second derivative end conditions. A and B should be defined by user.

Another important property of the above matrix is that it is a band matrix, therefore less amount of calculation is required to solve it (by using band matrix algorithms such as Thomas algorithm). Saturation data is modelled by using cubic spline curve fitting. For accurate curve fitting modelling a big quantity of data is used. Table 1.3.1 shows saturation data for R410A as an example. A big quantity of curve fitting coefficients are also required, but the coefficients are kept only in computer memory, they should not be known by the user.

**Table 1.3.1 R410A saturation coefficients to fit into cubic spline algorithm**

<table>
<thead>
<tr>
<th>Pressure P (Mpa)</th>
<th>Tb (degree C)</th>
<th>Td (degree C)</th>
<th>( \rho b ) (kg/m(^3))</th>
<th>( \mu b ) (m(^2)/s)</th>
<th>( \lambda b ) (W/m K)</th>
<th>( \sigma b ) (kJ/kg K)</th>
<th>( \nu b ) (mPas)</th>
<th>( \mu b ) (mN/m)</th>
<th>( \lambda b ) (W/m K)</th>
<th>( \sigma b ) (kJ/kg K)</th>
<th>( \nu b ) (mPas)</th>
<th>( \mu b ) (mN/m)</th>
</tr>
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<td>-88.14</td>
<td>1460.6</td>
<td>2.0989</td>
<td>76.56</td>
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<td>0.4588</td>
<td>2.0927</td>
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<td>0.668</td>
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<tr>
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<td>89.26</td>
<td>384.2</td>
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<td>2.0432</td>
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THERMAM 2016 – 1-3 September 2016, IZMIR, TURKEY

International Conference on Thermophysical and Mechanical Properties of Advanced Materials

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1.4 LEE KESLER EQUATION OF STATE

One problem in creating computer modelling of equation of states is that they are usually given as a function of density (or specific volume) and temperature. If a different set of data given (such as temperature and pressure), curve fitting methods should be applied in order to solve problem. Due to phase change (liquid and vapor densities are quite different) initial estimation of nonlinear curve fitting is a difficult process. As a general equation of state Lee-Kesler EOS can be used for species free first estimation of initial curve fitting process.

Benedict-Webb-Rubin (BWR) equation of state is one of the most successful equation of state. The success of the original BWR equation of state has led to a number of studies wherein the modified form of the equation has been generalized to apply to many types of compounds. Lee and Kesler developed a modified form of BWR. This equation of state is developed based on two reference fluids, the first one is called simple fluid (eccentricity factor \( \omega = 0 \)) and those of n-octane as a reference fluid. Assume that \( Z = \frac{PV}{T} \) compressibility factor is to be calculated for a fluid at some temperature and pressure. First using critical properties of this fluid, determine
\( T_r = \frac{T}{T_{ref}} \) and \( P_r = \frac{P}{P_{ref}} \) reduced temperature and pressure. Then determine an ideal reduced volume of a simple fluid with

\[
\frac{P_r V_r^{(0)}}{T_r} = 1 + \frac{B}{V_r^{(0)}} + \frac{C}{(V_r^{(0)})^2} + \frac{D}{(V_r^{(0)})^3} + \frac{c_4}{T_r^2 (V_r^{(0)})^2} \left[ \beta + \frac{\gamma}{(V_r^{(0)})^2} \right] \exp \left[ -\frac{\gamma}{(V_r^{(0)})^2} \right]
\]

(1.4.1) where

\[
B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}
\]

(1.4.2)

\[
C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3}
\]

(1.4.3)

\[
D = d_1 - \frac{d_2}{T_r}
\]

(1.4.4)

\[
V_r^{(0)} = \frac{P_r V_r^{(0)}}{RT_c}
\]

(1.4.5)

Properties of simple and reference fluid (n-octane) is given in table 1.3.1.
Table 1.3.1 Lee Kesler coefficients for simple and reference fluids

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Next, using the same reduced temperature and pressure $V_r^{(R)} = \frac{PV_r^{(R)}}{RT_r}$ for reference fluid is solved by using the same basic Lee-Kesler equation

\[
\frac{PV_r^{(R)}}{T_r} = 1 + \frac{B}{V_r^{(R)}} + \frac{C}{(V_r^{(R)})^2} + \frac{D}{(V_r^{(R)})^5} + \frac{e_4}{T_r^3 (V_r^{(R)})^2} \left[ \beta + \frac{\gamma}{(V_r^{(R)})^2} \right] \exp \left[ -\frac{\gamma}{(V_r^{(R)})^2} \right]
\]

(1.4.6)

, then compressibility factors for both simple and reference fluids are calculated.

\[
Z^{(0)} = \frac{PV_r^{(0)}}{T_r} \quad (1.4.7) \quad Z^{(R)} = \frac{PV_r^{(R)}}{T_r}
\]

(1.4.8)

The compressibility factor $Z$ for the fluid of interest is then calculated by

\[
Z = \frac{PV}{RT} = Z^{(0)} + \left( \frac{\omega}{\omega_R} \right) (Z^{(R)} - Z^{(0)})
\]

(1.4.9)

Where eccentricity factor $\omega_R = 0.3978$. In hydrocarbon calculations primary error of the equation is in the range of less than 2% for both vapor and liquid phases.
1.5 CURVE FITTING METHODS

In order solve EOS with known variables other than density and temperature curve fitting methods should be applied. Various curve fitting methods are applied in solving equation of states some of the most used ones will be given here:

Newton method:

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \quad (1.4.1)$$

Hasan[41] proposed several higher order methods that is relatively more economical to use (relatively less function calculations) Some of them are listed here.

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \quad (1.4.2)$$

$$x_{n+1} = x_n - \frac{2f(x_n)}{f'(x_n) + f'(x_n) - f(x_n)} \quad (1.4.3)$$

$$x_{n+1} = x_n - \frac{2f(x_n)}{f'(x_n) + f'(x_n) - f(x_n)} \quad \text{where } \alpha + \beta = 1 \quad (1.4.4)$$

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n) + \frac{1}{r} f'(x_n) \log \left( \frac{f'(x_n)f'(x_n) - f(x_n)f'(x_n)}{f'(x_n)f'(x_n)} \right)} \quad (1.4.5)$$

In the saturation region of ISO 17584-2005 EOS the following equations can be used to obtain saturation thermodynamic properties.

$$P(\tau, \delta_{\text{saturated liquid}}) = P(\tau, \delta_{\text{saturated vapor}}) \quad (1.1.21)$$

$$g(\tau, \delta_{\text{saturated liquid}}) = g(\tau, \delta_{\text{saturated vapor}}) \quad (1.1.22)$$

As it is seen from these equations a system of non-linear equation solving method is needed. The simplest method of Newton method is used

One dimensional Newton-Raphson Formula was:
\[ x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \]  \hspace{1cm} (1.4.1)

If the equation format changed a little, it can be written in the form of

\[ \Delta x_{n+1} = x_{n+1} - x_n = -\frac{f(x_n)}{f'(x_n)} \]  \hspace{1cm} (1.4.6)

\[ f'(x_n) \Delta x_{n+1} = -f(x_n) \]  \hspace{1cm} (1.4.7)

Now the same equation can be considered for a system of non-linear equation

\[
\begin{bmatrix}
\frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \frac{\partial f_1}{\partial x_3} & \ldots & \frac{\partial f_1}{\partial x_n} \\
\frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \frac{\partial f_2}{\partial x_3} & \ldots & \frac{\partial f_2}{\partial x_n} \\
\frac{\partial f_3}{\partial x_1} & \frac{\partial f_3}{\partial x_2} & \frac{\partial f_3}{\partial x_3} & \ldots & \frac{\partial f_3}{\partial x_n} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\frac{\partial f_n}{\partial x_1} & \frac{\partial f_n}{\partial x_2} & \frac{\partial f_n}{\partial x_3} & \ldots & \frac{\partial f_n}{\partial x_n}
\end{bmatrix}
\begin{bmatrix}
\Delta x_1 \\
\Delta x_2 \\
\Delta x_3 \\
\vdots \\
\Delta x_n
\end{bmatrix} =
\begin{bmatrix}
f_1 \\
f_2 \\
f_3 \\
\vdots \\
f_n
\end{bmatrix} \hspace{1cm} (1.4.8)

\[ \{\Delta x\} = \{x\} - \{f\} \]  \hspace{1cm} (1.4.9)

So multidimensional Newton-Raphson equation becomes

\[ [\nabla f] \{\Delta x\} = -\{f\} \]  \hspace{1cm} (1.4.10)

The equation can be solved by using methods such as gauss elimination. An initial estimate for all the x values are required to start iterative solution. All derivatives are taken numerically.

**2.0 SIMULATION OF THE EQUATION OF STATES**

Programs in java programming language developed to calculate **ISO 17584-2005, PRSV and other** equation of states. Java is an object oriented programming language, so two main object is developed in order to calculate the EOS. All class codes can be obtained from website [www.turhancoban.com](http://www.turhancoban.com). List of the classes and the duty they are carried out is given in the following list:
### Table 2.1  Program code list

<table>
<thead>
<tr>
<th>Class name</th>
<th>class performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>ref_CS3</td>
<td>Saturation data by using cubic spline curve fitting of actual data</td>
</tr>
<tr>
<td>refrigerant.java</td>
<td>Equation of states such as ISO 17584-2005, PRSV to calculate properties of refrigerants</td>
</tr>
<tr>
<td>ref_CS_Data3</td>
<td>Stored data structure for ref_CS3</td>
</tr>
<tr>
<td>reflISO17584</td>
<td>Equation of states for ISO 17584-2005</td>
</tr>
<tr>
<td>reflISO17584_mix</td>
<td>Equation of states for ISO 17584-2005 refrigerant mixtures</td>
</tr>
<tr>
<td>refModel</td>
<td>Arrange table form in Graphic user interface program</td>
</tr>
<tr>
<td>refTable</td>
<td>A GUI program to run property EOS</td>
</tr>
<tr>
<td>refrigerationcycle</td>
<td>Simple refrigeration cycle</td>
</tr>
<tr>
<td>refrigerationTable</td>
<td>A GUI program to run refrigerationcycle</td>
</tr>
</tbody>
</table>

Utilization of class refrigerant in your own class is very simple all you have to do is construct class and then call property method. While you are calling the property method you have to give known thermodynamic pair and double values of this pair such as:

```java
refrigerant g=new refrigerant("R410A");

double a[]=g.property("px",600.0,0.0);;
```

Known thermodynamic pairs and meaning of the properties double array is carried out is given below:
### Table 2.2 Known property pairs for program refrigerant and their meanings

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>tv</td>
<td>Temperature-volume</td>
</tr>
<tr>
<td>tp</td>
<td>Temperature-pressure</td>
</tr>
<tr>
<td>th</td>
<td>Temperature-enthalpy</td>
</tr>
<tr>
<td>tu</td>
<td>Temperature-internal energy</td>
</tr>
<tr>
<td>ts</td>
<td>Temperature-entropy</td>
</tr>
<tr>
<td>tx</td>
<td>Temperature-quality</td>
</tr>
<tr>
<td>pv</td>
<td>Pressure - volume</td>
</tr>
<tr>
<td>pt</td>
<td>Pressure - temperature</td>
</tr>
<tr>
<td>ph</td>
<td>Pressure enthalpy</td>
</tr>
<tr>
<td>pu</td>
<td>Pressure – internal energy</td>
</tr>
<tr>
<td>ps</td>
<td>Pressure- entropy</td>
</tr>
<tr>
<td>px</td>
<td>Pressure-quality</td>
</tr>
<tr>
<td>vp</td>
<td>Specific volume-pressure</td>
</tr>
<tr>
<td>vt</td>
<td>Specific volume-temperature</td>
</tr>
</tbody>
</table>

### Table 2.3 Class refrigerant property method double matrix meanings

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a[0]</td>
<td>P pressure kPa</td>
</tr>
<tr>
<td>a[1]</td>
<td>T temperature degree C</td>
</tr>
<tr>
<td>a[2]</td>
<td>v specific volume m$^3$/kg</td>
</tr>
<tr>
<td>a[3]</td>
<td>h enthalpy KJ/kg</td>
</tr>
<tr>
<td>a[4]</td>
<td>u internal energy KJ/kg</td>
</tr>
<tr>
<td>a[5]</td>
<td>s entropy KJ/kgK</td>
</tr>
<tr>
<td>a[6]</td>
<td>x quality kg vapor/kg total mix</td>
</tr>
<tr>
<td>a[7]</td>
<td>ρ density kg/m$^3$</td>
</tr>
</tbody>
</table>
A small example program to empathize this point

Program

```java
import java.io.*;
import javax.swing.*;

class reftest {
    public static void main(String arg[]) {
        refrigerant g = new refrigerant("R410A");
        double a[] = g.property("px", 600.0, 0.0);
        System.out.println(g.toString(a));
    }
}
```

---------- Capture Output ----------

```
> "C:\java\bin\javaw.exe" reftest
P : 600.0 kPa
T : -8.739999999999998 degree C
v : 8.30896071764108E-4 m^3/kg
h : 186.89000000000001 KJ/kg
u : 186.39146235694156 KJ/kg
s : 0.9517999999999999 KJ/kg K
x : 0.0 kg vap/kg mix.
ro: 1203.5199515107356 kg/m^3

> Terminated with exit code 0.
```

If we would like to take only the output results without actual values, results can directly be called
import java.io.*;
import javax.swing.*;

class refest
{
    public static void main(String arg[])
    {
        refrigerant g=new refrigerant("R410A");
        Text.print(g.toString("px",600.0,0.0));
    }
}

Graphic user interphase program (refTable) is also introduced for users to directly check thermodynamic properties on screen Input/Output of this program:
Once thermodynamic tables are established correctly, they can be used to calculate thermodynamic cycles such as standard refrigeration cycle. Program refrigerationcycle and user GUI refrigerationTable is produced for this table.
I would like to also note that all this effort is part of the PhD. level course “Numerical Thermodynamics” I’ve been given at Ege University, Mechanical Engineering department for years.

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PREPARATION AND MECHANICAL PROPERTIES OF GRAPHENE OXIDE (GO)/ POLYVINYLCHLORIDE (PVC) COMPOSITES

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Abstract: Graphene Oxide (GO)/Polyvinyl Chloride (PVC) composites were prepared by colloidal blending method. The characterization of the composites was made by X-Ray Diffraction (XRD), Field-Emission Scanning Electron Microscope (FE-SEM), Differential Scanning Calorimetry (DSC), tensile tests and microhardness measurements. XRD and FE-SEM results showed that GO sheets were well dispersed within the PVC matrix resulting in a filled porous structure. The tensile strength and microhardness improved with the addition of GO sheets although a stable variation in the composite elongation at break (%) was observed.

Keywords: GO/PVC composites; Colloidal blending; Mechanical properties.

1 INTRODUCTION
PVC is a common thermoplastic and has many application areas such as flooring, cable insulation, roof tiles, packaging material, bottle and medical products because of its good mechanical and corrosion properties, chemical and water resistances, low flammability, and low cost [1-2]. However PVC without plasticizers or fillers is typically brittle and is not suitable for use in many fields [3-4]. Recently, graphene–based fillers such as Graphene Oxide (GO), Reduced Graphene Oxide (RGO), Modified Graphene Oxide (MGO) and Multi-Layer Graphene (MLG) are widely used in the production of polymer composites or nanocomposites [5-6]. Especially, the easy synthesis and good degree of dispersion of GO as an inexpensive filler material are preferred by many researchers [5,7-8]. GO is highly hydrophilic due to its hydroxy, epoxide, carboxy surface groups (see figure 1.a) [9-10]. The high surface area of the GO sheets is a suitable location for strong interaction with the polymers to form GO-intercalated or GO - exfoliated composites [11-12]. These kinds of polymer composites containing low loadings of filler have shown important improvements in elastic modulus, tensile strength, electrical conductivity and thermal stability [6]. Recently, the improvement in thermal, electrical and mechanical properties of PVC matrix with graphene –based fillers has been reported in many literatures [3-5,13-15]. Wang et al. [3] found that the presence of MLG improved the wear resistance along with decreasing microhardness of the MLG/PVC composites. Hu et al. [4] and Salavagione and Martinez [14] prepared PVC nanocomposites with GO derivatives (RGO and MGO) and they reported that the interfacial interactions between the GO derivatives and the
PVC matrix increased mechanical properties and thermal stability of PVC nanocomposites. Hasan and Lee reported [13] that Graphene/ PVC nanocomposite films showed greater thermo-mechanical stability than PVC. Vadakumply et al. [15] also reported that the presence of graphene nanoflakes in PVC matrix provided 58% and 130% increase in the elastic modulus and tensile strength composites, respectively. Specially, studies on the mechanical properties of GO/PVC composite are scarce. Deshmukh and Joshi [5] prepared GO/PVC nanocomposite films with an interconnected network of macro-pores morphology by using colloidal blending method, and they reported that the strong interaction between PVC and GO and homogeneous distribution of GO significantly improved thermal stability, tensile strength and elastic modulus of the composites whereas elongation % decreased as a function of GO loading. The objective of this work is to synthesis and to investigate the structural and mechanical properties of GO/PVC composites with the use of minimum amount of fillers.

![Figure 1.](image)

Figure 1. Chemical structure of graphene oxide [16].

2. EXPERIMENTAL

2.1 Materials and Synthesis

For the synthesis of GO; GF (natural graphite with 45µm nominal particle size), concentrated sulfuric acid (98% H₂SO₄), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂) and hydrochloric acid (HCl) were purchased from Merck. GO was synthesized using the modified Hummers method [17] and the details of the process were given previously [18]. PVC was obtained from Sigma. The GO/PVC composites have been prepared by mixing with Tetrahydrofuran (THF) that was obtained from Merck. GO/PVC composites were prepared by a colloidal blending method. PVC (1gr) was first dissolved in THF at 70 °C and was cooled to room temperature. GO powder was separately dispersed in THF at 25ºC. The two solutions were stirred for 2 h at 60ºC. The synthesis process of GO/PVC composites is illustrated in figure 2. The GO content in the GO/PVC composite was varied from 0.1–1 wt. % (see Table 1).
Table 1. Ratios and codes of GO in the composites.

<table>
<thead>
<tr>
<th>Composites</th>
<th>GO Content (in weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO/PVC-0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>GO/PVC-0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>GO/PVC-0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>GO/PVC-1</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 2. Synthesis process of GO/PVC composites.

2.2 Characterization

Structural analyses of the composites were carried out by X-Ray Diffraction (XRD, PAN analytical, Empyrean) in the range of 10–60°. The morphology of the as-prepared composites was observed using a Field-Emission Scanning Electron Microscope (FE-SEM) equipped with an Energy Dispersive Spectroscopy (EDS). Glass transition temperature of the composites were determined by Differential Scanning Calorimetry (DSC, STA 409, Netzsch) at a scanning rate of 20 °C/min from 20 to 600 °C under nitrogen atmosphere. Tensile properties of the composites were performed on a tensile testing machine (AG-IC 100 kN, Shimadzu, Tokyo, Japan) at a
speed of 20 mm/min. Microhardness measurements were performed in a microhardness testing machine DuraScan20 (EmcoTest, Germany) with a load of 0.1 N.

3. RESULTS AND DISCUSSION

3.1 XRD

Figure 3 showed the XRD pattern of GF, GO and GO/PVC composites with different amounts of GO. The basal reflection peak of GF at 2θ = 26.4° was shifted to 2θ = 9.9° in the GO spectrum because of the intercalation of oxygen-containing functional groups in the interlayer spacing of GO. This leads to an increase of d-spacing from 0.33 (26.4°) to 0.88 (9.9°) nm and a decrease in the diffraction intensity. This situation indicated that GO was successfully synthesized from GF by a Hummers method [19]. For the GO/PVC composites, their XRD patterns only showed PVC peak coming from PVC, but the GO peak disappeared and the reflection shape of GO/PVC composites is almost exactly the same because of the low intensity of PVC and low amounts of added GO [15]. This clearly demonstrated the formation of fully exfoliated structures and the homogeneous distribution of GO layers in the PVC matrix.

![XRD patterns of GF, GO, pure PVC and GO/PVC composites](image)

3.2 FE-SEM

FE-SEM characterization was also used to investigate the structures of GF, GO, pure PVC and GO/PVC composites and distribution of GO layers in PVC matrix, as shown in figure 4(a-e). GF presented a thin layer structure (see figure 3a) [20]. GO showed bulky agglomerates due to Van der Waals forces [21]. According to EDS results of the GF and GO, oxygen content increased from 22.59 atom % to 47.95 atom %. These results suggested that the GF was oxidized. The FE-
SEM micrograph of pure PVC was characterized with smooth surface as shown in figure 4c, but on the surface of GO/PVC-0.1 composite porosity began to form (see figure 4d). As shown in figure 4e, small craters with average pore size of 4-5µm formed on the GO/PVC-0.5 and this was ascribed to polymer growing in the pores and galleries of GO [5].

Figure4.FE-SEM images of (a) GF, (b) GO, (c) pure PVC, (d) GO/PVC-0.1, (e) GO/PVC-0.5 (magnification 10,000X).
3.3 DSC

The effect of GO addition on the glass transition temperature of the PVC matrix was investigated via DSC and given figure 5. As shown in figure 5, it could be observed that the pure PVC and composites exhibited glass-transition temperature (T_g) at around 59°C. It is evident that GO does not influence the mobility of the polymer chains.

![Graph showing T_g values of GO/PVC composites with different amounts of GO.](image)

**Figure 5.** T_g values of the GO/PVC composites with different amounts of GO.

3.4 Microhardness

Figure 6 showed the variation of microhardness values with the increase of GO into PVC. It could be noticed that the microhardness of the GO/PVC composites increased with the increase of GO. The addition of 1 wt.% GO increased the microhardness of pure PVC from 45.8 to 52.4, corresponding to an increasing amount of about 14.4%. It was indicated that low additions of GO sheets could obviously enhance the hardness of PVC. Such a high hardness for these composites was closely associated with good PVC-GO interaction and well-dispersed GO layers in PVC matrix [22]. Additionally, it is known that filled pores are an important parameter improving mechanical properties [23]. The FE-SEM images confirmed the presence of PVC filling the pores and galleries of GO in the composites. (see figure 4d-e).
3.5 Tensile Properties

The effect of GO on the tensile properties of GO/PVC composites was plotted in figure 7a, b. From figure 7a, the tensile strength decreased until 0.1 wt.% of GO have been added to the PVC matrix, above which, the tensile strength values start to increase. The tensile strength varies from 9.43 (MPa) for pure PVC to 17.39 (MPa) for GO/PVC-1 composite. The GO/PVC composite with 1 wt. %GO had the maximum value, corresponding to an improvement of 84% compared to pure PVC. The improvement in the tensile strength can be attributed to the uniform dispersion of GO in the PVC matrix [5]. Also, XRD results (see figure 3) and FE-SEM images (see figure 4d, e) supported this result. On the other hand, the percentage elongation values of GO/PVC composites remain relatively stable. This phenomenon was reflected as the stable in the Tg of the composites (see figure 5).
4 CONCLUSIONS

Colloidal blending method was used to prepare GO/PVC composites, where GO sheets were well dispersed into PVC matrix. Small addition of GO (1 wt.%) to the PVC matrix improved the microhardness and tensile strength; however, the percentage elongation and Tg values of the GO/PVC composites remained relatively stable.

Acknowledgments-The financial support of the research foundation (Project no.: 2015-02.BŞEÜ.07-01) of Bilecik S.E. University. The author would also like to thank the officials of the Central Research Laboratory of Bilecik S.E. University for their precious contribution.
REFERENCES


THERMAL PERFORMANCE OF A MULTI-HOLED BRICK
CONSIDERING DIFFERENT HOLE SHAPES AND HOLE
ARRANGEMENTS

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Abstract: In this work, heat transfer characteristics of multi-holed bricks is investigated numerically. A conjugate heat transfer excluding and including surface to surface radiative heat transfer is studied. Computations are performed for three different shapes of air-filled cavity holes: square, circle and rhombus. Besides, the number of holes of a given fixed size brick is varied in the parallel and vertical directions of heat flow to determine the most effective configuration of the holes. Computational results show that although the thermal resistance of the bricks improves with the increase in number of holes thus void fraction of air, the highest improvement is achieved for the square-shaped cavities followed by circular-shaped and rhombus-shaped cavities, respectively. It is found that for the same hole shape and the same void fraction of air, increasing the number of holes in the perpendicular direction of heat flow rather than in the parallel direction to heat flow is more effective in terms of thermal insulation.

Keywords: multi-holed brick, energy saving, thermal optimization, thermal performance

Nomenclature

\( A \) \hspace{1cm} \text{Heat Transfer Area (m}^2\) \hspace{1cm} \( x \) \hspace{1cm} \text{Cartesian coordinate (m)}

\( c_p \) \hspace{1cm} \text{Specific heat at constant pressure, (kJ/kgK)} \hspace{1cm} \( y \) \hspace{1cm} \text{Cartesian coordinate (m)}

\( g \) \hspace{1cm} \text{Gravitational acceleration, (m/s}^2\)

\( k \) \hspace{1cm} \text{Thermal Conductivity (W/mK)}

\( k_{\text{eff}} \) \hspace{1cm} \text{Effective Thermal Conductivity (W/mK)}

\( \Delta T \) \hspace{1cm} \text{Temperature Difference (°K)}

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1. Introduction

A considerable amount of energy is required for heating and cooling of the residential buildings. This energy is mostly produced with fossil fuels that are harmful to the environment. In order to reduce the usage of fossil fuels, The European Union (EU) created new directives in 2012 [1]. According to these directives, EU is facing unprecedented challenges due to increasing dependence on energy imports and scarce energy resources. As a candidate of the European Union, Turkey also amended new standards for “Thermal Insulation Requirements for Buildings” (TS 825) and recently has begun to comply with European legislation on buildings. However, the energy consumption of the new buildings constructed according to the recent regulations in Turkey is two times higher than that of in EU countries [2]. In order to comply the rules and legislations, exterior wall of buildings must have an extra insulation layers which can be pricey. In order to increase thermal resistance of the wall, one of the most common ways is to use bricks with multi air-filled holes which makes it both light and cost effective. For that purpose, the engineers and scientists have been trying to further increase the thermal resistance performance of multi-holed bricks. Locating a partition midway of the cavity resulted in maximum heat leak reduction compared to fully insulating the enclosure with a porous material [3]. A similar study was conducted by Antar and Baig [4] where conjugate heat transfer across a hollow brick is numerically studied. It is shown that increasing number of cavities while keeping the block width constant increases R-value significantly and a maximum number of six cavities can fit the building block without compromising the strength. Besides, they stated that with this number of cavities, no insulation would be needed to fill the cavities as a result of the reduced effect of natural convection. However, they did not consider radiation in the calculations. Alhazmy [5] proposed to insert a folded sheet in each cavity of hollow bricks to divide it into several triangles in order to suppress the natural convection inside the voids. It was shown that heat flux through the cavity decreases as the number of partitions increases and the convection is nearly diminished when the number of partitions is increased to six. Also, it was reported that
Inclined partitions can reduce the heat flux by 37-42% depending on the number of partitions and their material. Costa [6] conducted a numerical study to improve the thermal performance of red clay holed bricks, considering protuberances to inhibit natural convection and radiation heat transfer inside the brick holes and reported that overall heat transfer reduction can be up to 23%. Li et al. [7] investigated equivalent thermal conductivity of a multi-holed clay brick for 50 different kinds of combination of holes and arrangements. They examined the effect of hole surface radiation, the width-wise and length-wise hole numbers and indoor-outdoor temperature difference. They reported that radiation between hole surfaces has effect on the equivalent thermal conductivity and thermal conductivity may decrease or increase with the hole number. Soria et al. [8] investigated numerically the behavior of differently heated cavities for both two-dimensional and three-dimensional cases. It was concluded that 2D simulations are sufficient to capture the main features of natural convection flows. Diaz et al. [9] attempted to improve the thermal efficiency of walls made up of multi-holed bricks with large recesses. They carried out a numerical study to optimize several hollow brick geometries using the average mass overall thermal efficiency and the equivalent thermal conductivity. Arendt et al. [10] studied the influence of the cavity concentration in hollow bricks on static and dynamic thermal parameters: a time lag, a decrement factor, an equivalent thermal diffusivity and an equivalent thermal conductivity. Cavity shape of hollow bricks is optimized to reduce the intensity of radiation and convective heat exchange. They reported that in order to obtain the optimum thermal parameters, a total cavity area to a gross brick area must be 30-45% for bricks made from low thermal conductivity materials whereas it increases up to 45-65% for bricks made from relatively high thermal conductivity materials. Sun and Fang [11] studied numerically heat transfer performance of a hollow brick for several different configurations. The effect of enclosure configurations with the same void volume fraction on equivalent thermal conductivity was conducted. It was reported that the relative enhancement of radiation heat transfer on the equivalent thermal conductivity ranged from 7.41% to 25.39%, and the natural convection from nearly zero to 22.50%, depending on the enclosure numbers and their arrangement configurations. They concluded that for the enclosure width 1.16 cm and length 6 cm, the contribution of the natural convection on the effective thermal conductivity is less than 0.10% and can be ignored.

In the present work, heat transfer characteristics of a hollow brick which is widely used in the building construction in Turkey are investigated. It is aimed to obtain the optimum configuration of holes which provides the highest thermal resistance thus the lowest effective conductivity. Computations are carried out for three different cavity shapes: square, circular and rhombus together with different number of cavities in the parallel and vertical direction of heat transfer in order to determine optimum configuration of the cavities in terms of thermal resistance.
2. Problem description

In this study, the heat transfer characteristics of a brick in size of 190mmx135mmx190mm which is one of the most used brick type in the construction sector in Turkey is investigated. Three different shapes of cavities of hollow bricks i) circle ii) square iii) rhombus are considered. In the course of designing all cavity configurations, it is taken into accounted that the thickness of the of any shell should not be less than 11 mm and that of any web should not be less than 8 mm to maintain strength of the structure [12]. The size of holes are kept constant. However, number of the holes in the brick is varied both in the horizontal direction (3, 5 and 7) and in the vertical direction (1, 3 and 5) of the heat transfer to generate different configurations. That is, 9 different configurations are considered for the each shape of the cavity. Three examples from the investigated configuration are presented in Figure 1 together with their denotations where V and H represents vertical and horizontal directions and numbers represents the number of holes in the relevant direction. For instance, “V3H5 Circle” represents the brick with 3 rows of circular cavity holes in the vertical direction and 5 columns of circular cavity holes in the horizontal direction (totally 15 number of holes). Hereinafter, the same denotation system is to be used in the rest of manuscript. It is noted that although the number of holes are the same for the each hole shape, the void fraction of air differs from each other due to different cross-sectional area.

![Figure 1 Three examples from investigated cavity configuration](image)

a) V1H3 Square  b) V3H5 Circle  c) V5H7 Rhombus

3. Mathematical Model and Numerical Approach

It is assumed that the flow in the holes is two dimensional, steady-state, incompressible and laminar. Thus, the depth of brick is not considered in analyses. All thermophysical properties of both porous clay and air are assumed to be constant except the density of air which is treated by Boussinesq approximation. The thermophysical properties are given in Table 1. It is shown in [13] that when the indoor–outdoor temperature difference varies from 20°C to 50°C, the
equivalent thermal conductivity of the investigated hollow bricks does not vary significantly, usually within ±5%. Therefore, it is assumed that the left and right surfaces of the bricks are maintained at 5°C and 25°C constant uniform temperatures, respectively while bottom and top surfaces are assumed to be adiabatic.

Table 1: Thermophysical properties of materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Density ($kg/m^3$)</th>
<th>Specific Heat ($C_p$) ($J/kgK$)</th>
<th>Thermal Conductivity ($W/mK$)</th>
<th>Viscosity ($kg/ms$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>-</td>
<td>1005,9</td>
<td>0,025219</td>
<td>1,7965E-5</td>
</tr>
<tr>
<td>Clay</td>
<td>600</td>
<td>900</td>
<td>0,32</td>
<td>-</td>
</tr>
</tbody>
</table>

Based on the assumptions given above, the governing equations are given as follows:

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0
\]  

(1)

\[
u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial P}{\partial x} + \nu \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)
\]  

(2)

\[
u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = \nu \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) - g \beta (T - T_\infty)
\]  

(3)

\[
u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \alpha \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right)
\]  

(4)

The governing equations are solved iteratively by using a finite volume based code, ANSYS FLUENT 15.0. Convective terms in momentum and energy equations are discretized by Second order upwind scheme. Pressure and velocity terms are coupled by SIMPLE algorithm. Calculations are also carried out for both excluding and including radiative heat transfer inside the air-filled cavities. Radiation between the surfaces of cavities are taken into account using the Surface to Surface (S2S) radiation model which assumes that air in the cavity is non-participating medium for radiation. Emissivity of the cavity surfaces is assumed to be 0.93. No slip boundary condition is imposed on the cavity walls.

Since hollow bricks consist of the solid part of clay and the air cavities, effective thermal conductivity ($k_{eff}$), which is defined in (5), is used to determine the insulation performance.
\[ k_{\text{eff}} = \frac{Q L}{A \Delta T} \]  

(5)

where \( Q \) is the heat transfer rate through the brick, \( L \) is the thickness of the brick, \( A \) is the heat transfer area of the brick and \( \Delta T \) is the temperature difference between the brick surfaces.

A non-uniform structured grid was generated for the fluid regions in order to resolve velocity gradients near the solid wall. A grid independency test was performed by a systematic decrease in the grid size while observing the effective thermal conductivity. It was found that the number of grid nodes varies between 6504 to 45489 depending on the number of holes in order to obtain optimum grid. A typical grid independency test is presented in Figure 2 for the V5H3 square configuration.

![Figure 2 An example of grid independency test (V5H3 square)](image)

4. Results and discussion

Calculations are performed for three different cavity shapes. Besides, nine different arrays of cavity configurations are considered for the each cavity shape. The obtained results is discussed in this section. Table 2 shows the effect of radiative heat transfer on the \( k_{\text{eff}} \) for some sample configurations. As seen in the table, the effect of radiation on the \( k_{\text{eff}} \) is insignificant for the cases with the low number of holes. However, as number of holes increases, the difference between \( k_{\text{eff}} \) obtained by excluding and including radiative heat transfer increases, since the solid surfaces that participates radiative heat transfer increases. The increase in \( k_{\text{eff}} \) reaches up to 22.56%, 14.74% and 8.00% for the square, circle and rhombus shape cavities, respectively. It can be easily concluded that radiative heat transfer plays a significant role for the configurations with relatively high number of holes particularly for the square-shaped cavities. Therefore, radiation is to be taken into consideration in the rest of analysis.
Table 2: The effect of including radiation into calculation on the $k_{eff}$

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Cavity shape</th>
<th>$k_{eff}$ (excl. radiation) (W/mK)</th>
<th>$k_{eff}$ (incl. radiation) (W/mK)</th>
<th>Increase in $k_{eff}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1H3</td>
<td>Square</td>
<td>1.033</td>
<td>1.049</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>Circle</td>
<td>1.045</td>
<td>1.056</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Rhombus</td>
<td>1.056</td>
<td>1.062</td>
<td>0.60</td>
</tr>
<tr>
<td>V3H5</td>
<td>Square</td>
<td>0.859</td>
<td>0.930</td>
<td>8.17</td>
</tr>
<tr>
<td></td>
<td>Circle</td>
<td>0.914</td>
<td>0.962</td>
<td>5.32</td>
</tr>
<tr>
<td></td>
<td>Rhombus</td>
<td>0.960</td>
<td>0.990</td>
<td>3.11</td>
</tr>
<tr>
<td>V5H7</td>
<td>Square</td>
<td>0.616</td>
<td>0.755</td>
<td>22.56</td>
</tr>
<tr>
<td></td>
<td>Circle</td>
<td>0.711</td>
<td>0.815</td>
<td>14.74</td>
</tr>
<tr>
<td></td>
<td>Rhombus</td>
<td>0.811</td>
<td>0.876</td>
<td>8.00</td>
</tr>
</tbody>
</table>

Temperature contour for three chosen configurations are presented in Figure 3. It is seen that temperature decreases gradually from hot right side to cold left side of the brick. A careful inspection of the figure shows that isotherms for the V1H3 square hole are distorted at the air-filled cavities due to convection currents (although weak) whereas it is nearly vertical in the solid domain. With the increase in number of holes, such as for the V5H7 rhombus, the isotherms are observed to be nearly parallel to each other such as pure conduction.

![Temperature contour](image)

Figure 3 Temperature distribution for three chosen cavity configurations
The effect of number of holes on the $k_{\text{eff}}$ is presented in Figure 4 for different hole shapes. As seen in Figure 4, the highest thermal resistance is attained for the square-shaped holes which is followed by the circular-shaped and rhombus-shaped holes, respectively for all the investigated hole arrangements. Besides, it can clearly be seen that as number of holes increases, $k_{\text{eff}}$ decreases due to higher thermal resistance of air compared to that of clay. However, it is seen that for the V1HX (X is the number of holes in horizontal direction) hole arrangements, the $k_{\text{eff}}$ is slightly above 1 W/mK for all the cases, and the maximum effect of the hole shape on the $k_{\text{eff}}$ is only 2.3%. As the number of holes increases, the effect of hole shape gains importance due to the increase in void fraction of air and radiative heat transfer. For instance, the effect of hole shape on $k_{\text{eff}}$ can be up to 7.80% and 16.07% for the V3HX and V5HX hole arrangements. Also, it is observed that thermal resistance of V3H3 square-shaped holes (totally 9 holes) are almost the same as that of V5H3 rhombus-shaped holes (totally 15 holes).

The $k_{\text{eff}}$ values of V3H5 and V5H3 hole arrangements where the number of holes thus void fraction of air is the same for each hole shape is compared in Figure 4 in order to determine whether increasing the number of holes in the parallel or perpendicular direction of heat flow is more effective. As seen in Figure 5, for all cavity shapes, the $k_{\text{eff}}$ values of the V5H3 configuration is lower than that of V3H5 configuration where the largest difference is observed in the square-shaped cavities.
5. Conclusions

In this study, heat transfer characteristics of a multi-hole hollow brick with different hole configurations is investigated numerically. A fixed size of a brick which is widely used in the building construction in Turkey is considered. Three different cross sections of holes i) square b) circular c) rhombus are considered. The size of holes is kept constant whereas number of the holes is varied both in the horizontal direction (3, 5 and 7) and in the vertical direction (1, 3 and 5) of the heat flux to generate different configurations for the each hole shape.

Computational results show that thermal insulation performance of brick enhances with the increase in the number of air-filled cavity holes for all the cases considered. However, the highest performance is achieved for the square-shaped cavities followed by circular-shaped and rhombus-shaped ones. The amount of heat transfer rate by radiation is significant particularly for the configurations with high void fractions. It is found that for the same hole shape and with the same void fraction, higher thermal resistance is attained by increasing the number of holes in the perpendicular direction of heat flow compared to that of parallel direction to heat flow for all three hole shapes considered. The largest thermal resistance of multi-hole brick is obtained for the V5H7 square-shaped configuration where the thermal effective conductivity is reduced down to 0.75 W/mK.

References


PARAMETRIC TRANSIENT ANALYSIS OF THERMAL INSULATING PLASTER FOR EXTERIOR WALL

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Abstract: To achieve heat control between indoor and outdoor environments, design and thermal behavior of the exterior facades of building is significantly important for energy efficient consideration. Application of heat insulation to the facades of the building is most remarkable solution of the entire set of policies related to the regulations on global scale. To provide the effective use of thermal insulation systems should be set as one of the most critical objectives of sustainable buildings. Achieving high levels of insulating materials to building external walls are getting thinner and also increasing the building usage area. Thermal insulating plaster can be one of the possible solutions for energy restriction and labor of the building facades. New kinds of thermal insulating plaster application is flexible to construct and can be suitable for any architectural solution. This research aims to understand time-dependent thermal behaviors of the exterior façade using autoclaved aerated concrete as a thermal insulating plaster. For that purpose, thermophysical properties of the plaster and aerated concrete are measured and used in a software code for parametric analyses to compare cement and gypsum plaster wall thicknesses under climatic conditions of Izmir located in hot-humid climate zone in Turkey. As a result of this study, similar thermal performance was obtained by using 0.5cm insulating plaster besides of 2cm common plaster.

Keywords: Thermal insulation, Insulation thickness,

1. Introduction

The built environment needs to provide the necessary comfort conditions for healthy and satisfied life for us, besides just sheltering. One of the most important of these conditions is the thermal comfort. Reduction and overutilization of available resources day by day is the biggest challenge facing the World. Hence, after the use of the wrong material in the process of the construction, heating and cooling loads increase and as a consequently, mechanical air-conditioning systems brings with it an increase in fossil fuel consumption. Due to this problem, people has led to the revision of material for building energy consumption. Therefore, strategy of environment friendly design and sustainable products have developed.

Annual heating and cooling transmission loads are the main specifications for analyzing of the optimum insulation thickness. Many authors investigated the optimum thickness of insulation materials with different climate zones. Some of these studies are developed under static conditions, but this method does not consider the impact of thermal inertia of building [1]. On the contrary, transient heat transfer through the exterior walls reflects the thermal inertia [2-11].
This one dimensional transient heat transfer method provides results which almost agree the exact solution (depends on the solution method).

In this study, the influence of insulating plaster under the unsteady environmental conditions was investigated thermally. Two different plaster configurations were compared each other by using one-dimensional transient heat conduction equation. For that purpose, thermophysical properties of each layers, autoclaved aerated concrete and insulating plaster, were measured their thermal conductivity, specific heat and density properties individually.

2. Measurements of the Thermal Properties of the Materials

2.1 Thermal conductivity

The hot wire method is broadly acknowledged as the essential device to measure the insulating materials’ thermal conductivity. The QTM-500 quick thermal conductivity meter (Kyoto Electronics Manufacturing Co. Ltd.) has been used for the experiments. This meter measures the thermal conductivity rate by the transient heater wire method (Figure 1) which is ASTM C 113-90. The sensor consists of a single heater wire and a thermocouple [12] The hot wire method is based on an ideal, infinitely long and thin continuous line source generated heat flux per length to applied in an infinite, homogenous and incompressible medium [13].

![Figure 1 Schematic view of the hot wire method](image)

Autoclaved aerated concrete and 2 insulating plaster samples were used for the thermal conductivity tests. The thermal conductivity for each sample was acquired by calculating the average thermal conductivity measured on the two sides. The average for the 2 autoclaved aerated concrete and 2 insulating plaster of each composition were then calculated. The variation of thermal conductivity of autoclaved aerated concrete and insulating plaster is shown in Table 1.
As it can be seen from the table, the autoclaved aerated concrete and the insulating plaster have quite similar thermal conductivity values, namely 0.11W/mK versus 0.13W/mK, respectively. Temperature values given in Table 1 shows the steady-state measurement after unsteady heat flux input from the hot wire source.

Table 1: Measured thermal conductivity values of the selected materials

<table>
<thead>
<tr>
<th></th>
<th>AAC*</th>
<th>Tm (°C)</th>
<th>Plaster</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Front Side</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k1(W/mK)</td>
<td>0.1151</td>
<td>30</td>
<td>0.1322</td>
<td>30</td>
</tr>
<tr>
<td>k2(W/mK)</td>
<td>0.1139</td>
<td>30</td>
<td>0.1234</td>
<td>32</td>
</tr>
<tr>
<td>k3(W/mK)</td>
<td>0.1072</td>
<td>31</td>
<td>0.138</td>
<td>33</td>
</tr>
<tr>
<td><strong>Back Side</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k4(W/mK)</td>
<td>0.1405</td>
<td>31</td>
<td>0.1451</td>
<td>34</td>
</tr>
<tr>
<td>k5(W/mK)</td>
<td>0.0975</td>
<td>31</td>
<td>0.139</td>
<td>34</td>
</tr>
<tr>
<td>k6(W/mK)</td>
<td>0.0915</td>
<td>31</td>
<td>0.1438</td>
<td>34</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>0.11</td>
<td></td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td><strong>Std. Dev.</strong></td>
<td>0.0171</td>
<td></td>
<td>0.008</td>
<td></td>
</tr>
</tbody>
</table>

* Autoclaved aerated concrete

2.2 Specific Heat

Specific heat is a property of a substance which can be described the energy requirement for inducing a certain change in the temperature of a unit mass of the material. A differential scanning calorimeter method was used for measuring that value. A modulated differential scanning calorimeter (Q10, TA Instruments, Inc.) [14] was employed to characterize the specific heat of each sample. Heat input and the temperature increase of a sample are measured and conpared with the reference substance for defining the specific heat. The test parameters are comprised of sampling interval 0.10 s/pt (seconds/point sampling), equilibrate value is defined as -35.00°C, the ramp is 5.00°C/min and the final temperature is up to 60.00°C. In this study, the specific heat values are determined 1320 J/kgK and 1340 J/kgK for autoclaved aerated concrete and insulating plaster, respectively. Inside environment temperature is assumed for specific heat value as 20°C and 24°C for winter time and summer time in order of January and July data for İzmir.
2.3 Density

Density is defined for two specimens of each sample. Firstly, samples were dried in an oven at 40°C for at least 24 hours. These weight measurements were recorded as the dry weights of the samples \( m_{\text{dry}} \) with precision balance equipment (AND HF-3000G). The samples water was evaporated in a vacuum oven (Lab-Line 3608-6CE Vacuum Oven) [15]. The saturated weights are defined \( m_{\text{sat}} \) and the Archimedes weights \( m_{\text{arch}} \) in water by using precision balance equipment. Bulk Density of samples were calculated by using the Equation 1.

\[
\rho = \frac{m_{\text{dry}}}{m_{\text{sat}} - m_{\text{arch}}}
\]

where

\( \rho \): Density \((\text{g/cm}^3)\), \( m_{\text{dry}} \): Dry weight \((\text{g})\), \( m_{\text{sat}} \): Saturated weight \((\text{g})\)

\( m_{\text{arch}} \): Archimedes weight \((\text{g})\), \( m_{\text{sat}} - m_{\text{dry}} \): Porous weight \((\text{g})\)

Basic physical properties of autoclaved aerated concrete and insulating plaster could be described by density values is in Table 2. The density values of both types of materials are 396.56 kg/m\(^3\) and 559.57 kg/m\(^3\), respectively.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Dry Weight</th>
<th>Saturated Weight</th>
<th>Archimedes Weight</th>
<th>( \rho ) (g/cm(^3))</th>
<th>Average (kg/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autoclaved Aerated Concrete Sample 1</td>
<td>32.08</td>
<td>92.47</td>
<td>11.57</td>
<td>0.3965389</td>
<td>396.56</td>
</tr>
<tr>
<td>Autoclaved Aerated Concrete Sample 2</td>
<td>35.24</td>
<td>101.35</td>
<td>12.49</td>
<td>0.3965789</td>
<td></td>
</tr>
<tr>
<td>Insulating Plaster Sample 1</td>
<td>12.48</td>
<td>26.62</td>
<td>4.34</td>
<td>0.5601436</td>
<td>559.57</td>
</tr>
<tr>
<td>Insulating Plaster Sample 2</td>
<td>12.6</td>
<td>26.46</td>
<td>3.92</td>
<td>0.5590062</td>
<td></td>
</tr>
</tbody>
</table>

3 Mathematical Formulation

The one dimensional heat conduction equation in a parallel, isotropic and homogeneous multilayered wall for transient and no heat generation condition, can be described as;
The boundary and the initial conditions were also defined as:

\[
\begin{align*}
\text{for } t > 0, & \quad \text{at } x = 0, \quad \leftrightarrow \quad -k_0 \frac{\partial T}{\partial x} |_{x=0} = \alpha l + \sigma \varepsilon (T_{sky}^4 - T_s^4) + h_o \left(T_{\infty, o} - T_{s, 0}\right) \\
\text{for } t > 0, & \quad \text{at } x = L, \quad \leftrightarrow \quad -k_L \frac{\partial T}{\partial x} |_{x=L} = h_i \left(T_{s, L} - T_{\infty, i}\right) \\0 \leq x \leq L, & \quad \text{at } t = 0 \quad \leftrightarrow \quad T(x, 0) = T_{\text{initial}}
\end{align*}
\]  

(3)  

(4)  

(5)

where \(k_0\) represent the thermal conductivity of the outside surface plaster material. \(\alpha\) is the outside surface radiation property, the absorption coefficient and it is supposed to be 0.4. \(I\) represent the solar radiation value and it is defined by using reference numbered [16] for İzmir and the vertical surface at South direction. Effective sky temperature, \(T_{sky}\) was calculated using the reference numbered 17. Photovoltaic Geographical Information System - Interactive Maps using for developed solar radiation value [18]. With this interactive maps data for the subcontinent of European was developed using the solar radiation model and certain programs identified with the GIS software called namely GRASS [19]. The solar radiation algorithms are based on equations published in the European Solar Radiation Atlas [20].

4. The Structure of Composite Walls

To compare of the numerical model solution for two composite walls structure of 3 parallel layers of different materials and thicknesses are in related with inside and outside temperature. In Figure 2a called Wall 1, this section is intentionally not-insulated with insulating plaster. This composite wall situation is respectively, 2 cm cement plastering on outside, 13.5 cm autoclaved aerated concrete and 2 cm gypsum plastering on inside.
Figure 2a Composite walls with cement and gypsum plastering: Wall 1

Figure 2b Composite walls with insulating plaster: Wall 2

That composition mentioned in Figure 2a is satisfied to the insulation regulation of Turkey for Izmir based on TS 825 and the overall heat transfer coefficient, U is calculated as 0.678 W/m²K which is lower than 0.7 W/m²K. Hence these plasters’ thermophysical properties were defined by using TS 825 and [21] and shown in Table 3.

Table 3: Thermophysical properties of the plasters used in the Wall 1 [22].

<table>
<thead>
<tr>
<th>Material name</th>
<th>Thickness (m)</th>
<th>Conductivity (W/mK)</th>
<th>Specific Heat (J/kgK)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outside Gypsum plastering</td>
<td>0.02</td>
<td>0.7200</td>
<td>840</td>
<td>1860</td>
</tr>
<tr>
<td>Inside Gypsum Plastering</td>
<td>0.02</td>
<td>0.3800</td>
<td>1090</td>
<td>1120</td>
</tr>
</tbody>
</table>

For comparison, the same size autoclaved aerated concrete is used with the insulating material having 0.5 cm thickness which is satisfied the TS825 and U value is calculated as 0.677 W/m²K for Wall 2 shown in Figure 2b.

5. Results and Discussion

The one dimensional time dependent heat transfer equation was solved via implicit finite difference method with Visual Basic Program for the determination of the building energy consumption for heating and cooling loads. Simulations are performed with regard to temperature distribution across the wall thickness at different time of the day and also hourly variation of inside surface heat flux of two types of the walls structure under optimal insulation conditions were also investigated for south facing exterior wall for January and July months in
Izmir. The meteorological data were used as an outside boundary condition for İzmir. Figure 3 shows the lowest and highest daily average temperatures of months which were January and July, respectively [23]. Figure 4 shows the global irradiance on a fixed vertical wall (W/m²) according to the selected orientation at South in January and July. The peak of South facing slopes occurs in January receive the more solar radiation compared with in July.

Figure 3 Monthly Average of the Daily Meteorological Data at January and July for İzmir.

Figure 4 Monthly Average of the Daily Solar Radiation at January for South Façade in İzmir

Figure 5 shows the variation of temperature differences based on the wall thickness. It presents the temperature distribution of cement plaster autoclaved aerated concrete and gypsum plaster combination wall for south orientation in İzmir with January data. Indoor air temperature is accepted 20°C in January time. In this figure, the verified times are 24.00, 18.00, 12.00 and 06.00 based on temperature. The breaking points symbolize the cement plaster and gypsum plaster. Figure 6 presents the Wall 1 temperature distribution across the wall thickness at different time of the day for south facing wall in July data in İzmir, Turkey. Indoor air temperature is approved to be at 24°C in July for summer period.

Figure 5 Wall 1 temperature distribution across the wall thickness at different time of the day for south facing wall in January in İzmir.
Figures 6 and 7 show the calculated hourly variations of heat flux on the inside surface (mentioned continuous line) of the exterior wall combined with cement and gypsum plaster. Heat flux from exterior surface and the heat storage are shown with the dashed lines. Climatic conditions are used for two representative days: one of a winter period is January and the other figure represent the summer period in July as a monthly average daily data were used as an outside temperature. It is seen that the maximum heat flux peak load is in antemeridian time in winter which gives the fluctuations of peak gain in Figure 7. Figure 8 demonstrates the hourly variation of inside surface heat flux of plaster (mentioned continuous line) combined wall structures at south facing for July in İzmir. The fluctuation of heat flux values at the outside surface and the stored heat energy have wide range according to Figure 7. Also $Q_{storage}$ is equal to the total of heat flux at indoor surface and outdoor surface of the wall.
Temperature distributions from the insulating plaster autoclaved aerated concrete and insulating plaster combination wall at four different times in a day in winter period of January shown in Figure 9. And energy use of exterior wall overall heat transfer coefficient (U-value) of the autoclaved aerated concrete and insulating plaster are approximately same. So in Figures 9 and 10 have no breaking point between two materials, since they have similar thermophysical properties.

![Figure 9 Wall 2 temperature distribution across the wall thickness at different time of the day for south facing wall in January in İzmir.](image1)

![Figure 10 Wall 2 temperature distribution across the wall thickness at different time of the day for south facing wall in July in İzmir.](image2)

Figures 11 and 12 represent the heat fluctuations of insulating plaster autoclaved aerated concrete and insulating plaster wall for south orientation in İzmir in January and July, respectively. Also the wall structure’s thermophysical properties is accepted based on ASHRAE Standard 55 Thermal Environmental Conditions for Human Occupancy. [22]
Figure 11 Hourly variation of inside surface heat flux of Wall 2 structures under optimal insulation conditions for January south facing in İzmir.

Figure 12 Hourly variation of inside surface heat flux of Wall 2 structures under optimal insulation conditions for July south facing in İzmir.

The results given in Table 4 show that the similar value is obtained in two types of combination of the wall which is integrated with cement plaster and gypsum plaster and the other one is insulating plaster walls. Table 4 exemplify the Wall 1 and Wall 2 heat gain and loss are experienced as regards in İzmir for south façade.

Table 4: Overall daily heat transfer for exterior wall compositions based on different plaster usage in January and July.

<table>
<thead>
<tr>
<th></th>
<th>Qout-January (Wh/m²day)</th>
<th>Qout-July (Wh/m²day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall 1</td>
<td>-141.8</td>
<td>98.6</td>
</tr>
<tr>
<td>Wall 2</td>
<td>-142.4</td>
<td>98.5</td>
</tr>
</tbody>
</table>
6. Conclusion

The numerical heat transfer model based on the one-dimensional time-dependent heat conduction equation is investigated by solving via implicit finite difference method to determine of the transient heat transfer through two types of multilayered walls for summer and winter climatic conditions with south orientation in İzmir, Turkey. In this study, the first and second wall types calculated overall heat transfer coefficient, U value are almost same. However, based on an optimum insulation thickness and the U value calculation according to TS-825, Thermal Insulation Standard in Buildings, the thickness of Wall 1 and Wall 2 are 0.175m and 0.145m, respectively. Insulating plaster is a one coat application was developed as a way of taking advantages of the reduced labor of cement and gypsum plastering application. It also leaves more space to use at the inside environment.

7. References


EXPERIMENTAL INVESTIGATION ON BOLTED NATURAL FIBRE REINFORCED COMPOSITES

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Abstract: Aim of the study is an investigation on the failure behaviour of bolted joints which are natural fibre reinforced polymeric composites under tensile loading condition. For this aim composite plates were designed as eight layers orientation angels of biaxial jute fabric (0/90)8 and epoxy resin. The jute fabrics were pH 7 treated before composite production. Alkali treatment was applied by 1% NaOH solution during two hours and litmus papers were used to adjust the pH value of fabrics. Vacuum assisted resin infusion method (VARIM) was used for composite production. After epoxy resin impregnation, at 80 °C during 8h curing process was applied. Fibre volume fraction of composites obtained approximately 38%. Then the composite plates were cut by circular saw and the holes were drilled according to ASTM D5961M-13 standards dimensions. Five specimens were tested under tensile loading and results were given by graphs. Failure mode were occurred the same in all specimens as net-tension mode.

Keywords: Bolted composite, natural fibre, vacuum assisted resin infusion method (VARIM).

1. Introduction

As it is well known stress concentration zones play an important role in failure behavior of materials which have any hole. On the other hand, bolted joints are one of the crucial joints for the designs which need to disassemble for maintenance or transportation, because of low cost and simplicity. Furthermore, fiber reinforced polymeric composites have more advantages on metallic materials as high strength-to-weight and stiffness to-weight ratios they are getting more and more application areas such as automotive, air vehicle and marine vessels. Thus, fiber reinforced polymeric composites with bolted joints were subjected to detailed investigation in the literature [1-9].

Dano et al. investigate the effect of failure criteria and material property degradation rules on the behaviour of pinned-joint in graphite/epoxy composite laminates two sets of failure criteria and degradation rules were adopted to examine their influence on the predicted load–bolt displacement curves and the strains around the hole [1]. Xiao and Ishikawa made experimental investigation to offer the basic data for design and strength prediction of bolted composite joints and clarify the relationship between bearing strength and damage behavior of two different polymer base matrix and carbon fiber reinforced plastics [2]. Experimental and finite element analyses were used to investigate the influence of the distance from the free edge of plate to the
diameter of bolt hole (E/D) ratio and the width of the specimen to the diameter of bolt holes (W/D) ratios on failure response of bolted single-lap composite joint [3]. The bearing strengths depending on E/D and W/D ratios for different preloading moments such as 0, 2.5, and 5Nm have been determined on glass fiber reinforced epoxy laminates experimentally [4]. Failure behavior of glass fiber-epoxy laminated composite bolted-joints experimentally investigated to obtain the effects of joint geometry, torque and stacking sequence of laminated composite plates on the failure strength, maximum failure load and failure mode [5]. Experimental investigation was carried out for the failure response of bolted glass fiber reinforced-epoxy composite plates at various preload moments, the effects of plyorientations and a range of geometrical parameters [6]. In another study, the behavior of woven glass fiber-epoxy pin joints both numerically and experimentally investigated to the sensitivity of the model to different parameters such as ply orientation and geometry [7]. The influence of the failure criteria and the inclusion of geometric and shear non-linearities is discussed and the proposed model is used to predict the bearing response of composite plates with different stacking sequences [8]. To examine the effect of the preload moment, the edge distance to the pin diameter ratio and the specimen width to pin diameter ratio on the strength of a pinned-joint E-glass/epoxy composite plate another experimental study was carried out [9]. By the way, failure modes of bolted joints in laminated composite plates under tensile loads generally occur in four basic types as cleavage, net-tension, shear-out and bearing modes are shown in Fig. 1 [ASTM D 5961].

Natural-fibre composites combine good mechanical properties with a low specific mass (approximately 1.2± 1.5 g/cm³). But their high level of moisture absorption, poor wettability and an inadequate level of adhesion between untreated fibres and a non-polar polymer matrix lead to debonding with age [10]. On the other hand, many automotive components (interior and exterior) are now made from bio-fibre reinforced composite materials which are mainly based on poly(propylene) with reinforcing bio fibres jute, flax, hemp, kenaf and wood. Of primary importance to the automotive industry is the weight reduction of the components, which is
possible up to 30% when using bio-fibres. Therefore the future opportunities of using biofibres as replacements for glass fibres in automotive applications are enormous [11]. Thus, bio-fibres need to enhance mechanical properties to make possible to use in. In the literature alkali surface treatment seems one of the most efficient methods on the removal of lignin and hemicelluloses from jute fibres [12-18].

The primary objective of the study is to investigate experimentally bolted joints bearing strength and failure mode of natural fibre reinforced epoxy composites. For this purpose alkali surface treated jute fibre/epoxy single bolted joints are produced by VARIM and tested tensile loading conditions according to ASTM D 5961.

2 Materials and Methods

2.1 Production of Specimens

As reinforcement material cross ply jute fabrics was used from local market, Izmir, Turkey. The fabric had 300 g/m² density and five wraps six wefts in 1 cm. XB 3585 ES epoxy resin and 3486 BD hardener by Hunstman was used as matrix material. Mix ratio which was given in datasheet 100 unit of epoxy and 32 unit of hardener by weight. Weight measurement was done by a scale which had 30 kg capacity and 1g accuracy. Composite plates were produced by alkali treated jute fabrics/epoxy. Alkali treatment process was applied by 1% NaOH solution during 2h. After then the fabric was cleaned in distilled water to reach pH value of 7 by checking with litmus papers. An oven was used to drying to the fabrics at 80°C during 2h. Jute/epoxy composite plates were produced by vacuum assisted resin infusion method (VARIM). Lay-ups for the composite production were (0/90°)₈. After resin impregnation curing process was started for 8h at 80°C. Fibre volume fraction of produced composites was calculated according to Eq. (1), [19]. pH7 jute/epoxy had fibre volume fraction of 38%.

\[ v_f = \frac{\rho_c}{\rho_f} \times m_f \]  

(1)

Where; \( \rho_c \) is the composite density, \( \rho_f \) is the fibre density and \( m_f \) is the mass fraction of the fibre.

Specimen dimensions were 135 mm length, 36 mm wide and a 6mm diameter hole was drilled to one side without countersink to at 18mm far from two edges (\( e=\frac{w}{2} \)), Fig. 2. Average thickness of five specimens was 4.6 mm and standard deviation is 0.1.
2.2 Experimental Procedure

Two-piece single-fastener test specimens without support fixture were prepared and tensile tests were applied to pH7 treated jute/epoxy bolted composites according to ASTM D 5961M-13. 6x8 steel bolts, nuts and washer (just at backside of specimens) were used for joints and preloaded at 2.8Nm by a torque meter. Experiments were carried out five times by Shimandzu AG-X 100kN, Fig. 3.

The test machine was equipped with data acquisition systems which records 10 point per second. The crosshead speed of test was chosen 1mm/min. Ultimate bearing strength, bearing strain, sample mean, sample standard deviation and sample coefficient of variation were calculated according to Equation (2)-(4), respectively [ASTM D 5691].
\[
\sigma_{bru} = \frac{F_{\text{max}}}{kDh} \quad (2)
\]
\[
\epsilon_{br} = \frac{\Delta \delta}{Kd} \quad (3)
\]
\[
\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} \quad (4)
\]

Where; \( F_{\text{max}} \) is force at failure, \( k \) is 1 for Procedure B type test (ASTM D 5961), \( D \) is hole diameter, \( h \) is thickness, \( \delta \) is hole displacement, \( K \) is 2 for Procedure B type test (ASTM D 5961), \( x_i \) is measured property, \( n \) is number of specimen.

3. Experimental Results

Alkali treated \([0/90]_8\) lay-up sequences jute/epoxy single bolted composites under 2.8 Nm preload were tested and diagrams are given in Fig. 4-5. It is obvious from the diagrams that after tests started tensile load and bearing stress increase linearly. When the first failure occurred which was matrix failure small amount of load decreased then the loading processes continue until the final failure of composites.

![Figure 4. Tensile load vs. time diagram of pH7 treated jute/epoxy bolted specimens.](image-url)
Tests results of five specimens are given in Table 1. Average ultimate bearing strength and ultimate bearing strain of five jute/epoxy single bolted specimens are 103 MPa and 26.4 %, respectively.

Table 1: Mechanical properties and failure modes of pH7 treated bolted jute/epoxy joints

<table>
<thead>
<tr>
<th>Number of Specimen</th>
<th>Failure Load (kN)</th>
<th>Ultimate bearing strength (MPa)</th>
<th>Ultimate bearing strain (%)</th>
<th>Failure Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.93</td>
<td>104.1</td>
<td>30.0</td>
<td>Net tension</td>
</tr>
<tr>
<td>2</td>
<td>2.60</td>
<td>96.5</td>
<td>25.2</td>
<td>Net tension</td>
</tr>
<tr>
<td>3</td>
<td>2.48</td>
<td>86.1</td>
<td>23.4</td>
<td>Net tension</td>
</tr>
<tr>
<td>4</td>
<td>3.04</td>
<td>112.5</td>
<td>25.2</td>
<td>Net tension</td>
</tr>
<tr>
<td>5</td>
<td>3.20</td>
<td>115.9</td>
<td>28.0</td>
<td>Net tension</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>2.85</strong></td>
<td><strong>103.0</strong></td>
<td><strong>26.4</strong></td>
<td></td>
</tr>
</tbody>
</table>

For an example photograph of 3rd specimen after failure is given in Fig. 6. The failure mode is the net-tension mode [1-9] and the same for all other specimens. There were no delamination seen on the failed region of bolted specimens because the failure occurred by abruptly ruptures.
4. Conclusion

In this study failure behaviour of jute fiber reinforced bolted joints investigated under tensile loading condition. Alkali surface treatment was applied to jute fabric and then pH7 adjusted by distill water. Composite specimens were produced as eight layers orientation angels of biaxial jute fabric \((0/90^\circ)_8\) and epoxy resin by VARIM and approximately 38 % volume fibre fraction achieved. By repeating the test five times stress-strain diagram, average ultimate strength and strain values obtained. From the obtained results it can be concluded that:

- Jute fiber reinforced epoxy composites show 103 MPa average ultimate bearing strength and 26 % average ultimate bearing strain with parameters of \(e/D=3\), \(w/D=6\). Although ultimate bearing strength seems less value than E-glass/epoxy bolted composite, green composites still under demand of various industries.
- Further study will be focus on variety of different surface treatment conditions on jute fibres such as different pH values or treatment durations to obtain as close as E-glass/epoxy bearing strength.

Figure 6. The failure mode of 3rd specimen.
5. References


EFFECT OF POLYMER CONCENTRATION ON THE RELEASE CHARACTERISTICS OF THYME OIL MICROCAPSULES

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Abstract: Essential oils have been used as food preservatives due to their antioxidant, antimicrobial and anti-insect properties. However, one of the limitations of using essential oils as active agents is their volatility. In this research thyme oil containing gelatin/acacia gum microcapsules were prepared by complex coacervation and the effects of variations in gelatin/acacia gum concentrations of thyme oil loaded microcapsules were examined. Effect of variations in gelatin/acacia gum ratio, on the oil load (%), oil content (%), encapsulation efficiency (%) and release rate of thyme oil from microcapsules were determined. The thyme oil-loaded microcapsules were smooth and spherical in shape as revealed by scanning electron micrograph. Results of Fourier transform infrared spectroscopy indicated stable character and showed the absence of chemical interaction between the thyme oil and gelatin/acacia gum blends.

Keywords: Gelatin, acacia gum, complex coacervation, microencapsulation, release rate

1. Introduction

Essential oils, commonly used as fragrances and flavoring agents for foods and beverages, are gaining great popularity and scientific interest in the agricultural and pharmaceutical industries because of their natural and safe status [1,2]. The excessive and indiscriminate use of synthetic chemically synthesized preservatives has resulted in a growing number of severe problems of antimicrobial resistance and environmental pollution with potential risks to human health. In recent years, there has been an increasing interest in the uses of essential oils for their various functional properties such as environmentally friendly, biodegradable, antibacterial, antifungal, and antioxidant [1,3]. Thyme essential oil, which is extracted from Thymus vulgaris L., is used in medical and pharmaceutical industries as well as in flavor and food industries [1,4]. One of the limitations of using essential oils as active agents is their high volatility and chemically unstable in the presence of air, light, moisture and high temperatures [1,5,6]. As a result, increasing their activity and stability using microencapsulation technique by polymeric wall materials has always been considered crucial in order to improve their functional characteristics and minimize environmental damage, thus providing them with a longer shelf life [1,4].
Microencapsulation is defined as an effective method for the oxidative stabilization of edible oils, and is widely used in the food industry in order to achieve various goals: protect sensitive ingredients from oxidation or hydrolysis, mask unpleasant taste, transform liquid droplets into solid particles, and allow controlled release of food additives [7,8]. It is required that the polymer shell or walls is thick and rigid in order to ensure an efficient separation of the inner core and the surrounding medium, slow down the diffusion of the active ingredient to the external medium, and build a mechanically rigid layer that provide a powder consistency to the dry microcapsules [2,7]. Microencapsulation most often relies on building a continuous coating of polymer wall around core material [7,14].

Numerous techniques for microencapsulation for various core materials have been reported in the literature. Among the microencapsulation methods, complex coacervation is the most commonly used to produce microcapsules [1,2,9]. The major advantage of complex coacervation over other methods is its very high payload (up to 99%) and controlled release possibilities [8]. Encapsulation by complex coacervation consists in the precipitation of an insoluble material, a coacervate, and its deposition at the surface of oil droplets so as to build a wall of polymer material [7]. Complex coacervation is a phase separation phenomenon induced by electrostatic interactions between polymers of opposite electrical charge, most often biopolymers such as proteins and polysaccharides [7,8]. Complex coacervation takes place in the mixed solution of two polymers when a shift of the pH across the isoelectric point of one polymeric partner leaves the two polymers with opposite electrical charges. The association of the macromolecules induces the formation of insoluble complexes that undergo an associative phase separation into liquid droplets made of water-swollen complex species [7].

The microcapsule wall material can be formulated by using a wide variety of materials including natural and synthetic polymers [2]. The selection of the microcapsule wall material is of the utmost importance, as its constitutes the main critical point for providing stability and cost efficiency to the system and must be compatible with the microencapsulating technique followed [2]. Gelatin is an abundant protein which is biocompatible, biodegradable, edible and soluble at the body temperature and therefore it is an ideal material for food and pharmaceutical applications [2,11]. Acacia gum is a complex polysaccharide composed of three distinct fractions with variable protein contents as well as molecular weights [20]. Gelatin/acacia gum system is the oldest polymeric wall materials for complex coacervation process where its use as a delivery matrix has many advantages including its abundance and its biodegradability [7,8]. Gelatin/acacia gum coacervates exhibit a wide range of useful functionalities for the development of food products such as thickening, gelling, foaming and emulsifying abilities [12].
The current study was set to evaluate the effect of variation of gelatin/acacia gum ratio on the oil load (%), oil content (%), encapsulation efficiency (%) and release rate of thyme oil from gelatin/acacia gum microcapsules.

2 Materials and Methods

2.1 Materials

Gelatin from bovine skin, type B with gel strength of approximately 225 g bloom, acacia gum, thyme oil, tannic acid and Tween 80 were purchased from Sigma-Aldrich. Double-distilled water was used throughout the study. Other reagents used were of analytical grade.

2.2 Methods

2.2.1 Preparation of microcapsules

Aqueous solutions gelatin 3 %(w/w) and acacia gum 3 %(w/w) were prepared at ambient temperature under magnetic stirring. 100 mL of gelatin dispersion was heated at 55 °C under moderate stirring rate (300 rpm); 10 g of thyme oil were added into the solution of gelatin and emulsified for 15 min at 1000 rpm. After the formation of the emulsion, 100 mL of hot acacia gum solution was added into the emulsion at the stirring speed of 300 rpm. The pH was 5.0 at this stage. The pH of the mixture was adjusted to 4.0 with 10% (v/v) acetic acid followed by stirring the mixture. After coacervate microcapsules have been observed by optical microscopy, the solution was cooled down to 5 °C. An appropriate volume of 10% (w/w) aqueous solution of tannic acid was finally added to the system and the temperature was increased to 25 °C. After a cross-linking time of 2.5 h, stirring was stopped, the microcapsules were allowed to cream to the top, they were collected, rinsed with deionized water and kept in aqueous suspension for storage.

2.2.2 Calibraton curve of thyme oil

A calibration curve is required for the determination of encapsulation efficiency and release rates of the thyme oil from microcapsules. A known concentration of thyme oil containing 0.3% Tween 80 in double distilled water was scanned in the range of 200–500 nm by using UV visible spectrophotometer (UV 1601 Shimadzu). For thyme oil having concentration in the range 0.05–5 g/100 mL, a prominent peak at 230 nm was recorded. The absorbance values at 230 nm obtained
with the respective concentrations were recorded and plotted. From the calibration curve, the unknown concentration of thyme oil was obtained by knowing the absorbance value.

2.2.3 Determination of the oil load, oil content and encapsulation efficiency

1.0 ± 0.001 g of accurately weighed microcapsules completely crushed in a porcelain mortar was carefully placed in a volumetric flask containing 100 ml of 0.3% Tween 80 (in distilled water). The flask was shaken all night in a shaker to ensure complete extraction of oil in Tween 80 solution. The encapsulation efficiency (%), oil content (%), and the oil load (%) were determined using the calibration curve and the following formulae [2]. Three parallel experiments were conducted and data were expressed as mean ± standard deviation.

Oil load (%) = \( \frac{w_2}{w_3} \times 100 \)

Oil content (%) = \( \frac{w_1}{w} \times 100 \)

Encapsulation efficiency (%) = \( \frac{w_1}{w_2} \times 100 \)

where \( w \) = weight of microcapsules; \( w_1 \) = actual amount of oil encapsulated in a known amount of microcapsules; \( w_2 \) = amount of oil introduced in the same amount of microcapsules; \( w_3 \) = total amount of polymer used including crosslinker.

2.2.4 Oil release studies

The rate of thyme oil released from gelatin/acacia gum microcapsules prepared with three different gelatin/acacia gum ratios were determined as a function of time using a UV-VIS spectrophotometer. A known quantity of microcapsules was placed in the Erlenmeyer flask with 0.3% Tween 80 and shaken at room temperature. After filtering the 5 ml microcapsule-Tween 80 mixture at appropriate time intervals, oil release rate at the fixed \( \lambda_{\text{max}} \) value of 230 nm was measured. In order to keep the volume of the microcapsule-Tween 80 mixture constant, the 5 ml 0.3% Tween 80 solution was transferred back into the Erlenmeyer flask after the UV measurements. All experiments were carried out in triplicate and expressed as mean values plotted with standard deviation errors.
2.2.5 Microscopy studies

Electron microscope images of the gold-palladium coated microcapsules were obtained with a Philips XL-30S FEG scanning electron microscope.

2.2.6 FTIR study

Fourier transform infrared (FTIR) spectra of gelatin, acacia gum, thyme oil and microcapsules were characterized by FTIR spectrometer (Perkin-Elmer Spectrum BX) in the frequency range of 4000-650 cm\(^{-1}\) using the attenuated total reflection (ATR) method.

3 Results and Discussion

3.1 Effects of variation of gelatin/acacia gum ratio

Three sample formulations (F1, F2, F3) of microcapsules with different gelatin/acacia gum concentrations were fabricated, and the oil load (%), oil content (%) and encapsulation efficiency (%) results are summarized in Table 1.

<table>
<thead>
<tr>
<th>Sample Formulations</th>
<th>Oil load (%)</th>
<th>Oil content (%)</th>
<th>Encapsulation efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>244.14</td>
<td>48.80 ± 1.53</td>
<td>52.58 ± 1.34</td>
</tr>
<tr>
<td>F2</td>
<td>244.14</td>
<td>54.46 ± 1.88</td>
<td>55.28 ± 1.28</td>
</tr>
<tr>
<td>F3</td>
<td>244.14</td>
<td>65.47 ± 1.26</td>
<td>70.09 ± 1.86</td>
</tr>
</tbody>
</table>

*Total polymer = 6 g; tannic acid = 10 ml; thyme oil = 10 ml; water = 100 ml; Temperature = 42 ± 1 °C.

An examination of the values obtained reveals that, as the gelatin concentration increased in the gelatin/acacia gum ratio, the oil content (%) and encapsulation efficiency (%) values of the microcapsules increased (Table 1).

3.2 Oil release studies
Thyme oil release profiles of microcapsules examined are displayed in Figures 1. From Figure 1, it can be seen that thyme oil release (%) from gelatin/acacia gum microcapsules is characterized by two different phases. Initially, all sample formulations (F1, F2, F3) demonstrated an initial burst release of about 15-20% of thyme oil up to 0-75 min, followed by a gradual and sustained release phase for the following 72 h. This initial fast release might be the result of oil absorbed on the capsule surface [15,16]. After the burst release period, the release mechanism of thyme oil from the gelatin/acacia gum complex was significantly reduced. The burst effect can be due to volume expansion polymer when immersed in liquid media [17].

![Figure 1](image)

Figure 1 The effect of variations in gelatin/acacia gum ratio on the release rate. (♦) F1; (■) F2; (◄) F3.

The release rate data in Figure 1 indicates that microcapsules containing higher amount of gelatin concentration in gelatin/acacia gum ratio exhibited more prolonged release rates than those containing a lower amount of gelatin. The oil release from microcapsules is quite fast and large at small amounts of gelatin (F1), whereas release is slower at higher amounts of gelatin (F3).
3.2 Structure of microcapsules

The morphology of gelatin/acacia gum microcapsules has been studied by means of scanning electron microscopy. From the scanning electron microscopy micrograph shown in Figure 2, it was observed that dried capsules after the lyophilization process have a spherical form without forming agglomerations. The microcapsules had continuous walls with no cracks or apparent porosities, indicating that the lyophilization process was adequate, since it did not cause damage to the particles. These results are consistent with reports from other researchers [18,19].

![Figure 2 Scanning electron microphotograph of microcapsules (650 X magnification).](image)

3.3 Fourier Transform Infrared (FTIR) study

The compatibility of thyme oil with gelatin/acacia gum polymers was evaluated through FTIR analysis. FTIR spectra of gelatin (a), acacia gum (b) and thyme oil (c) and thyme oil containing gelatin/acacia gum microcapsules (d) are shown in Fig. 3.
In our study, it was found that the strong absorption peak of the thyme oil was at a wavelength of 1733 cm\(^{-1}\) in the FTIR spectrum. Gelatin is an amphoteric polymer composed of different molecular weight polypeptide and acacia gum is a highly branched polysaccharide composed of L-arabinose, L-rhamnose, D-galactose and D-glucuronic acid [18]. FTIR spectrum of gelatin (Fig. 3a) revealed the presence of characteristic functional group at 3435 cm\(^{-1}\) for amino group and other notable peaks observed by its carbonyl peak and amino band appeared at 1642 cm\(^{-1}\) and 1547 cm\(^{-1}\), respectively. The bands of acacia gum at 1025 cm\(^{-1}\) are belongs to asymmetric stretching of C–O–C structure. In the FTIR spectrum of the gelatin/acacia gum microcapsules containing thyme oil as shown in Figure 3, the carbonyl stretching bands of the thyme oil remain unchanged at a wavelength of 1733 cm\(^{-1}\). Therefore, it was concluded that the thyme oil was encapsulated successfully by the gelatin/acacia gum, and that gelatin/acacia gum microcapsules containing thyme oil were obtained. Further, the appearance of a new band in the microcapsules at 1539 cm\(^{-1}\) indicated the formation of gelatin/acacia gum polyelectrolyte complex. It was also found that there was no significant interaction evident between the thyme oil and the gelatin/acacia gum complex.

4. Conclusion

The control of the complex coacervation requires that each step is mastered since all of the different steps have a significant impact on the final properties of the microcapsules. In this study, the production parameters for gelatin/acacia gum complex membrane microcapsules, and the release effects of encapsulated thyme oil with variation of gelatin/acacia gum ratio investigated. The microcapsules exhibit higher oil content (%) and encapsulation efficiency (%) values and prolonged release with the increase of gelatin concentration in the gelatin/acacia gum ratio. Analyses by scanning electron microscopy have confirmed the spherical nature of the microcapsules. FTIR study shows that there was no significant interaction between thyme oil and the gelatin/acacia gum complex, and that there was an interaction between gelatin and acacia gum during the formation of polyelectrolyte complex.
5. References


SYNTHESIS AND CHARACTERIZATION OF ZN$_{0.98}$AL$_{0.02}$O
POWders BY SOL-GEL METHOD

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Abstract: In this paper, synthesis and characterization of Zn$_{0.98}$Al$_{0.02}$O powders were systematically investigated by sol-gel method for high temperature thermoelectric generator applications. Solution characteristics were examined by Turbidity and pH measurements using turbidimeter and pH meter. Thermal properties of the powders were characterized by Differential Thermal Analysis-Thermogravimetry (DTA-TG) in order to obtain appropriate calcination regime. Structural properties of the powders were fulfilled by X-ray Diffraction (XRD). X-ray Photoelectron Spectroscopy (XPS) was used to specify chemical composition and empirical formula of the elements existed within the powders. According to the DTA-TG results, process optimization was performed by clarifying temperatures of drying, oxidation and phase transformation processes. DTA curve exhibited that endothermic and exothermic reactions take place between temperatures of 200 °C and 345 °C. XRD study confirmed that the powders consist of Zn$_{0.98}$Al$_{0.02}$O phase. It can be seen from the phase spectrum that 2θ peaks are matching with typical ZnO peaks (periclase, JCPDS: 01-089-1397) and compatible with the literature.

Keywords: Sol-gel processes, photoelectron spectroscopies, thermal analysis, X-ray diffraction

1. Introduction

Thermoelectric (TE) materials have become important in terms of thermoelectric power generation applications because of converting waste heat directly into electricity [1]. Recently, TE modules composed of intermetallic compounds have been delayed for high temperature applications due to problems of their low decomposition temperatures, including harmful elements, and their cost. On the other hand, oxide TE materials have attracted much attention extinguishing these problems for high temperature thermoelectric generator (TEG) applications [2]. Among oxide TE materials, Ca$_3$Co$_4$O$_9$ [3] and ZnO [4] have become important candidates for p- and n-type TE materials because of their high figure of merit (ZT) at high temperatures. In the last few decades, many studies have been implemented in order to enhance ZT of these materials. The major approach to enhance ZT in bulk materials has been doping techniques [5]. Through these studies, highest ZT values for bulk oxide TE materials have been obtained as 0.5
at 1000 K and 0.65 at 1247 K for p-type Ca$_2$.7Ag$_{0.3}$Co$_4$O$_9$/Ag-10 wt.% composite [6] and n-type Zn$_{0.96}$Al$_{0.02}$Ga$_{0.02}$O [7], respectively.

Over the past decades, many synthesis methods of solid state reaction method [8], self-ignition method [9], combustion synthesis method [10], and sol-gel method [11] have been used to synthesize Ca$_3$Co$_4$O$_9$ and ZnO powders. Through these methods, sol-gel synthesis has many advantages of better stoichiometry control and homogeneity, low reaction temperature and process cost, easier process and possibility to use high-purity precursors [12].

In this study, ZnO was doped with Al using sol-gel method for the first time to enhance its thermoelectric properties for TEG applications. Synthesis and characterization of Zn$_{0.98}$Al$_{0.02}$O were methodically fulfilled using Zn and Al based precursors, and solutions of these precursors were prepared with their solvents and chelating agents. Methodology of this paper shall be presented in the way of identification of solution characteristics, process regime, structural properties and elemental composition. Within this context, solution characteristics were investigated by pH and turbidity measurements. Thermal properties of the powders were characterized by Differential Thermal Analysis-Thermogravimetry (DTA-TG) in order to obtain appropriate calcination regime. Structural analysis of the Zn$_{0.98}$Al$_{0.02}$O powders was carried out using X-ray Diffraction (XRD) and results were compared with literature. In addition, X-ray Photoelectron Spectroscopy (XPS) was used to specify elemental composition and empirical formula of the elements found in the powders.

2 Experimental Procedure

Synthesis of Zn$_{0.98}$Al$_{0.02}$O powders by sol-gel method was executed by that way: First of all, all the precursors were dissolved in their solvents and solutions of the precursors were prepared adding their chelating agents. Characteristics of the solutions were investigated by pH and turbidity measurements. After gelation process, xerogel was dried at 200 °C for 2 h and powders were obtained. Hereafter, DTA-TG analysis were achieved to specify thermal attributes of the powders and XRD analysis were managed to state structural analysis. Finally, elemental composition of elements within the powders was assigned by XPS.

So as to fabricate 0.1 mole of Zn$_{0.98}$Al$_{0.02}$O powders, precursors of N$_2$O$_6$Zn.6H$_2$O (99%, Alfa Aesar) and Al(NO$_3$)$_3$•9H$_2$O (Alfa Aesar) were used in stoichiometric ratios and amounts of the precursors, solvent and chelating agent were given in Table 1. Distilled water was used as the solvent to dissolve precursors. The solutions were magnetically stirred at 100 °C to get
homogeneous solutions and glacial acetic acid was added as the chelating agent for gelation process. After gelation, obtained xerogel was dried at 200 °C for 2 h and residual constituent and undesired gases such as HCl were taken away by the drying process.

Table 1. Stoichiometric ratios used for 0.1 mole of Zn$_{0.98}$Al$_{0.02}$O powders.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Molecular Weight (g/mole)</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc nitrate hydrate</td>
<td>297.47</td>
<td>29.1521 g</td>
</tr>
<tr>
<td>Aluminum nitrate nonahydrate</td>
<td>375.13</td>
<td>0.7503 g</td>
</tr>
<tr>
<td>Distilled water</td>
<td>18.00</td>
<td>200 ml</td>
</tr>
<tr>
<td>Glacial acetic acid</td>
<td>60.05</td>
<td>20 ml</td>
</tr>
</tbody>
</table>

A turbidimeter and a pH meter were used to ascertain the turbidity and pH values of the solutions, respectively, to specify the solution characteristics. Turbidity of the solutions were measured by a VELP TB1 model turbidimeter and 0-1000 ntu (nephelometric turbidity unit) was measurement range for the turbidity measurement. After the dispersion process, acidic and basis characteristics of the final solution was determined by measuring its pH value using a WTW Inolab pH 720 model pH meter.

DTA-TG analysis was carried out from ambient temperature to 800 °C in air atmosphere with a heating rate of 10 °C/min by a Perkin Elmer STA 6000 model DTA-TG instrument to define thermal behavior of the dried Zn$_{0.98}$Al$_{0.02}$O powders. With DTA-TG analysis, solution evaporation, decomposition and phase formation of the powders were procured. Before performing XRD analysis, the powders were calcined at 600 °C for 4 h in order to obtain final sol-gel processed powders. Phase structure of the Zn$_{0.98}$Al$_{0.02}$O powders was identified by a Thermo Scientific ARL model X-ray diffractometer. While executing this analysis, Cu K$_\alpha$ irradiation (wavelength, $\lambda = 1.540562$ Å) was used to record XRD pattern in the range of $5^\circ \leq 2\theta \leq 90^\circ$ at a speed of 2°/min. A Thermo Scientific K-Alpha model XPS device was used to specify elemental composition and quantities of the elements existed within the powders with an Al K$_\alpha$ X-ray source between the energy range of 0-1350 eV.
3 Results and Discussion

Turbidity measurements are important in terms of describing if powder precursors are dissolved completely in solutions or not by inspecting ntu values of the solutions between the turbidity range of 0-1000 ntu. If the turbidity value approaches to 0, it is said that the powder precursors are dissolved very well in solutions and a homogeneous solution has been obtained; if the turbidity value approaches to 1000, it is said that the powder precursors are not dissolved completely in solutions [13]. Besides, the pH value of the solution affects the formation of the gel and it should be regarded during the preparation of the solution. In this study, turbidity and pH values of the prepared solution were 0.32 ntu and 1.13, respectively, and given in Table 2. The turbidity result of the solution in this study means that the precursors were dissolved very well in the solution. The pH value of the solution explains that the solution in this case shows acidic characteristics and a branched structure is formed during the gelation process.

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>Turbidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$<em>{0.98}$Al$</em>{0.02}$O</td>
<td>1.13</td>
<td>0.32 ntu</td>
</tr>
</tbody>
</table>

Powders dried at 200 °C for 2 h in air were heated with an increment of 10 °C per minute in air atmosphere until 900 °C and results of their thermal behavior is shown in Fig. 1. DTA curve in the figure exhibited that since the powders were dried at 200 °C, endothermic and exothermic reactions take place between the temperatures of 200 °C and 345 °C. One of the biggest endothermic peaks between 200 °C and 250 °C is regarded to burning out of organic groups with C based materials. The other biggest endothermic peak between 260 °C and 300 °C is oxidation peak of Zn and Al. A significant weight loss starts with the temperature of 200 °C with respect to these peaks and continues until 345 °C with a weight value of 60%. Phase formation of Zn$_{0.98}$Al$_{0.02}$O powders starts after 345 °C on the DTA curve and any weight losses is not observed after this temperature.
XRD pattern of Zn$_{0.98}$Al$_{0.02}$O powders manufactured by sol-gel method is depicted in Fig. 2. Sharp diffraction peaks showed that crystalline structure of Zn$_{0.98}$Al$_{0.02}$O particles was excessively formed. It can be seen from the phase spectrum that 2θ peaks at 31.70°, 34.36°, 36.20°, 47.48°, 56.54°, 62.82°, and 67.90° correspond to typical ZnO peaks (periclase, JCPDS: 01-089-1397) and compatible with the literature [10]. Any other phases were not observed in the detection of diffractometer. In addition, using the intensities of the primary peaks of reflection at 2θ=36.20°, average crystalline size of Zn$_{0.96}$Al$_{0.02}$O particles were determined by the Debye-Scherer equation [14] that is $D = 0.9\lambda/\beta\cos\theta$. Here, $D$ is the average crystalline size, $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half the maximum intensity, and $\theta$ is the Bragg’s diffraction angle. Using this equation, average crystalline size of the Zn$_{0.98}$Al$_{0.02}$O particles was calculated as 55.7 nm.
A broad scan XPS spectra of Zn$_{0.98}$Al$_{0.02}$O powders was evaluated within the range of 0-1350 eV with an energy step size of 1.0 eV and is given in Fig. 3. Sharp peaks corresponding to Zn, Al, and O can be seen from the spectra confirming the presence of these elements in the powder sample. Moreover, Table 3 gives elemental ID and quantification of Zn$_{0.98}$Al$_{0.02}$O powders including binding energies (BE) in eV for the components of Zn2p3, O1s, and Al2p, with their corresponding full-width at half maximum (FWHM) accompanying the respective atomic concentrations. It can be noticed from the table that binding energies which Zn, O, and Al are formed at are 1022.74 eV, 532.51 eV, and 76.21 eV, respectively. Although the peaks in the XRD pattern show pure ZnO, presence of Al dopant can be detected in the XPS spectra. Hence, doping of Al into ZnO was achieved.

Table 3. Elemental ID and quantification of Zn$_{0.98}$Al$_{0.02}$ powders.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position BE (eV)</th>
<th>FWHM (eV)</th>
<th>Area (cps eV)</th>
<th>Amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn2p3</td>
<td>1022.74</td>
<td>1.778</td>
<td>532796.03</td>
<td>32.35</td>
</tr>
<tr>
<td>O1s</td>
<td>532.51</td>
<td>3.498</td>
<td>226537.41</td>
<td>57.63</td>
</tr>
</tbody>
</table>
Al2p | 76.21 | 3.721 | 9122.25 | 10.02

Fig. 3. Wide survey XPS spectra of Zn_{0.98}Al_{0.02}O powders.

4. Conclusion

In this study, Zn_{0.98}Al_{0.02}O material for high temperature thermoelectric applications was successfully synthesized using sol-gel method. In order to specify the solution characteristics, results of the turbidity and pH measurements showed that the precursors were dissolved excellently in the solutions and a branched structure was formed during the gelation process. According to the DTA-TG results, endothermic and exothermic reactions took place between the temperatures of 200 °C and 345 °C in terms of thermal behavior of the Zn_{0.98}Al_{0.02}O powders dried at 200 °C. On the other hand, a notable weight loss occurred in the same temperature interval until the weight value of 60%.

Phase formation of Zn_{0.98}Al_{0.02}O powders started after 345 °C as seen on the DTA curve. High diffraction peaks in the XRD pattern of Zn_{0.98}Al_{0.02}O powders showed that crystalline structure of Zn_{0.98}Al_{0.02}O particles was excessively formed and 2θ peaks corresponded to typical ZnO peaks (periclase, JCPDS: 01-089-1397) compatible with the literature. In addition, average crystalline size of the Zn_{0.98}Al_{0.02}O particles was calculated as 55.7 nm. The peaks corresponding to Zn, Al, and O in the wide survey XPS spectra of Zn_{0.98}Al_{0.02}O powders verified the presence of these elements in the powder sample. Although
the peaks in the XRD pattern showed pure ZnO, presence of Al dopant could be detected in the XPS spectra. As a result, manufacturing of Zn$_{0.98}$Al$_{0.02}$O material for high temperature thermoelectric applications was succeeded with Al doping.

5. References


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Acknowledgements

This work was promoted by the Center for Production and Application of Electronic Materials (EMUM) in Dokuz Eylul University in Izmir, Turkey. Financial part of the study was compensated by the Scientific and Technological Research Council of Turkey (TUBITAK) under the project numbered 115M579.
**ABSTRACT:** Silicon is the essential material in solar cell application and the production of solar cell has many exhausting steps such as CZ process, diamond wire saw, lapping, polishing, dicing, texturing, formation of p-n junctions, metallization. Texturization step has a critical factor on the reflectance performance of the silicon solar cell efficiency. However, diamond wire saw, lapping and polishing steps are consuming too much time, material and requiring high technological equipment before the texturing process. Therefore, preparation cost of wafers for the texture step is increasing extremely. In this study we have determined the cutting parameters in order to obtain smoother surface after the diamond wire saw. Furthermore, instead of chemical mechanical lapping and polishing process, we applied a chemical polishing process in order to decrease the duration and consumed material. Chemically polished wafers are exposed to micro etching. Reflectance and SEM measurements are employed in the study and reflectance results are satisfactory and micro pyramids are obtained uniformly.

**Keywords:** Solar cell, silicon wafer, lapping, polishing, slicing, chemical polishing, texturing

1. Introduction

In the last few years there are many researches about the improving the solar cell performance. The most common methods are based on the reducing the reflection ratio and increasing the light trapping because the reflection and the light trapping are two essential parameters effect the solar cell efficiency[1]. Obtaining a good surface without cracks and defects is very important of the texture step in order to decrease the reflection and increase light trapping.

Conventional silicon solar wafer production starts with the Czochralski (CZ) process including melting and re-solidification of pure silicon after diced as 200-350 microns thick wafers by using diamond wire saw[2]. Cutting the wafers by diamond wire saw is now widely used in the wafering process, applied by a steel wire with abrasive slurry [3-5]. At this step, diamond wire saw is damaging the surface and creating some cracks or defects at the surface of the wafer while cutting the silicon ingot. This causes the breakage of the wafer during the cutting process or creating weak regions for next processes[4].
The saw damage must be removed by chemical or mechanical remove methods. Mechanical methods are required both of technological equipment and people for using these mechanical systems. In mechanical methods firstly, surfaces of the wafers are lapped on the lapping and polishing system. There could be several problems such as un-lapped parts of surface, arranging difficulties in speed of rotation and quantity of the supplied abrasive slurry. Also high consumption of the expensive slurries and long duration of the lapping generate additional problems. Furthermore, thin wafers in the lapping machine are broken into pieces due to the pressure of lapping machine.

After the lapping step, polishing is applied in order to obtain a mirror like wafer surface. During the polishing process another expensive slurry is supplied to the system. Also the risks in the lapping process are always valid for the polishing process. All these problems cause high cost,

Figure 1. The cost distribution for a typical installation of a silicon solar system [2]

long duration and much material consumption for the next studies, lose so many wafers before the further processes and waste so much time of the researchers.

An enormous deal is existing in order to reduce the materials and manufacturing costs PV systems to provide economic sustainability [6]. Figure 1 gives some opinions about the cost distributions of the steps for PV systems. It shows that ingot/wafer and cell production occupy the biggest ratio in the pie[2]. This paper investigates the alternative ways of to decrease the biggest cost ratios of the cost pie such as wafer production and cell manufacture in order to obtain high quality wafer surface for micro texturization of solar cell applications. First of all, the parameter study of the diamond wire saw was done and the optimum cutting parameters were obtained. Secondly one group wafer subjected to lapping and polishing processes and optimum parameters were obtained, another group wafer was subjected to chemical polishing. Lastly all wafers were textured in order to obtain high quality wafer surface for solar cell applications. The results of the two groups are compared.
2. Experimental

Preparing a silicon wafer in order to build a solar cell requires several processes. Firstly, diamond wire saw damages have to be minimum in order to decrease lapping duration and consumption of lapping liquid[7]. In this step n type mono crystal silicon ingot in 100 mm diameter and STX 1202 diamond wire saw machine were used. Several cutting processes were performed in order to obtain the optimum surface roughness due to the slicing duration have been performed under different z axis speed conditions. For the spool speed the maximum capacity of the cutting machine is applied. Dogit cutting oil was used as coolant supplied on the diamond wire. The coolant oil was applied as a mixture of DI water and oil with the ratio of 7:3. Z axis speed, wire spool speed of the cutting processes are given in Table 1. Cutting cycle is scheme of the STX 1202 is given in Figure 2.

Table 1: Z axis speed, wire spool speed and duration of the processes

<table>
<thead>
<tr>
<th>Z axis (mm/min)</th>
<th>0.55</th>
<th>0.6</th>
<th>0.65</th>
<th>0.7</th>
<th>0.75</th>
<th>0.75</th>
<th>0.8</th>
<th>0.85</th>
<th>0.9</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spool (m/s)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

During the lapping and polishing step Logitech lapping and polishing machine is used. For the abrasive slurry alumina powder (Al₂O₃) was mixed with diluted water 1:10 by volume. For the experimental process of the polishing process 3-micron particle size cerium oxide (CeO₂) is solved in deionized water in the volume ratio of 9,5% and applied on the plate at 10 ml/min flow rate[7].

![Figure 2. Schematically presentation of diamond wire cutting system](image-url)
The first group wafers subjected to micro texture process after the lapping process the second group wafers are subjected to micro texture process before the lapping and polishing process.

After a good cutting, lapping and polishing of the double surfaces of the wafers are textured. Before the texturization the wafer is diced into 20 mm square pieces in dicing machine and cleaned in acetone and HF. First group the dice sized wafer pieces was boiled in NaOH-IPA solution for 30-45 minutes in 80-90°C[8]. Second group wafers are subjected to chemical saw damage removal in high concentrated NaOH solution in order to remove most of the damages. Then the wafers subjected to texturing process same as the first group. The all application steps are summarized in Figure 3.

![Figure 3. Application steps of the preparing solar wafer](image_url)

The surface qualities of the two groups were characterized by the way of measurements of reflectance and scanning electron microscope (SEM).

### 3. Results and Discussion

Diamond wire saw experiments showed that increasing spool speed and decreasing z axis speed are decreasing the surface roughness. Low roughness values are also decreasing the lapping and the polishing duration. Also z axis speed determines the cutting duration. On the other hand, the roughness values are determining the lapping and the polishing duration. When z axis speed exceeds 2 mm/min, the roughness values increased extremely and wafer breakages occurred. In addition, deep wire prints were formed and corrugated view is obtained. Finally exceeding 2 mm/min x axis speed is not only decrease and deforms the surface, but also extremely increase
the lapping and the polishing duration due to the deep wire prints and corrugated shape. Another disadvantage was increasing z axis speed more than 4 mm/min was caused increasing the stress of the diamond wire resulted partition. So there is existing a requirement to determine the minimum duration and minimum material consumption point. Table 2 shows the all the time durations in the minimum surface roughness.

Table 2: Z axis speed, wire spool speed and duration of the cutting lapping and polishing processes

<table>
<thead>
<tr>
<th>Cutting Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z axis (mm/min)</td>
<td>0.55</td>
<td>0.6</td>
<td>0.65</td>
<td>0.7</td>
<td>0.75</td>
<td>0.75</td>
<td>0.8</td>
<td>0.85</td>
<td>0.9</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Spool (m/s)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Cutting Duration (min)</td>
<td>182</td>
<td>167</td>
<td>154</td>
<td>143</td>
<td>134</td>
<td>134</td>
<td>125</td>
<td>118</td>
<td>112</td>
<td>100</td>
<td>50</td>
<td>33</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>Lapping Duration (min)</td>
<td>30</td>
<td>35</td>
<td>40</td>
<td>45</td>
<td>50</td>
<td>55</td>
<td>60</td>
<td>55</td>
<td>50</td>
<td>40</td>
<td>30</td>
<td>60</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>Polishing Duration (min)</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Final Polishing Duration (min)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Total Duration</td>
<td>262</td>
<td>252</td>
<td>244</td>
<td>238</td>
<td>234</td>
<td>239</td>
<td>235</td>
<td>223</td>
<td>212</td>
<td>190</td>
<td>130</td>
<td>143</td>
<td>150</td>
<td>160</td>
</tr>
</tbody>
</table>

Lapping time durations under the conditions number 1 and the number 11 are obtained exactly same. This shows that the surface roughness values are almost equal of these two experiment. But duration of 1st cutting condition is so long and the total process duration is extremely high. This causes also so much material consumption. After the 2 mm/min z axis speed although the cutting duration decreasing, lapping duration starts to increase seriously. According to the results in Table 2, optimum cutting parameter was obtained in the 11th cutting condition in terms of surface quality, duration and material consumption.

Second group wafers are cut with parameters determined above and subjected chemical to saw damage removal (SDR) process instead of mechanical damage removal process (Lapping and polishing). Wafers are firstly cleaned followed texturing process in high concentrated 80°C NaOH or KOH solution 10 minutes in order to remove most of the saw damages[9]. After the SDR standard texturing process is applied explained in the several other researcher’s studies before[9-12]. After the micro etching processes, SEM measurements and reflectance measurement have been done in order to understand the effect of the surface shape on the reflectance performance. At the end of micro texture processes, the uniform pyramidal shapes are covered the surface of the cell in the dimensions of 1.5-2.5 micrometers wide and height for
the two wafer groups. Figure 4 gives the reflectance values and figure 5 and 6 show SEM views of the two wafer groups respectively.

Figure 4. Reflectance values of two wafer groups

Figure 5. SEM view of the first wafer group

Figure 6. SEM view of the second wafer group
According to reflectance measurements given in Figure 4 the slopes seem almost identical for the two wafer groups. The green slope is representing the reference wafer surface polished mirror like and not exposed to texture. Between 300 and 400 nanometers reflectance values are decreasing sharply but after the 400 nm there is a slight change until the 800 nm and approach to %13 for the two groups. Finally, there is no difference between the mechanical polishing and the chemical polishing in points of the reflectance and the SEM views.

During the experiments there are important points to be considered while using the cutting machine, lapping and the polishing machine and the application of the texturing process. After every step the wafers must be cleaned in HF and diluted water. Dirty initial surface causes such cloudy viewed surface. The wafer never removed from the tool in the whole lapping and polishing steps in order not to lose the orientation of the wafer between the table of the machine. Removing the wafer during the processes from the tool causes unpolished final surface. Diluted water should be used in every cleaning and preparing solution steps.

4. Conclusion

In this study firstly optimum cutting parameters are determined for the STX 1202 cutting machine. After wafers investigated in two group. First group is subjected to lapping and polishing procedure and then textured. Second group is subjected to chemical polishing process. The results are compared in the point of the duration, reflectance and the SEM measurements. The experiment and the measurements showed that chemical polishing method is more profitable and easy because of the obtaining the same reflectance values, low material and time consumption. The results showed that in order to obtain approximately %13 reflectance value and homogeneously distributed pyramids on the surface, chemical polishing method is very useful and sufficient due to the reasons mentioned above. This experimental study will be a short road map for the researchers who study about decreasing the reflectance of the silicon solar cell.

References


**Acknowledgements**

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AN INFLUENCE OF THE NANOPARTICLES AL₂O₃ ADDITIVES IN ISOPROPYL ALCOHOL AND PROPYLENE GLYCOL ON HEAT CAPACITY IN THE LIQUID AND SOLID PHASES

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Abstract: New experimental data for the heat capacity on the saturation line for the pure isopropyl alcohol and nanofluids (solutions of the isopropyl alcohol and nanoparticles Al₂O₃) have been reported in the paper. We also present the description of the experimental setup that realizes method of direct heating in adiabatic calorimeter. The calorimeter has been used for experimental investigation of the heat capacity for pure isopropyl alcohol as well as for nanofluids (solutions of the isopropyl alcohol and nanoparticles Al₂O₃) in temperature range from 80 to 330 K at weight fractions of nanoparticles 2.008%, 5.107%, 9.958%. Procedure of fitting of the obtained experimental data is reported. Analysis shows that mean uncertainty of the measured heat capacity does not exceed 0.408%. Obtained results indicate that admixtures of nanoparticles Al₂O₃ lead to decreasing the heat capacity of the liquid and solid phase of isopropyl alcohol. In addition, the heat capacity in the glassy and metastable states is measured. For the first time information about structural changes for the studied solutions in the solid phase is presented.

Based on obtained experimental data we proposed new “3-phase” prediction model for the heat capacity of the nanofluids. Proposed model considering an excess mole heat capacity. This value can be determined as heat capacity of the surface layer which is formed on the surface of the nanoparticle due to sorption. The surface layer can be assumed as molecules of the base liquid. We would emphasize that value of excess heat capacity of the nanofluids correlated with changing of hydrodynamic radius of the nanoparticles.

Keywords: Heat capacity – Nanofluids– Nanoparticles Al₂O₃– Isopropyl alcohol – Experiment – Prediction Model

1 Introduction

Nanofluids are innovative new working fluids, obtained by dispersing solid nanoparticles in base liquids. Published results show that additives of the nanoparticles with high thermal conductivity improve the heat transfer in free and forced convection, boiling of nanoparticles in the evaporator and help to increase the efficiency of vapor compression refrigeration systems [1]. It should be noted that thermophysical properties of the nanofluids (TPN) cannot be predicted by rule of additivity (in contrast to regular suspensions), since this class of fluids has to be characterized as heterogeneous colloidal solutions.

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Experimental study of TPN connected with elimination of many methodological and experimental uncertainties. Main of them is the stability of the fluids under experimental conditions. The problem with correct evaluation of the uncertainties is reason of rather controversial results in experimental studies for the TPN. It can be argued with reasonable confidence that additives of nanoparticle increase the thermal conductivity and viscosity of the base fluids. An absence of reliable information about TPN properties complicates the practical implementation of nanotechnology in the energy industry and especially in refrigeration industry.

Heat capacity is one of the most important caloric properties for the working and heat transfer fluids since determine the efficiency for many technological processes. At the same time, experimental investigation of the heat capacity for the nanofluids are limited \cite{2}-\cite{7}. This fact hinders the possibility to develop the predicting model for the heat capacity of the nanofluids. In addition, information about the excess heat capacity makes it possible to analyze structural changes in nanofluid at variable thermodynamic parameters.

It is necessary to take into account two main factors before investigation the effect of nanoparticles on caloric properties. Firstly, data on the caloric properties of the base fluid should be very well investigated and available. Secondly, nanofluid samples have to meet the requirements for the stability over experimental parameters range.

2 Experimental section

Samples of nanofluids isopropanol (C\textsubscript{3}H\textsubscript{8}O) /Al\textsubscript{2}O\textsubscript{3} nanoparticles were prepared by mixing pure isopropanol GOST 9805-84 with the original sample nanofluid (702129 Aldrich) containing 80 wt.% isopropyl alcohol and 20 wt.% the Al\textsubscript{2}O\textsubscript{3} nanoparticles, the average size equal to 50 nm. In this way, three samples were prepared and contained 2.008, 5.107, 9.958 wt.% nanoparticles correspondingly. The nanofluids remained stable in the pilot study.

A scheme of low-temperature adiabatic calorimetric setup is given in Fig. 1. The immersion type cryostat is a vacuum chamber 2, which is placed into the Dewar vessel 1 with liquid nitrogen. The elements of the calorimetric system and the container 4 with the substance under investigation 3 are mounted inside the vacuum chamber. Radiation heat transfer is minimized due to the electrolytic silvering of the inner surfaces of the adiabatic shell 6 and covering the outer surface of the container 4 by polished aluminum foil.

Since the samples for investigation of the caloric properties are in liquid phase, a sealed stainless steel container with volume 72 mL was used. Calorimetric heater H\textsubscript{4} and resistant thermometer 5 are placed inside of the container. There is a micro valve 8 in the upper part of the container,
through which the test sample or heat transfer gas (when the thermal value of the calorimeter is determined) are filling.

Reduction of convective heat transfer between the calorimeter shell and the container is achieved by creating a pressure $10^5$ mm of mercury in the vacuum chamber. Vacuum system of the adiabatic calorimetric device is consisting of the roughing and diffusion pumps 22 and 18, vacuum traps 17 and 19, ionization and thermocouple pressure transmitters 16 and 20, and the leak valve 21. The vacuum chamber may be filled up with helium from the cylinder 15 to reach quickly the required temperature of the calorimetric system. The heat transfer through electric wires is decreased due to use the conductors of small diameter (0.05 to 0.08 $\text{mm}$) and using a temperature controlled ring 9. This ring is wound a wire section coming from the electrical input 12 to the adiabatic screen 6. The temperature of the temperature-controlled ring 9 is maintained equal to the temperature of the container 4 with the help of additional regulating heater $H_2$. External temperature control screen 7 is used to ensure constant conditions of heat transfer with adiabatic screen 6 in a wide temperature range.

Thus, all elements of the calorimetric system are enclosed in a shell with approximately the same temperature. Vacuum chamber 2 immersed in a Dewar vessel 1 with liquid nitrogen is equipped with massive copper screen 10, which has good thermal contact with the lid of the vacuum chamber 2. This design of the vacuum chamber prevents the radiative heat exchange between the calorimetric system and the external environment through the vacuum bridge 11. The design of the cryostat provides the reduction of radiant heat exchange between liquid nitrogen and the environment with the help of the screens 13.

Heat transfer between the elements of the adiabatic system was controlled by using copper-constantan differential thermocouple $\Delta T_1$, $\Delta T_2$, and $\Delta T_3$ (Fig. 1) with high sensitivity ($\frac{dE}{dT} = 20-40 \mu\text{V/K}$). In this design of the calorimeter is necessary to regulate the temperature difference between the following items: container with the substance under investigation – adiabatic screen (differential thermocouple $\Delta T_1$, $\Delta T = 0$); container with the substance under investigation – hot ring (differential thermocouple $\Delta T_2$, $\Delta T = 0$); hot ring – external screen (differential thermocouple $\Delta T_3$, $\Delta T \geq 0$). The signal from each of thermocouple is measured by a precision multimeter Rigol DM3064 at 6 sec. intervals and is transferred to the computer for further processing, display and saving the experimental results.
Figure 1 Schematic diagram of the low-temperature adiabatic calorimetric setup

1 – Dewar flask with liquid nitrogen; 2 – vacuum chamber; 3 – investigated sample; 4 – container; 5 – platinum resistance thermometer (TC); 6 – internal adiabatic screen; 7 – external temperature control screen; 8 – filling valve; 9 – thermo-regulating ring; 10, 13 – screens; 11 – vacuum tube; 12 – electric inputs; 14 – vacuum connector; 15 – a tank of helium; 17, 19 – vacuum trap; 18 – diffusion pump; 16, 20 – thermocouple and ionization pressure transmitters; 21 – the leak valve; 22 – the roughing pump; H1, H2, H3 and H4 – heaters of the thermostat screen, rings, adiabatic screen and container with sample, respectively; ΔT1, ΔT2, and ΔT3 – differential thermocouple; Rigol DM3064 – precision digital multimeter; PA – power amplifier; CR – model coil resistance; TCU – blocks, temperature controlled; UN – stable power sources.

A PRT (Platinum resistance thermometer) type platinum resistance thermometer 5 produced by TERA was used to measure the temperature of the container (see Fig. 1). The measurements of the calorimeter temperature by the PRT were carried out by the compensation method. The voltage drop on the thermometer and standard resistance and also time measurements were made using a digital multimeter (Rigol, see Fig. 1).

The first phase of the calorimetric experiments is refill of the container with the substance under investigation, which is performed on a separate stand. The container is evacuated before filling. Then the container is weighed on an electronic analytical balance AND GR-300 with uncertainties not exceeding 5·10⁻⁷ kg, is filled with the sample, re-weighted and installed in the adiabatic system. The vacuum chamber was filled with helium from the cylinder 15 to quickly reach a required temperature level. When the set temperature is reached, helium is pumped out from the vacuum chamber through the vacuum system.

The heat capacity of nanofluids was measured by the monotonic heating method. In the implementation of this method, heating rate of the samples in the calorimeter was changed within the range from 2.4·10⁻³ to 0.01 deg/s. While continuously transmitting power to the calorimeter heater not exceed 0.51 W.
The heat capacity of the samples was calculated from the ratio:

$$c_s = \frac{P_{sh} - P_{hl}}{m \cdot \Delta T} \frac{A(T)}{m}$$

(1)

where $P_{sh}$ is the average input power to the calorimeter, $W$; $P_{hl}$—power heat loss at average temperature of experiment $T_{av}$, $W$; $\Delta T$ is the temperature change of the calorimeter during the time $\Delta \tau$, $K$; $m$—mass of test sample, $kg$; $A(T)$ is the heat value of the calorimeter at average temperature of experiment $T_{av}$, $J/K$.

3. Analysis of experimental data

The experiments show the analyzed isopropanol / Al$_2$O$_3$ nanoparticles solutions should be cooled to the temperature of 90 K for measurements of the caloric properties in solid phase. The rate of cooling of the sample under investigation is important. We found that at cooling rate of 0.1 to 4.8*10^-2 deg/s the sample passed into the solid amorphous state. In this condition there is no expressed crystal lattice (the glassy state of substance). The validity of this statement confirms by trends shown in Fig. 2.

Multiple phase transitions can be clearly seen from Fig. 2. The phase transitions are realized during the heating of isopropanol / Al$_2$O$_3$ nanoparticle samples, those are cooled at a rate of 0.1 to 4.8*10^-2 deg/s to the temperature 86 K (see plot thermogram 1-2). The parameters of reference points on the thermogram are given for sample that has the composition of isopropanol 94.893 wt.% / nanoparticles 5.107 wt. %. Heating of the sample (the rate of temperature change from 0.009 to 0.007 deg/s), which is in the glassy state, is shown by the line 2-3. At point 3, the solutions are beginning to move in the supercooled liquid state. On the line 3-4 of the thermogram, there is a continuous transition of substance from a glassy state to supercooled liquid. This process is accompanied by partial destruction of the intermolecular bonds. Therefore, the rate of temperature changing of the samples in the temperature range from 112 to 135 K decreases from 0.007 to 0.005 K/s. In this case, the effective heat capacity of supercooled liquids increases approximately from the value of 1027.5 kJ/kg to the 1640 kJ/kg (Fig. 2).

It should be noted the lager concentration of Al$_2$O$_3$ nanoparticles in the sample leads to insignificance of the effective heat capacity. This result is quite reasonable since the heat capacity of Al$_2$O$_3$ nanoparticles is less compare to heat capacity of the base fluid. Line 4-5 on the thermogram reflects the phase transition of supercooled liquid–solid phase. This phase transition is accompanied by a large heat liberation caused the increase temperature of the sample from 136 K to the temperature of phase transition solid phase – liquid. Experiments show that re-cooling of the samples (line 6-7) is required in order to transit test samples to a solid phase. Parts 7-8 of the thermogram reflect the process of increasing the temperature of the sample in solid phase, melting (8-9) and increase temperature of the sample in the liquid phase (9-10). Structural phase transitions were not observed up to the melting temperature at re-heating (7-8) of the sample in solid phase.
The presented model of the structural transformations confirms by temperature dependence of the effective heat capacity, which is demonstrated in Fig. 3. It should be mentioned the effective heat capacity can be interpreted as amount of heat required to raise the temperature of samples per degree at the experimental conditions (including thermal effects of the phase transitions during crystallization and melting).

Figure 2 Thermogram of phase transitions in the study of the caloric properties of nanofluids

Figure 3 Temperature dependence of the effective heat capacity during heating of nanofluids samples

As follows from data given in Fig. 4 and 5, the presence of nanoparticles in isopropyl alcohol leads to reduce the heat capacity in both solid and liquid phases.

Figure 4 Temperature dependence of the heat capacity for the samples of isopropyl alcohol/ Al₂O₃ nanoparticles in the solid phase

Figure 5 Temperature dependence of the heat capacity for the samples of isopropyl alcohol/ Al₂O₃ nanoparticles in the liquid phase
In contrast the heat capacity of samples in glassy state is higher by 7.5-10.5% than the heat capacity of samples for the same concentration in the crystalline state (see Fig. 6). The effective heat capacity of nanofluids in a metastable state in the temperature range 120-135 K is higher approximately by 32-40% than the heat capacity of the samples in the crystalline state (see Fig. 7).

Information obtained on the heat capacity of the samples in the crystalline state, glassy state (plot images 2-3) and metastable liquid phase (plot images 3-4) makes it possible to evaluate the thermal effects of the phase transitions. The results are given in Fig. 6 and 7.

The effect of Al₂O₃ nanoparticles on the temperature and heat of fusion is shown in the Figs. 8 and 9. It is seen that additives of nanoparticles in isopropyl alcohol reduce the melting temperature and heat of fusion.
At the heating mode the latent heat of phase transition can be calculated by following correlation:

$$\lambda = \frac{(P_{sh} - P_{hl}) \cdot \Delta \tau - A \cdot \Delta T}{m}$$

(2)

where $\Delta \tau$ is the time of energy supply to tested sample determined by duration of almost horizontal section on thermogram, $s$; $A$ is the thermal value of the calorimeter at an average temperature of phase transition, $J/K$; $\Delta T$ is the temperature change on the part of the phase transition associated with presence of impurities in the sample, $K$.

The analysis for the obtained experimental data shows that the average uncertainties for the temperature measurement is equal to 0.03 K (individual graduation), for the concentration of nanoparticles is equal to 0.1, heat of fusion is equal to 0.025% and for the heat capacity does not exceed 0.408%, at confidence probability of 0.95.
4 Model for predicting heat capacity of nanofluids

We found that existing correlation for prediction of the heat capacity at the saturation line do not adequately reproduce experimental data. The values for the heat capacity of nanofluids calculated by correlations reported in [9], [10] always lie above experimental data.

According to our opinion, this is a reasonable result since correlation presented in [9], [10] do not consider that any sustained in time nanofluids are colloidal systems in which the molecules of the base fluid (isopropyl alcohol) adsorbed on the surface of nanoparticles. In this paper we consider the nanofluid as a thermodynamic system consisting next phases:

- base liquid – dispersed medium, thermal properties correspond to properties of a pure substance at specified temperatures;

- nanoparticles – dispersed phase, in first approach the thermal properties correspond to the material properties of nanoparticles;

- the surface layer of nanoparticles – molecules of the base fluid adsorbed on the surface of nanoparticles. Thermophysical properties of the base fluid are different from the properties of the dispersion medium. According to ideas presented in [11], the density and heat capacity of the surface layer can be taken equal to the properties of the dispersion medium at the melting temperature as a first approach.

Considering assumptions mentioned above the value of the molar heat capacity for the nanofluid can be calculated by formula:

\[ c_s = c_{np}x_{np} + c_{bf}(1 - x_{bf}) + \Delta c_{sl}x_{sl}, \]  

(3)

where \( c_s \) is the heat capacity of nanofluid, \( J/mol\cdot K \); \( c_{np} \) is the heat capacity of nanoparticle material (Al\(_2\)O\(_3\)), \( J/mol\cdot K \); \( x_{np} \) is the mole fraction of the material of the nanoparticles in nanofluid, mol/mol; \( c_{bf} \) is the heat capacity of the dispersion medium (base liquid – isopropyl alcohol) in nanofluids, \( J/mol\cdot K \); \( x_{bf} \) is the mole fraction of the dispersion medium in nanofluids, mol/mol; \( \Delta c_{sl}x_{sl} \) is the excess heat capacity of the dispersion medium in the surface layer of nanoparticles; \( x_{sl} \) is the mole fraction of the dispersion medium in the surface layer of nanoparticles, mol/mol.
In first approach $\Delta c_d = c_{mt} - c_{bf}$, where $c_{mt}$ is the heat capacity of the dispersion medium at the temperature of melting, $J/mol\cdot K$; $c_{bf}$ is the heat capacity of the dispersion medium at the temperature of nanofluid, $J/mol\cdot K$. The structure of the (3) represents the thermodynamic equation for a nonideal solution where third term of the equation is the excess heat capacity.

In the frame of assumptions mentioned above we may assume that nanoparticles have a spherical shape, and correspondingly, molecules of the dispersion medium adsorbed on the surface of the nanoparticles and then form a spherical layer. Therefore, it is possible to determine the diameter of the surface layer around the nanoparticles (hydrodynamic diameter) by calculating the excess heat capacity from obtained experimental data:

$$D_h^3 = D_{np}^3 \left(1 + \frac{c_{exp} - c_{np} x_{np} + c_{bf} \left(1 - x_{np}\right)}{x_{np} \left(c_{np} - c_{bf}\right)} \frac{\rho_{np}}{\rho_{np} \cdot M_{np}}\right)$$

where $D_h$ is the hydrodynamic diameter of nanoparticles, nm; $D_{np}$ is the diameter of nanoparticles, nm; $c_{exp}$ is the measured heat capacity of nanofluid (3), $J/mol\cdot K$; $\rho_{mt}$ is the density of the dispersion medium at the temperature of melting, $kg/m^3$; $\rho_{np}$ is the density of nanoparticle, $kg/m^3$; $M_{np}$ is the molar mass of the material of the nanoparticles, $kg/mol$; $M_b$ is the molar mass of the base fluid, $kg/mol$.

The analysis shows that value of the hydrodynamic diameter calculated from experimental data (see (3) and (4)) agrees satisfactorily with the data reported in [12].

The difference between the heat capacity of the nanofluids and pure isopropyl alcohol is shown in Fig. 10. The concentration dependence of the specific heat of nanofluids is shown in Fig. 11. The comparison of calculated values of the hydrodynamic radius and the data reported in [12] is shown in Fig. 12 and 13.
As follows from the Fig. 12 and 13, the hydrodynamic radius of nanoparticles in isopropyl alcohol varies from temperature and concentration. Therefore, for the description of experimental data in the model (3), we propose to calculate the concentration of base fluid in the surface layer by the following fitting equation:

\[ x_{sl} = \frac{x_{np}}{a} \exp \left( -\frac{T}{b} \right) \]  \hspace{1cm} (5)
where the coefficients $a = 0.0017703 \text{ mol/mol}$, $b = 48.0188 \text{ K}$.

The absolute and relative deviations of experimental data for the heat capacity of nanofluids isopropyl alcohol / $\text{Al}_2\text{O}_3$ nanoparticles from data calculated by proposed model (3) are shown in Fig. 14.

![Figure 14](image_url)

**Figure 14** Absolute and relative deviation of the experimental heat capacity data of nanofluids (isopropyl alcohol/ $\text{Al}_2\text{O}_3$ nanoparticles) from data calculated by model (3), (4)

Based on information presented in Fig.14 we can conclude that the deviations of calculated data by (3), (4) for the specific heat of the solutions of isopropyl alcohol / $\text{Al}_2\text{O}_3$ are comparable with the experimental uncertainty. Thus, model (3) can be recommended to fitting and prediction of the heat capacity for the nanofluids.

The paper also shows the experimental data on the thermodynamic properties of propylene glycol and propylene glycol / $\text{Al}_2\text{O}_3$ nanoparticles.

**5. Conclusions**

The description of experimental setup (adiabatic calorimeter), technique of the experiment and processing of the obtained data on the heat capacity for the nanofluids isopropyl alcohol/ $\text{Al}_2\text{O}_3$ nanoparticles are given.

It is shown that additives of $\text{Al}_2\text{O}_3$ nanoparticles leads to a decrease of the heat capacity of isopropyl alcohol in the liquid and solid phases. In addition, the heat capacity of the samples in the glassy state is higher by 8-10% than the heat capacity of samples at the same concentration in
the crystalline state. The effective heat capacity of nanofluids in a metastable state in the temperature range from 119 to 134 K is higher about 32 - 40% than the heat capacity of the samples in the crystalline state.

The temperature dependence for the specific heat of isopropyl alcohol/ Al₂O₃ nanoparticles solutions and temperature dependence of the specific heat of isopropyl alcohol are almost equidistant. New information about structural phase transitions in the solid phase solutions of isopropyl alcohol/Al₂O₃ nanoparticles (glassy state - metastable liquid), which are realized in the temperature range from 111 to 118 K is reported.

We propose to use new "three phase" model for predicting the heat capacity of nanofluids. The model contains the excess molar heat capacity. The value of the excess molar heat capacity is determined by the heat capacity of structurally oriented layer of molecules of the base fluid on the surface of nanoparticles. We believe that changing in absolute value of the excess heat capacity for the nanofluids correlated with changing of the hydrodynamic radius of the nanoparticles. Deviations of calculated data by proposed model for the specific heat of nanofluids isopropyl alcohol / Al₂O₃ nanoparticles are comparable with the experimental uncertainty.

**Literature**


GRAIN SIZE EFFECT ON FATIGUE LIFE OF WC-Co40 MAINLY USED IN COLD FORGING TOOLS

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Abstract: Life cycle of forging dies used in cold forging industry has always been a limitation in tool design process. Changes in binder ratio of the material and grain size, directly affects the mechanical behaviour of forging dies. Thus makes wide range possibilities and service behaviors of forging tools. Aim of the studies was to determine fatigue behavior of WC-Co 40 for making life prediction of forging tools. Three point bending fatigue test were carried out at constant stress ratio on a fine and coarse grained WC-Co which were used in cold forging industry. Mainly two different aspects which were the grain size effect on lifecycle and surface roughness on fatigue life were investigated and comparative results obtained from experimental tests was given in the study.

Keywords: WC-Co, Fatigue life, Grain size, Cold forging dies

1. INTRODUCTION

Die life has always been a research target for many companies and R&D centers. Research based on estimating fatigue life of WC-Co, which were mainly used in die inserts, has a wide parameter range which can not be simulated precisely. Understanding the mechanical behavior of WC-Co will lead companies to decide the best composite structure of the material for different production processes. As known, surface roughness has a direct influence on fatigue life of metallic materials. Several studies carried out to find effects of binder ratio, grain size, surface roughness, working temperature, pre-stressing and many more parameters on service life of forging tools. Torres et al. [1], studied the fatigue behavior of cemented carbides with a perspective of fatigue crack growth and fatigue life. Mikado et al [2] investigated the effect of stress ratio based on fatigue life time of carburized materials. Li et al [3] worked on a fatigue test based on 3 point bending and find out the effects of notch sensitivity. A research based on crack initiation and growth of forging die was investigated by Ebara [4]. Bronsted and Hansen [5] also worked on mechanical and fatigue behaviour of high strength materials which are used the most in die insert material. Klünsner et al [6] Has made some important studies based on fracture mechanics and crack growth for WC-Co materials. Ferreira et al [7] also examined the mechanical behaviour of WC-Co material with different test methods. Lee et al [8] made some researches on predicting fatigue life cycle of cold forging tools based on High-cycle fatigue theory. Okamoto et al [9] Also worked on larger grains size effects on mechanical behaviour of cemented carbides. Kawahara et al [10] worked on fatigue life of carbide tools with a different surface finishing processes. Experimental studies were made during past 30 years for
understanding the fatigue behavior of Tungsten Carbides. Fracture toughness and fatigue life approach was considered the most reliable method to understand fatigue behaviour of hard materials.

2. EXPERIMENTAL PROCEDURE

The experimental study was based on WC-Co 40 material, which’s Cobalt ratio was % 20. The specifications of the material from the catalogue is given in Table 1 [11]. For comparison test, fine (CTF40) and coarse (CTE40) grain sized carbides with polished surface conditions were prepared. Test samples of 20x6.5x5.25 which is given in Fig. 1, was chosen based on ISO 3327:2009 Type B (Determination of Transvers rupture strength-Hard metals) [12]. Stress amplitude calculation was done for a stress ratio of R=0,1 with the equation given below in Eq. (1).

\[
TRS = \frac{3.PJ}{2.b.h^2}
\]  

(1)

Table 1: Material catalogue value

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness (HV10)</th>
<th>Average Grain Size (µm)</th>
<th>Transvers Rupture Strength (MPa)</th>
<th>Fracture Toughness (MPa*m(1/2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-Co 40 Coarse Grain (CTE 40)</td>
<td>850</td>
<td>2.5-&lt;6.0</td>
<td>2900</td>
<td>24.0</td>
</tr>
<tr>
<td>WC-Co 40 Fine Grain (CTF 40)</td>
<td>1070</td>
<td>0.8-&lt; 1.3</td>
<td>3400</td>
<td>18.0</td>
</tr>
</tbody>
</table>

Fatigue life tests were carried on 3 point bending fixture, described in Figure 1, with resonating fatigue testing machine Zwick Roell Amsler 250 HFP 5100. Each experimental test contains 5 different stress amplitude value and 3 tests for each amplitude value. Specimens were polished with 50, 30, 15, 3 grades diamonds at a total of 12 minutes for each side.
Vickers hardness measurements were carried on 3 different test specimens to determine the difference between coarse and fine grained WC-Co 40 and comparative result was given in Figure 2. From the comparative result it is obvious that fine grained carbide is much harder than the coarse one. Obtained result was approximately the same as the catalogue value of the supplier firm. It is also known from the literature that finer grain sized carbides has a higher value of hardness.

Figure 2. Vickers hardness test results of CT40 and CTF40
Comparative surface roughness test result based on Ra, Rz, Rq of coarse grained polished and unpolished specimens were given in Figure 3. The common surface roughness indicator Ra has a huge difference between two specimens as expected.

![Surface roughness results of unpolished and polished CTE40](image)

Figure 3. Surface roughness results of unpolished and polished CTE40

For determining the grain size of the material microstructural investigation was done to coarse and fine grained specimens. Metallographic specimen preparation was done by using ASTM B657 standard of “metallographic determination of microstructure in cemented tungsten carbides” [13]. Hard material binder phase and metallic binder phase for fine and coarse grain carbide can be seen in Figure 4.

![Metallographic examination of ctf 40 and cte 40 materials.](image)

Figure 4. Metallographic examination of ctf 40 and cte 40 materials.
Fatigue life test were carried on different stress amplitude at 0.1 stress ratio. Based on the experimental result it is revealed that surface condition of the material has an essential role on the fatigue life of WC-Co 40. Test results of unpolished coarse grained and polished coarse grained experiment is given in Figure 5. Comparative results also given in Figure 6. From experimental tests it could be said that surface roughness directly effects life cycle of the material. It is obvious that surface conditions has a key role on fatigue lifetime.

Figure 5. 3point bending fatigue test results of polished and unpolished CTE 40

Figure 6. Fatigue life comparison of polished and unpolished specimens
Figure 6 shows the S-N curves of experimental tests conducted on fine grained and coarse grained WC-Co 40. Both specimens had been polished before conducting fatigue life test. Furthermore, from the experimental results given in Figure 7 it is evident that fatigue life decrease with finer grain sized carbides.

![Image of S-N curves](image_url)

Figure 7. S-N diagram of CTF 40 on the left and comparison with CTE 40 results on the right

### 3. CONCLUSION

The results obtained from the experimental study shows some important parameters for cold forging die material WC-Co 40. The most important parameter effecting the fatigue life is surface conditions. For long fatigue life, all forging die surfaces must be polished delicately. Also, it could be said that for long fatigue life, coarse grain sized material has to be considered instead of fine grade material. For Hardness needed application instead of fatigue life, fine grain sized carbides could be a better choice. The current study has only examined the surface effect and grain size on fatigue life cycle of WC-Co 40. Further research in this subject regarding the role of other parameters has to be done for more precise and accurate life cycle prediction in forging die.

### 4. REFERENCES


**Acknowledgements**

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PERFORMANCE ANALYSES OF ENVIRONMENTALLY FRIENDLY LOW-GWP REFRIGERANTS

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Abstract: Refrigeration systems transferring heat from a low-temperature space to a region having high-temperature are of great importance to us in our daily life. The period starting from Montreal Protocol in 1987 and Kyoto Protocol in 1997 to the European Directive 2006/40/EC in 2006 and EU Regulation No 517/2014 in 2014 show the environmental aspects of the refrigerant selection in addition to the performance criterion. Montreal Protocol aimed to phase out the chlorofluorocarbon (CFC) refrigerants due to their ozone depletion potential (ODP); while Kyoto Protocol focused on reducing the emission of the greenhouse gases thereby pointing out the low global warming potential (GWP) working fluids in the refrigeration applications. Nowadays, deadlines with regard to the stringent limits on the GWP values by EU legislation result in the high demand of environmentally friendly refrigerants fulfilling the requirements of the regulations. Therefore originating from the advances induced by the pressure of the EU normative, the subject of this paper is zero ODP and low-GWP refrigerants. The main objective is comparing the performance of them and selecting the most promising candidates considering also their safety class according to ASHRAE standard. This study proposes a list including candidate refrigerants from the potential groups, i.e., (i) low-GWP hydrofluorocarbons (HFCs), (ii) natural refrigerants, (iii) hydrofluoroolefins (HFOs), and (iv) fluorinated ethers and alcohols and makes a performance comparison for refrigeration and air-conditioning operation conditions. Although some of those working fluids are investigated in detail in the previous literature studies, there aren’t any analyses that they are gathered together to be evaluated on a comparative basis regarding different operation conditions. Moreover, this study would be beneficial for the researchers and manufacturers involved in this sector to clarify the preliminary performance questions about the comparison of these candidate refrigerants. The thermodynamic model of the vapor compression refrigeration cycle is constructed in Matlab®. In conclusion, when considering the environmental issues, high performance, and safety criteria, R152a is a promising candidate. Moreover, although R1234yf and R1234ze(E) have less COP values when compared to the others, they are environmentally friendly and safe refrigerants of the future.

Keywords: Refrigeration, Air-conditioning, Coefficient of Performance (COP), Low-GWP refrigerants, the EU Normative.

1. Introduction

There has been an ongoing investigation as to environmentally friendly refrigerants more than a century beginning with the Montreal Protocol and the Kyoto Protocol and lasting with the European Directive 2006/40/EC [1] in 2006 and EU Regulation No 517/2014 [2] in 2014. One of the target of the Montreal Protocol is to eliminate the chlorofluorocarbon (CFC) group refrigerants because of their ozone depletion potential (ODP) while the intention of the Kyoto Protocol is reducing the emission of the greenhouse gases including most of the refrigerants having high global warming potential (GWP).
The European Directive 2006/40/EC [1] declared that refrigerants having GWP values higher than 150 cannot be used in the air conditioning systems of the motor vehicles that are introduced from 2011 and produced from 2017. EU Regulation No 517/2014 [2] also known as F-gas Regulation puts the other restriction on the GWP values of the refrigerants. Figure 1 lists briefly refrigerant related aspects of the environmental protocols and regulations. Natural refrigerants, hydrofluoroolefin (HFO) group refrigerants, some of the hydrofluorocarbons (HFCs), HFO based mixtures comprised of HFC and HFO components, fluorinated ethers and alcohols are proposals mainly attained from the literature as the solution of the low-GWP refrigerant problem. Hence, new generation refrigerants from all groups other than any blend options are the subject of this study.

Figure 7. Phase-out stages of the refrigerants due to the environmental concerns.

There are similar performance evaluation studies in the literature. Next, some examples accompanied by the distinctive points of this study are presented. Mota-Babiloni et al. [3] emphasized the restrictions applied by F-gas Regulation and investigated various refrigerant mixtures proposed by Air-Conditioning, Heating, and Refrigeration Institute (AHRI). As for the results of their research from the theoretical analyses, most of the mixture alternatives in question couldn’t reach a better performance level than the regarding pure HFC component. Eyerer et al. [4] showed that R1233zd-E, a low-GWP alternative, could be used in the Organic Rankine Cycle (ORC) systems as a replacement for R245fa and yielded in high efficiency as well. Pigani et al. [5] investigated ammonia (NH₃), carbon dioxide (CO₂), R1234yf and R1234ze(E) to make a comparison with R407F which is commonly used in the marine refrigeration systems. Yana Motta et al. [6] experimentally investigated HFO-1234yf and HFO-1234ze in a small refrigeration equipment, i.e, vending machine. Pham and Rajendran [7] aimed to investigate R32 and HFO blends as a substitute for R410 to propose a low GWP and low Life Cycle Climate Performance (LCCP) refrigerant option to be utilized in air conditioning and heat pump applications. Jarall [8] analyzed the performance of the HFO-1234yf elaborately in terms of the cooling effects, COP, compressor efficiency, and the heat transfer characteristics in a plate heat exchanger. Bivens and Minor [9] investigated fluorinated ethers, alcohols, amines, silicon, and sulfur compounds benefiting from the literature findings in terms of toxicity, nonflammability, stability, atmospheric lifetime, refrigeration performance, and manufacturing issues and the cost of the fluids as they might be zero ODP alternatives to the HFCs. Wu et al.
[10] studied the performance of R161 to be utilized in a residential air conditioner under various operation conditions.

The literature consists of this kind of comprehensive investigations and only some of them are given here to highlight that a good deal of research into finding an appropriate new generation refrigerant with regard to the EU normative is strongly going on since refrigerants having GWP values higher than 150 even cannot be used in the air conditioners of the cars in a couple of months. More research and development activities are compulsory, hence main objective of this paper is collecting low GWP refrigerant options from the literature and making a performance comparison among them to propose the most promising candidates. Due to the strict deadlines regarding the GWP values depending on the refrigeration applications, these kinds of comparison studies are of great value particularly for the people involved in this sector.

A mathematical model of the vapor-compression refrigeration cycle is established to calculate the performance coefficients of the refrigerants in Matlab® and the thermodynamic properties of the them are obtained via REFPROP version 9.1 [11]. The REFPROP program developed by the National Institute of Standards and Technology (NIST) uses the most appropriate equations of states and models in order to obtain the thermodynamic and transport properties of the important fluids.

2. Environmental Regulations regarding the Refrigerants

F-gas Regulation limits GWP values of HFCs depending on the applications versus years as summarized in Table 1. F-gas Regulation came into effect in 2015 and according to the European Directive any refrigerant having GWP value higher than 150 cannot be used in any motor vehicles by the beginning of 2017. Two deadline examples show the great importance of seeking an appropriate refrigerant compatible with the normative.

<table>
<thead>
<tr>
<th>Refrigeration Application</th>
<th>Date of Prohibition</th>
</tr>
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<tbody>
<tr>
<td>Domestic refrigerators and freezers that contain HFCs with GWP of 150 or more</td>
<td>1 January 2015</td>
</tr>
<tr>
<td>Refrigerators and freezers for commercial use (hermetically sealed equipment) that contain HFCs with GWP of 2500 or more</td>
<td>1 January 2020</td>
</tr>
<tr>
<td>that contain HFCs with GWP of 150 or more</td>
<td>1 January 2022</td>
</tr>
<tr>
<td>Movable room air-conditioning equipment that contain HFCs with GWP of 150 or more</td>
<td>1 January 2020</td>
</tr>
<tr>
<td>Single split air-conditioning systems containing less than 3 kg of fluorinated greenhouse gases that contain fluorinated greenhouse gases with GWP of 750 or more</td>
<td>1 January 2025</td>
</tr>
<tr>
<td>Multipack centralised refrigeration systems for commercial use with a rated capacity of 40 kW or more that contain fluorinated greenhouse gases with GWP of 150 or more</td>
<td>1 January 2022</td>
</tr>
<tr>
<td>Refrigerants to be used in the air conditioners of the motor vehicles with GWP higher than 150</td>
<td>1 January 2017</td>
</tr>
</tbody>
</table>
Table 2 shows the allowed quantities defined in accordance with the percentages based on the years. The target is decreasing the HFC use to 21% by 2030.

### Table 2. Maximum quantities defined by percentages according to the years.

<table>
<thead>
<tr>
<th>Years</th>
<th>Percentages to calculate the maximum allowed quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td>2015</td>
<td>100%</td>
</tr>
<tr>
<td>2016-17</td>
<td>93%</td>
</tr>
<tr>
<td>2018-20</td>
<td>63%</td>
</tr>
<tr>
<td>2021-23</td>
<td>45%</td>
</tr>
<tr>
<td>2024-26</td>
<td>31%</td>
</tr>
<tr>
<td>2027-29</td>
<td>24%</td>
</tr>
<tr>
<td>2030</td>
<td>21%</td>
</tr>
</tbody>
</table>

#### 3. Candidate Refrigerants

Most of the refrigerants would be eliminated owing to their high GWP values. The GWP comparison among some of the commercially available refrigerants, their mixtures, HFOs and their blend options, natural refrigerants, and fluorinated ethers and alcohols are shown in Figure 2. The red lines in Figure 2 display the critical GWP values of 150, 750, and 2500 and the emphasize the limited number of the refrigerants fulfilling the requirements. Only pure low GWP alternatives are selected from Figure 2 and performance analysis is carried out to compare them practically. Refrigerant list of this investigation is comprised of the natural refrigerants, HFOs, low GWP HFCs, and only one refrigerant from the fluorinated ethers and alcohols group to create a comparison database.

![Comparison of various refrigerant groups](image_url)
Table 3 displays the investigated refrigerants of this study and their basic thermodynamic properties.

**Table 3. Refrigerants and their thermodynamic properties (n.a.: non-available, a: [12], b: [10], c: [16], d: [2], e: [9], and f: [11]).**

<table>
<thead>
<tr>
<th>Refrigerants</th>
<th>ASHRAE Safety Group(^{a,b,c})</th>
<th>GWP(^{a,d})</th>
<th>ODP(^{a,b,e})</th>
<th>Critical Pressure (MPa)(^f)</th>
<th>Critical Temperature (°C)(^f)</th>
<th>Normal Boiling Point (°C)(^f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R134a</td>
<td>A1</td>
<td>1430 (**)</td>
<td>0</td>
<td>4.06</td>
<td>101.06</td>
<td>-26.07</td>
</tr>
<tr>
<td>R600a</td>
<td>A3</td>
<td>3 (*)</td>
<td>0</td>
<td>3.63</td>
<td>134.66</td>
<td>-11.75</td>
</tr>
<tr>
<td>R717</td>
<td>B2L</td>
<td>0 (*)</td>
<td>0</td>
<td>11.33</td>
<td>132.25</td>
<td>-33.33</td>
</tr>
<tr>
<td>R290</td>
<td>A3</td>
<td>3 (*)</td>
<td>0</td>
<td>4.25</td>
<td>96.74</td>
<td>-42.11</td>
</tr>
<tr>
<td>R1270</td>
<td>A3</td>
<td>2 (*)</td>
<td>0</td>
<td>4.56</td>
<td>91.06</td>
<td>-47.62</td>
</tr>
<tr>
<td>R32</td>
<td>A2</td>
<td>675 (**)</td>
<td>0</td>
<td>5.78</td>
<td>78.11</td>
<td>-51.65</td>
</tr>
<tr>
<td>R152a</td>
<td>A2</td>
<td>124 (*)</td>
<td>0</td>
<td>4.52</td>
<td>113.26</td>
<td>-24.02</td>
</tr>
<tr>
<td>R161</td>
<td>A3</td>
<td>12 (*)</td>
<td>0</td>
<td>5.01</td>
<td>102.1</td>
<td>-37.55</td>
</tr>
<tr>
<td>R1234yf</td>
<td>A2L</td>
<td>4 (*)</td>
<td>0</td>
<td>3.38</td>
<td>94.7</td>
<td>-29.45</td>
</tr>
<tr>
<td>R1234ze(E)</td>
<td>A2L</td>
<td>7 (*)</td>
<td>0</td>
<td>3.63</td>
<td>109.36</td>
<td>-18.97</td>
</tr>
<tr>
<td>RE143a</td>
<td>n.a.</td>
<td>756 (**)</td>
<td>0</td>
<td>3.64</td>
<td>104.77</td>
<td>-23.58</td>
</tr>
</tbody>
</table>

Table 4 is a quick display concerned with the definitions of the ASHRAE safety classes mentioned in the second column of Table 3.

**Table 4. Definition of the ASHRAE safety classes [16].**

<table>
<thead>
<tr>
<th>Safety group</th>
<th>A3</th>
<th>B3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher flammability</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower flammability</td>
<td>A2</td>
<td>B2</td>
</tr>
<tr>
<td></td>
<td>A2L*</td>
<td>B2L*</td>
</tr>
<tr>
<td>No flame propagation</td>
<td>A1</td>
<td>B1</td>
</tr>
</tbody>
</table>

*Lower toxicity Higher toxicity*

*\(A2L \) and \(B2L \) are lower flammability refrigerants with a maximum burning velocity of \(\leq 10 \) cm/s.*
4. Theoretical Model

Vapor-compression refrigeration cycle is modeled in Matlab®. The governing control volumes are shown in Figure 3. Energy balance is applied to all components, namely compressor, condenser, expansion valve, and the evaporator.

Theoretical Model

Vapor-compression refrigeration cycle is modeled in Matlab®. The governing control volumes are shown in Figure 3. Energy balance is applied to all components, namely compressor, condenser, expansion valve, and the evaporator.

![Diagram of a refrigeration cycle](image)

**Figure 9.** Vapor-compression refrigeration cycle and the control volumes of the components to be analyzed.

The first law or energy balance relation for a general steady-flow device on a unit-mass basis is given by [17]

\[ q - w = (h_i - h_o) + \frac{V_i^2 - V_o^2}{2} + g(z_o - z_i) \]  

It is assumed that the mass flow rate is conserved throughout the cycle and kinetic and potential energy changes of the components are negligible. Energy balance equation for the compressor is defined as [18, 19]

\[ w_{in} = (h_2 - h_1) \]  

Compressor isentropic efficiency is expressed by a correlation accounting the inlet (low) and outlet (high) pressures of the component and stated as [20]

\[ \eta_s = 0.874 - 0.0135 \tau \]  

The throttling process across the expansion valve is isenthalpic. Similarly, energy balance equations for the condenser and the evaporator are as follows;
\[ q_H = h_2 - h_3 \]  
(4)

\[ q_L = h_1 - h_4 \]  
(5)

Coefficient of performance (COP) is one of the performance indicator of the system and \( \text{COP}_{\text{Carnot}} \) as well is an important value for the Carnot refrigerator as defined below

\[
\text{COP} = \frac{q_L}{w_{in}} 
\]  
(6)

\[
\text{COP}_{\text{Carnot}} = \frac{1}{T_H / T_L - 1} 
\]  
(7)

where \( T_L \) and \( T_H \) are cold refrigerated space and warm ambient temperatures of the cooling cycle, respectively. The thermodynamic properties of the refrigerants are obtained through REFPROP version 9.1 [11].

5. Results

Two operation conditions are defined for the evaporator and the condenser temperatures to represent a refrigerator and an air conditioner in a typical summer day as given in Table 5. Warm environment temperature is assumed to be 25 °C and 40 °C for the refrigerator and the air conditioner; whereas the cold space temperature is chosen as -3 °C and 17 °C for them, respectively. 7 °C and 15 °C temperature differences are estimated between the cold refrigerated space and the evaporator, and warm environment temperature and the condenser, respectively. The superheat and subcooling temperature differences are 3 °C expressed according to the evaporation and condensation temperatures.
Table 5. Operation conditions arranged for an air-conditioner and a refrigerator.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Refrigeration</th>
<th>Air-conditioning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Warm Medium Temperature ($T_H$)</td>
<td>25 °C</td>
<td>40 °C</td>
</tr>
<tr>
<td>Cold Refrigerated Space Temperature ($T_L$)</td>
<td>-3 °C</td>
<td>17 °C</td>
</tr>
<tr>
<td>Evaporation Temperature ($T_{evap}$)</td>
<td>-10 °C</td>
<td>10 °C</td>
</tr>
<tr>
<td>Evaporator Outlet Superheat Temperature Difference ($\Delta T_{sh}$)</td>
<td>3 °C</td>
<td>3 °C</td>
</tr>
<tr>
<td>Condensation Temperature ($T_{cond}$)</td>
<td>40 °C</td>
<td>55 °C</td>
</tr>
<tr>
<td>Condenser Outlet Subcooling Temperature Difference ($\Delta T_{sc}$)</td>
<td>3 °C</td>
<td>3 °C</td>
</tr>
</tbody>
</table>

Results are schematically shown in Figure 4 (a-b) for air-conditioning and refrigeration applications. Although this study focuses mainly on the performance evaluation, some more comments are added regarding the safety classes of the refrigerants according to the ASHRAE Standard 34 [16].

Pure refrigerants are superior to the refrigerant mixtures eliminating temperature glide problem during phase change and difficulty of recharging completely if any leakage occurs. That’s why only pure refrigerants are chosen for investigation in this study.

Generally speaking, refrigerator case results in lower COP values than the air-conditioner case as displayed in Figure 4. The refrigerants yielding the best performance in both of the applications are R717 (ammonia), R152a, R600a (isobutane), and R161. R717 has B2L safety class meaning that it has toxicity and lower flammability. R161 and R600a as well have flammability problems, as it is obvious from their safety class, A3. When considering GWP limit of 150 and the safety class criteria in addition to performance, R152a is the best option. R152a is in A2 safety class and this class includes lower flammability problems requiring auxiliary equipment.
Figure 10. Performance comparison of the refrigerants for air conditioning (a) and refrigeration (b) applications.

The HFO group refrigerant, R1234yf has the lowest COP in both of the working configurations. R1234ze(E) and RE143a have the same COP value in the air conditioning case and perform similarly in the refrigeration application.

In both of the schematics of Figure 4, HFOs, namely R1234yf and R1234ze(E) are displayed in different colors to distinguish them. Although R1234yf and R1234ze(E) display low performance when compared to the others, they are prominently decided to be utilized in the future products by the important brands. For example, Alarko Carrier made its choice on R1234ze(E). From December 2013, Swiss legislation bans refrigerants having GWP values higher than 10 for systems of 400 kW or more capacity. Carrier products in Switzerland fulfill the requirements due to this low GWP refrigerant [21]. Moreover, Toyota declared that R1234yf would be their future refrigerant [22]. These examples emphasize the popularity of the HFO group refrigerants.
6. Conclusion

The main conclusion of this study is that R152a could be proposed as a good alternative refrigerant in terms of environmental concerns and high performance. However, since R152a has flammability problems, refrigeration systems using this refrigerant must have safety measures. The HFOs, i.e., R1234yf and R1234ze(E), are preferably chosen by many brands as a result of the F-gas requirements or any current legislation though they perform less when compared to the other options. Good safety characteristics make these low GWP refrigerants prominent. However, low COP values create a trade-off and highlight the requirement to recover the losses caused by the irreversibilities to increase the performance of the systems utilizing the refrigerants under consideration.

COP\textsubscript{Carnot} for the air conditioning and refrigeration cases are 12.62 and 9.65, respectively. These are the maximum achievable performance coefficients independent of the refrigerants operating between those warm and cold temperature limits of the air conditioner and the refrigerator. Because of the characteristics of the refrigerants, each has its own irreversibility levels depending on the components of the vapor-compression refrigeration cycle. To that regard, actual COP values of the refrigerants vary from maximum achievable coefficients (COP\textsubscript{Carnot}) and comprehensive exergy analyses should be conducted to display the work loss (work destruction) of the components. In other words, improvement potentials could be displayed more apparently with the planned exergy analyses. Future achievements regarding this subject would focus on the exergy analyses of the refrigerants through the components of the vapor-compression refrigeration cycle to recommend new technologies for work recovery resulting in performance increase.

\textbf{Nomenclature:}

\begin{itemize}
  \item \textit{w}\textsubscript{in} \quad Compressor work input, kJ kg\textsuperscript{−1}
  \item \textit{w} \quad Work transfer, kJ kg\textsuperscript{−1}
  \item \textit{q} \quad Heat transfer, kJ kg\textsuperscript{−1}
  \item \textit{h} \quad Enthalpy, kJ kg\textsuperscript{−1}
  \item \textit{V} \quad Velocity, m s\textsuperscript{−1}
  \item \textit{g} \quad Gravitational acceleration, m s\textsuperscript{−2}
  \item \textit{z} \quad Elevation, m
  \item \textit{\eta}_{is} \quad compressor isentropic efficiency
\end{itemize}
\( \tau \) pressure ratio \( (\tau = \frac{HP}{LP}) \)

\( T \) Temperature, K

Subscripts:

\( i \) in

\( o \) out

1 Compressor inlet/evaporator outlet

2 Condenser inlet/compressor outlet

3 Condenser outlet/expansion valve inlet

4 Expansion valve outlet/evaporator inlet

\( H \) Warm heated space (environment)

\( L \) Cold refrigerated space (environment)

\textit{Carnot} Carnot refrigerator

Abbreviations:

COP coefficient of performance

HP High pressure

LP Low pressure

References


THERMODYNAMIC PROPERTIES OF REDOX-ISOMERIC COBALT COMPLEXES WITH O-SEMIQUINONIC LIGANDS

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Nina Skorodumova 1 and Gleb Abakumov 1, 2

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smirnova@ichem.unn.ru

Extensive studies have been performed on bistable molecules, which can transform their physical properties with an external stimuli, for developing molecule-based sensors [1-3]. It is known that some transition metal complexes with two semiquinone ligands undergo a redox-isomeric (valence-tautomeric) interconversion induced by temperature, light and pressure.

![Diagram showing two forms of a complex with low-spin and high-spin forms](image)

<table>
<thead>
<tr>
<th>Low-spin form</th>
<th>High-spin form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(III), d6, S = 0</td>
<td>Co(II), d7, S = 3/2</td>
</tr>
<tr>
<td>DBSQ, S = ½</td>
<td>DBSQ, S = 1/2</td>
</tr>
<tr>
<td>DBCat, S = 0</td>
<td>DBSQ, S = 1/2</td>
</tr>
</tbody>
</table>

where DBSQ – anion-radical of o-quinone,
DBCat – dianion of corresponding o-quinone;
Y – organic or elementoorganic bridge;
R – substituent.

The paper presents results of thermodynamic studies of some complexes which exhibit redox-isomerism.
I. INTRODUCTION

Redox-isomeric complexes combine redox-active ligands and transition metal ions with two or more accessible oxidation states, exhibiting two nearly degenerated electronic states with localized electronic structures. Charge distribution in such electronic isomers has an appreciable sensitivity to the environment so an external perturbation, like photons, temperature and/or pressure, may lead to an intramolecular electron transfer between both redox active units and therefore to a reversible interconversion between the two degenerated electronic states (Fig. 1). Moreover, since each electronic isomer exhibits different optical, electronic and/or magnetic properties, these complexes are being proposed as candidates for future use in molecular electronic devices, switches and sensors [4, 5].

In solid state redox-isomerism was discovered in o-semiquinonic cobalt complexes [6]. Currently, most of known redox-isomeric complexes were obtained with cobalt, and few of them with nickel, manganese and rhodium [7, 8]. It was revealed that transformation of semiquinonc-catecholate form of complex into bis-semiquinonic one is accompanied by phase transition.

So, precise vacuum calorimetry gives very useful quantitative information for the characterization of complexes displaying redox-isomerism as well as of redox-isomeric transformation itself.

The purpose of present work is to measure the low-temperature heat capacity by adiabatic calorimetry over the temperature range 6–350 K and by differential scanning calorimetry in the range 250–420 K of some o-semiquinonic cobalt complexes, to estimate their characteristics, to calculate the standard thermodynamic functions in wide temperature range and to investigate dependence of phase transition characteristics on acceptor ability of quinone fragment and nature of neutral ligands.
II. EXPERIMENT

A. Experimental set up

For measuring heat capacity, temperatures and enthalpies of transitions we have used an installation of calorimetric equipment, including adiabatic vacuum and differential scanning calorimeters.

A precision automatic adiabatic calorimeter (BCT-3) was used to measure heat capacities over the temperature range of $6 \leq T \leq 350$ K [9]. It was established that the apparatus and measurement technique were enable the determination of the heat capacity of substances with an error not exceeding $\pm 2\%$ within the temperature range $6-15$ K, $\pm 0.5\%$, between $15$ and $40$ K, $\pm 0.2\%$ within the temperature range of $40 \leq T \leq 350$ K. The phase transition temperatures were measured within about $\pm 0.01$ K and the enthalpies of transformations with the error of $\pm 0.2\%$.

To measure the heat capacity of the sample under study over the range from $250-420$ K the differential scanning calorimeter (DSC 204 F1 Phoenix, Netzsch, Germany) was used [10]. The heat capacity error didn’t exceed $\pm 2\%$. The heating and cooling rates were $5$ K/min, the measurements were carried out in argon atmosphere.

Measured samples were also studied with IR and EPR spectroscopies and by magnetic measurements. Elemental analysis reveals that the purity of measured compounds is about 99.5 per cents.

B. Experimental results

First redox-isomeric complex studied calorimetrically was $(bpy)\text{Co}(3,6-\text{DBSQ})_2$, where $(bpy)$ is 2,2-dipiridyl (Fig. 2, curve 2) [11]. Further, in order to try to control the parameters of transition we studied heat capacities of complexes similar to initial, having methoxy and chlorine substituents in position 4 of quinonic fragment (Fig. 2, curves 1, 3). Previously, it was established that methoxy substituent reduces acceptor ability and chlorine substituent increases acceptor ability of quinone compared with non-substituted one (Fig. 3).

![Fig. 2. Temperature dependence of heat capacity of $(bpy)\text{Co}(4-\text{MeO}-3,6-\text{DBSQ})_2$ [I] (1),](image-url)
(bpy)Co(3,6-DBSQ)$_2$ [II] (2), (bpy)Co(4-Cl-3,6-DBSQ)$_2$ [III] (3)

Obtaining (bpy)Co(4-Cl-3,6-DBSQ)$_2$ (Fig. 2, curve 3) doesn’t finish because of thermal destruction of the sample, so, decomposition of the compound makes impossible the determination of transition enthalpy. Data of magnetic measurements, Infrared and EPR spectroscopy fully confirm the existence of redox-isomerism in temperature ranges of transitions observed calorimetrically.

Table 1. Thermodynamic parameters of phase transition in I, II and III

<table>
<thead>
<tr>
<th></th>
<th>ΔT, K</th>
<th>$\tau_{m}^o$ ($C_{p,max}^o$), K</th>
<th>$\Delta H_{m}^o$, kJ/mol</th>
<th>$\Delta S_{m}^o$, J/K·mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>134–222</td>
<td>178.0</td>
<td>2.14</td>
<td>11.9</td>
</tr>
<tr>
<td>II</td>
<td>250–375</td>
<td>299.9</td>
<td>15.0</td>
<td>48.8</td>
</tr>
<tr>
<td>III</td>
<td>309–</td>
<td>370.0</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

If to use the 1,10-phenanthroline as neutral ligand instead of 2,2-dipiridyl we will obtain complex which heat capacity is presented in Fig. 4.
As we can see, minor distinction (of 2 carbon atoms) in neutral ligand leads to significant change in phase transition temperature, interval and steepness (Table 2).

Table 2. Thermodynamic parameters of phase transition in II and IV

<table>
<thead>
<tr>
<th></th>
<th>ΔT, K</th>
<th>$T^0_{tr}$ ( $C^p_{\text{max}}$ ), K</th>
<th>ΔH^0_p, kJ/mol</th>
<th>$\Delta S^0_{tr}$, J/K·mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>250–375</td>
<td>299.9</td>
<td>15.0</td>
<td>48.8</td>
</tr>
<tr>
<td>IV</td>
<td>234–281</td>
<td>254.5</td>
<td>6.32</td>
<td>24.8</td>
</tr>
</tbody>
</table>

For explaining different steepness (cooperativity) domain model proposed by Sorai and Seki for spin-crossover transitions was used [12]. Extent of cooperativity of transitions is highly important characteristics which should be studied in order to be able to control it for creating molecular devices, switches and sensors. Precise vacuum calorimetry is one of suitable methods which allow us to investigate cooperativity of redox-isomeric transitions.

III. CONCLUSIONS

The temperature dependence of heat capacity for some $\sigma$-semiquinonic cobalt complexes was studied by methods of calorimetry in 6–350(420) K temperature range.

Thermodynamic parameters of phase transition which accompanies redox-isomeric transformation semiquinone-catecholate form of the complex into bissemiquinonic one were determined. It was revealed, that increasing of acceptor ability of quinones leads to increasing transition temperature, enthalpy and steepness.

Substitution of neutral ligand dipyridil on phenanthroline leads to increasing the cooperativity extent of phase transition and decreasing the values of its enthalpy and entropy.

On the basis on experimental data standard thermodynamic functions were calculated for studied complexes in wide temperature range.
These studies contribute to development an approach of “tuning” properties of redox-isomeric systems for use in specific practical purposes. Peculiar redox-active character of semiquinonic transition metal complexes makes them appealing to design materials of potential technological interest.

IV. ACKNOWLEDGMENTS

We are grateful to the RFBR (grant № 16-03-00700-a)

V. REFERENCES

INVESTIGATION OF THE MECHANICAL BONDING EFFECTS ON MECHANICAL PERFORMANCE OF THE ADHESIVELY BONDED COMPOSITE MATERIALS

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Abstract: The purpose of this study is investigating mechanical bonding effects on adhesively bonded composite materials for different adhesive lengths ($l_a$), number of bolts ($n$), $E/W$ values and various bolt torques ($T$). In this study, the damage behaviors of composite plates were investigated using experimental method. Glass-fibre reinforced epoxy laminated composites $(0/90)_{6}$ were used as composite material and samples dimensions were $100 \times 20 \times 2.3 \text{ mm}$. For adhesion process, two components of epoxy adhesive EA 3430 was preferred and M5 steel bolts were used for mechanical bonding. Three different tightening torques ($T=5, 10, 15 \text{ Nm}$) were chosen for the bolted joints in the experiments. Also different adhesive lengths ($l_a=20, 30 \text{ mm}$) and $E/W$ values ($0.5$, $0.75$) were chosen. Tensile test was applied through a centroidal axis on each sample. Load – displacement curves were drawn and datas were shown with graphics. Results were commented about adhesive length ($l_a$), number of bolts ($n$), $E/W$ values and bolt tightening torques ($T$) in this study.

Keywords: Composite materials, mechanical bonding, adhesively bonding, torque effect, adhesive length

1 Introduction

A composite material can be specified as a combination of two or more materials that results in better properties than those of the individual components used alone. Each material keeps its separate chemical, physical, and mechanical properties. The two components are a reinforcement and a matrix. Composite materials are becoming a necessary part of today’s materials because they offer advantages such as low weight, corrosion resistance, high fatigue strength, faster assembly, etc. Also composite materials have high specific strength, high wear resistance, high dimensional stability and the flexibility in designing complex shapes. Composites are used for different sectors from making aircraft structures to golf clubs, electronic packaging to medical equipment, and space vehicles to home building. Moreover composite materials submit this advantages in economic aspects. In such applications composites are generally fastened either to composites or to metals by adhesive bonding or by mechanical bolts. [1-3]

Connection of polymer matrix composite materials has conventionally been achieved by mechanical fastening or adhesive bonding. Combining these methods has been considered unneeded in terms of structural performance as the adhesive supplies a stiffer load path and thus transfers the greater part of the load. However, these assumptions are generally related to special aerospace connections where long adhesive length and high modulus epoxy adhesives are used.
In other basic applications, joining polymer matrix composites using alternative methods such as hybrid joints combining mechanical fastening and adhesive bonding could be prompted. [4]

The important parameters considered in hybrid joint design include the number and diameter of the fasteners, diameter of the fastener head or washer size, clamping torque, adhesive length and position of hole on material. Optimum combinations of these parameters can cause to increase in bearing strength. [5]

Aydin [6] has presented a master thesis on the effect of environmental conditions on the mechanical performances of bonded composites. Aydin has examined mechanical performances of composite materials which are connected by adhesive bonding and have constant thickness according to various temperatures. Beside this, Aydin also has examined the effects of various bonding lengths. Tension tests have been applied to bondings in various temperatures and lengths.

In this experimental study, specimens which punched were bolted only. Adhesively bonded composite material experimental study datas were quoted from Aydin’s article.

2 Experimental Study

2.1 Manufacturing of the laminated composite plates

In this experimental study, glass-fibre reinforced epoxy laminated composites (0/90)₆ were used. Glass-fibre reinforced epoxy material was manufactured by vacuum-assisted resin infusion system.

In the production of laminated composite plate, as a reinforcement material 300 g/m² (0/90) woven E - glass fiber fabric is used. Matrix was chosen as the material is a two-component epoxy. The epoxy hardener is used at 100:34 ratio.

![Figure 11: (0/90) E-Glass Fibre](image-url)
2.2 Specimen Preparation

In order to observe the effects of the factors we mentioned, it was studied with 2 different sample geometries. In these geometries; adhesive lengths \((l_a)\), the location of holes and E/W ratios were different. For each geometry, three specimens was prepared to converge to the correct results. Three different tightening torque values \((T=5, 10, 15\ Nm)\) were applied for each sample geometries.

![Figure 12: Specimen geometries (geometry 1 and geometry 2) for different adhesive lengths and E/W ratios](image)

In specimens preparation phasae, glass-fibre reinforced epoxy laminated composites \((0/90)_6\) were cut to specified size by cold saw and specimens were punctured with drills at specified points. To perform an accurate test, the force that applied should be transmitted as linear on test specimens. Therefore, affixion parts were affixed to both ends of the specimens by *Pattex 2C Proffesional Rapid Adhesive*.

Later on cutting, punching and affixation process, specimens were attached with two-component epoxy adhesive *Loctite EA 3430*. In bonding process, adhesive lengths \((L_a)\) were different for two different specimen geometries. All bonding operations were performed at room temperature. Physical properties were shown in Table 1.

**Table 1: Loctite EA 3430 - Physical Properties for 22°C**

<table>
<thead>
<tr>
<th></th>
<th>Tensile Strength [N/mm²]</th>
<th>Shear Strength [N/mm²]</th>
<th>Tensile Modulus [N/mm²]</th>
<th>Elongation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Loctite EA 3430</em></td>
<td>36</td>
<td>22</td>
<td>3.21</td>
<td>2</td>
</tr>
</tbody>
</table>
Right after bounding process, singular parts of specimens were bolted with different test torques (\(T=5, 10, 15 \, Nm\)). Torque meter was used when tightening bolts for precious torque value. Flat washers were used in bolting stage. After torquing operation, samples were kept waiting for 24 hours to curing adhesive. Thus, all specimens were ready for tension test.

![Figure 13: Examples of specimens](image)

### 2.3 Testing

All tests were carried out on an Shimadzu Autograph AG-X tensile testing machine (Fig 4a). The tests were run in displacement control at a rate of 2 mm/min. Loading continued for a while, after the damage had occurred on specimens. Each test configuration was repeated with three specimens. Prior to testing, the surfaces of all specimens were cleaned with alcohol to remove dust or grease. Force and displacement data were taken from Shimadzu Autograph AG-X tensile testing machine and graphs were shown in Trapezium X material testing software (Fig 3b).

![Fig 4.a Shimadzu AG-X Tensile Testing Machine](image) ![Fig 4.b Trapezium X material testing software](image)

### 3 Results And Discussion

The influence of mechanical bonding on adhesively bonded composite materials was investigated experimentally for various tightening torques (\(T = 5, 10, 15 \, Nm\)) applied on the bolted joints, various adhesive lengths (\(L_a = 20, 30 \, mm\)) and also E/W ratios of the specimens (0.5, 0.75) in this study.
3.1 Effect of Tightening Torque on Adhesively Bonded Composites

Increasing of tightening torque of bolted joint on adhesively bonded composite positively affects on the max. loads before damaging of the specimens preliminarily. On the other hand, if tightening torque exceeds a critical torque value, bolted joint is affected negatively. The reason of this effect is damage where under bolt head and nut places on specimens due to excessive clamping forces accordingly high tightening torque.

Figure 5: An example of load – displacement graphics for Geometry 1 (a) and Geometry 2 (b)

Fig.5 (a and b) depicts the effect of the different specimen geometries have different adhesive lengths \(L_a = 20, 30 \text{ mm}\) and E/W values \((0.5, 0.75)\) on the experimental results according to various tightening torques \((T = 5, 10, 15 \text{ Nm})\) as charts. From the figures, it is generally seen that the max. load increased by increasing the tightening torque from 5 Nm to 10 Nm for each geometry. Furthermore, max. load value for first damage decreased by increasing the tightening torque from 10 Nm to 15 Nm. The reason of this effect is damage where under bolt head and nut places on specimens due to excessive clamping forces accordingly high tightening torque for 15 Nm tightening torque. Fig. 6 shows max. loads for first damage on material.

Figure 6: Examples of damages accordingly high tightening torque as 15 Nm.
Table 2: Maximum damage load table for first damage on material

<table>
<thead>
<tr>
<th>E/W</th>
<th>La</th>
<th>Max. Damage Load [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Bonding + 5 Nm Torque</td>
</tr>
<tr>
<td>Geometry 1</td>
<td>0,5</td>
<td>20 mm</td>
</tr>
<tr>
<td>Geometry 2</td>
<td>0,75</td>
<td>30 mm</td>
</tr>
</tbody>
</table>

3.2 Effect of hole and E/W ratio

Aydin [5] has presented a master thesis on the effect of environmental conditions on the mechanical performances of bonded composites. In Aydin’s thesis, bonding effect was studied without bolt connection for the same material and temperature as this study. Solely, specimens widths are 5 mm more than this study, so average load should be more for our comparison. Fig 3. shows average loads for various adhesive lengths at 23°C.

Table 3: Average load values to adhesive length for 23°C (Aydin, 2014)

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Average Load [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E/W</td>
<td>La</td>
</tr>
<tr>
<td>0,5</td>
<td>20 mm</td>
</tr>
<tr>
<td>0,75</td>
<td>30 mm</td>
</tr>
</tbody>
</table>

Considering Table 2 and 3 together, hole effect and E/W effect can be seen. When tightening torque is 5 Nm, max. load values get close to adhesive bonding samples without bolt connection. Despite the 5 Nm torque, load values can’t rise significantly. Damage on composite material and high stress around hole is the reason for this.

Referring to the difference between geometries; hole effect can be seen greater for geometry 1 than geometry 2. If the hole places getting close to near, damage occurs at low loads gradually because of E/W effect.

3.3 Failure modes of joints

In the mechanical joints, it may appear in a variety of failure modes; net-tension, shear-out, bearing and cleavage. The damage may occur as a result of the combination of these modes.

As seen in this figure, the specimens generally damage as the bearing + shear out mode.
4. Conclusion

The influence of different torque values on adhesively bonded composite materials were investigated experimentally for various tightening torques (\( T = 5, 10, 15 \text{ Nm} \)) applied on the bolted joints and various adhesive lengths (\( L_a = 20, 30 \text{ mm} \)) and also E/W ratios of the specimens (0.5, 0.75) in this study. From the experimental results, it can be concluded that;

Hole for bolting connection affects max. load values negatively, on the other hand bolt tightening torque affects max. load values positively till a critical tightening torque value. After critical tightening value, damage occurs because of the extreme clamping forces. For ideal bolting connection, ideal bolt tightening torque should be determined.

When bolt tightening torque was increased 5 Nm to 10 Nm, max. load increased 74% for geometry 1 and 16% for geometry 2. This difference caused by variations of E/W ratios between geometries. Hole is positioned close the end of specimens so, negative hole effect is bigger for geometry 1 than 2. for 5 Nm tightening torque. Increase was bigger from 5 Nm to 10 Nm torques because of this E/W effect. Afterwards when torque value was increased 15 Nm, max load decreased 30% for geometry 1 and 36% for geometry 2. Decreasing values were close to each other, because reason are same for each 2 geometries.

Damage modes are entirely influenced from the geometric parameters of the specimens, such as E/D, W/D, or E/W. There are many studies about these parameters. However, since the width of the specimen is constant in this study, the changing of E/W ratio does not affect specially on the damage modes of the specimens. All of the specimens damage in forms of bearing, shear out or bearing + shear out modes without meaningful reason.
5. References


Acknowledgements

The author wish to express the particular thanks to Dokuz Eylul University, Engineering Faculty, Department of Mechanical Engineering in Izmir / Turkey, for their collaboration during manufacturing of the glass/epoxy laminated composite plates and testing specimens.
EFFECTS OF TALC ADDITIONS ON THERMAL CONDUCTIVITY AND DECOMPOSITION OF RIGID POLYURETHANE FOAMS

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2 Department of Mechanical Engineering, Energy Division, Pamukkale University, Denizli, Turkey

Abstract: Rigid polyurethane foams are used in thermal insulation applications due to their low thermal conductivities. Meanwhile, different inorganic minerals as fillers are incorporated into rigid polyurethane foams, especially to reduce production costs. However, it is required to investigate the effects of fillers on the properties of foams before their usage in industrial applications. In this study, talc which is a cheap inorganic mineral was added in rigid polyurethane foams up to 15 % in mass. Effects of talc addition on thermal conductivity and decomposition of rigid polyurethane foams were investigated. Experimental results showed that talc addition slightly increased the thermal conductivity of the foams. However, thermal stability of the foams was enhanced with the talc addition.

Keywords: Rigid polyurethane, talc, thermal conductivity, thermal decomposition.

1. Introduction

Rigid polyurethane foams are used in many applications such as automotive, transporting, constructions, furnishings etc. due to beneficial properties like low thermal conductivity, low density, good shock absorption and good chemical resistance [1-4]. But, they have low thermal decomposition resistance, low fire resistance and can be easily ignited [5, 6]. So, many studies have been performed for enhancing these properties bordering the usage of the foams [7-11].

One of the best way of enhancing the thermal and fire behaviours of the polyurethane foams is adding different flame retardants like alumina trihydroxide (ATH), magnesium hydroxide (MgOH), ammonium polyphosphate (APP) [12, 13]. In general, prices of the flame retardant materials are higher than those of the foam raw materials. Therefore, the higher production costs are inevitable with addition of flame retardants [14]. Furthermore, mineral fillers like calcite, clay, dolomite and talc are used mainly for reducing production costs of the foams. Meanwhile they can also enhance thermal behaviours of the materials [15-17]. However, it should be pay attention to the important properties of the fillers such as particle size, chemical composition or filler ratio before using them [11].
In this study, effects of 15 wt % talc addition on thermal conductivity and thermal degradation behaviours of the rigid polyurethane foams were investigated. Thermal conductivities of the neat and the talc filled foams were measured regularly once in a week for two months. Thermal degradation behaviours were investigated by thermogravimetric analysis in a nitrogen atmosphere.

2. Materials and Methods

2.1 Materials

The raw materials of rigid polyurethane foam (polyol-Evopur 1122-28, isocyanate-PMDI 92140) were purchased from TEKPOL Technical Polyurethane Ltd. (Turkey). The density and viscosity of the isocyanate at 25 °C are 1230 kg/m³ and 210 mPas, respectively. Meanwhile, the density and viscosity of the polyol at 25 °C are 1130 kg/m³ and 300 mPas, respectively. Talc was kindly supplied by OMYA Mining Ltd. (Turkey) and the average particle size (d_{50}) of the talc is 7 µm. Talc is mainly composed of SiO₂ (63.45 %), MgO (34.11 %) and CaO (1.46 %).

2.2 Sample Preparation

Talc was dried in an oven at 100 °C for 24 hours to remove the humidity. The density of the foam was kept at 40 ± 0.5 kg/m³ by reducing the amount of raw materials as the amount of talc addition. The detailed information about the samples is given in Table 1. Talc was poured into the polyol and homogenized with mechanical homogenizer (Heidolph Silent Crusher M Model) with a speed up 26,000 rpm for 5 min. Talc filled polyol and isocyanate were stirred at mechanical stirrer at 3000 min⁻¹ for 12 s. Then the mixture was poured into the pre-heated mold at 40 °C and the mold was kept for 25 min under the heated press at 40 °C. The samples were kept for 24 hours in the laboratory conditions to complete curing process. The samples were kept into the conditioning device at the temperature 23 ± 1 °C and relative humidity 50 ± 3 % for 48 hours before the tests.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Polyol (%)</th>
<th>Isocyanate (%)</th>
<th>Talc (%)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUR</td>
<td>46.0</td>
<td>54.0</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>PUR+TALC</td>
<td>39.1</td>
<td>45.9</td>
<td>15</td>
<td>100</td>
</tr>
</tbody>
</table>
2.3 Thermal Conductivity

Thermal conductivities were measured with Kyoto QTM-500 according to ASTM C1113 [18]. The results for each foam were given as the average of five measurements. The thermal conductivities were measured within 5 % accuracy.

2.4 Thermogravimetric Analysis

Thermogravimetric analysis (TG/DTG) were performed with Perkin-Elmer Diamond thermal analyser. The tests were performed between 40 and 800 °C and at a rate of 20 °C/min under nitrogen gas. Ceramic pans were used in the experiments. The real time weight loss and derivative weight loss were recorded via a special software during the experiments.

3. Results and Discussion

Figure 1 shows thermal conductivity coefficients of PUR and PUR+15TALC composites for first and fiftieth days. Thermal conductivity coefficient increased about 8 % with the talc addition for the first day. This increase can be explained with the broken cell walls by talc particles and decreasing the closed cells content [6, 19, 20]. Thermal conductivity coefficients of PUR and PUR+15TALC foams increased about 8.2 % and 9 % in 55th day, respectively. It is well known that the thermal conductivity coefficient of the foam increases by time due to the exchange of the cell gas used in the foam [21, 22]. The gas which has low thermal conductivity coefficient inside the cells is replaced with the air by diffusion effect by the time [23]. This results show that the talc addition does not significantly worsen the thermal insulation of the foam by the time.
Thermogravimetric analysis are important studies to clarify thermal decomposition characteristics of materials [24]. Figure 2 shows TG and Figure 3 shows DTG curves of PUR and PUR/TALC composites. Addition of the talc into the rigid polyurethane foam increased the maximum decomposition temperatures and decreased the maximum decomposition rates [25, 26]. The second maximum decomposition temperature for PUR material was obtained as 357.8 °C. This temperature value was 364.0 °C for 15 wt % talc added foam. The second maximum decomposition rate was decreased about 17 % with the addition of 15 wt % talc. Decreasing of decomposition rate can be explained with the barrier effect of talc particles which prevents the volatiles to leave from the material. The main loss temperature ($T_{50wt}$) of PUR was 360.6 °C and this temperature increased about 7.7 % for 15 wt % talc addition into the rigid polyurethane foam.

Figure 2 TG curves of PUR and PUR/TALC composites
4. Conclusions

Effects of 15 wt % talc addition on thermal conductivity and decomposition of rigid polyurethane foams were investigated. Although the talc addition slightly increased the thermal conductivity of the foam, thermal stability of the foams was enhanced with the talc addition. Since the price of the talc is fairly lower than that of the foam raw materials, it can be incorporated in the rigid polyurethane foam productions up to 15 wt % to reduce the production costs without significant negative effects in terms of thermal insulation and thermal stability.

5. References


**Acknowledgements**

The authors would like to thank the Pamukkale University Scientific Research Council for supporting this study under project contract no. 2014FBE026. Since some of the equipments and materials were provided with the support of TUBITAK (The Scientific and Technological Research Council of Turkey) under project contract no. 108T246, the authors would like to thank TÜBİTAK.
INVESTIGATION THE FIRE BEHAVIOUR OF RIGID POLYURETHANE FOAMS FILLED WITH TALC

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² Department of Mechanical Engineering, Energy Division, Pamukkale University, Denizli, Turkey

Abstract: In thermal insulation applications, rigid polyurethane foams are preferred due to their low thermal conductivities. However, the price of the rigid polyurethane foam is higher than that of other thermal insulation materials. Therefore, different cheap mineral matters are incorporated into the foams to reduce the production costs. Beside thermal conductivity and decomposition behaviours of the foams filled with different fillers, the fire behaviour of the foams should also be investigated for security of life and property.

In this study, the talc was added into rigid polyurethane foams at different loadings, namely 5, 10 and 15 wt % and fire behaviours of the foams containing the talc were investigated by using cone calorimeter burning test. The experimental results revealed that 5 and 10 wt % the talc additions do not significantly affect the fire resistance of the foams; however, it was found that the fire resistance of the foams can be enhanced with 15 wt % the talc addition.

Keywords: Rigid Polyurethane, talc, fire resistance, cone calorimeter

1. Introduction

In thermal insulation applications, rigid polyurethane foams are preferred due to their low thermal conductivities [1, 2]. However, the price of the rigid polyurethane foam is higher than those of other thermal insulation materials. Therefore, different cheap mineral matters are incorporated into the foams to reduce the production costs. Beside thermal conductivity and decomposition behaviour of the foams filled with different fillers, the fire behaviour of the foam should also be investigated for security of life and property [3, 4].

Cone calorimeter test is one of the most common method to investigate and enhance the fire behaviours of polymer materials [5, 6]. The parameters like heat release rate (HRR), total heat released (THR), time to ignition (TTI), peak heat release rate (PHRR) and also smoke and CO generations, CO₂ and NO emissions can be obtained from cone calorimeter tests.

Mineral fillers like talc, calcite, clay and dolomite are used to reduce the cost of production [7, 8]. Beside this, adding mineral fillers may enhance thermal, fire and mechanical properties of the materials [9-11]. Sizes of the particles of filler, the composition and the content of the filler are
the important parameters affecting the properties of the composite foam materials [12]. The big particles may break down the cell walls and make worsen the mechanical, thermal and fire behaviours of the composites [13].

In this study, combustion behaviours of neat and talc added rigid polyurethane foams were investigated with cone calorimeter tests. Heat release rate, total heat released, ignition time, smoke and CO productions of neat and talc filled polyurethane foams were examined.

2. Materials and Methods

2.1 Materials

Raw materials of the rigid polyurethane foam which are polyol and isocyanate were purchased from TEKPOL-Technical Polyurethane LTF. (Turkey). The density and viscosity of the polyol at 25 °C are 1130 kg/m$^3$ and 300 mPas, respectively. Meanwhile, the isocyanate is characterized by 31.2 % of NCO groups, with the density and viscosity of at 25 °C, 1230 kg/m$^3$ and 210 mPas, respectively. Talc which is mainly composed of SiO$_2$ (63.45 %), MgO (34.11 %) and CaO (1.46 %), was kindly supplied from OMYA Mining Ltd. (Turkey). Average particle size of the talc was about 7 µm.

2.2 Sample Preparation

Since the moisture content of the talc negatively affects the foam production, the talc was dried in an oven at 100 °C for 24 hours before production of the foams. The amount of raw materials was reduced as the amount of talc to keep the density of the foam at 40 kg/m$^3$. The detailed information about the samples is given in Table 1. Talc was poured into the polyol and a rotor-stator type of mechanical homogenizer with a speed up to 26,000 rpm was used for the dispersion. The mixture of talc/polyol/isocyanate was stirred at mechanical stirrer at 3000 min$^{-1}$ for 12 s. The mixture was poured into pre-heated aluminium mold at 40 °C. Then, mold was put under the pre-heated press and kept for 30 min. the samples were kept in the laboratory conditions for 24 hours to complete curing process after removing the samples from the mold. Before the tests, the samples were kept in the conditioning device at the temperature 23 °C and relative humidity 50 % for 48 hours.
Table 1 Formulations of PUR and PUR/TALC

<table>
<thead>
<tr>
<th>Sample name</th>
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<th>Total</th>
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<td>39.1</td>
<td>45.9</td>
<td>15</td>
<td>100</td>
</tr>
</tbody>
</table>

2.3 Cone Calorimeter

The cone calorimeter apparatus was used to investigate the fire behaviours of the samples. The cone calorimeter was manufactured according to ASTM E-1354 [14] and ISO 5660 [15] standards. The samples were cut into 100 x 100 x 50 mm and wrapped in 2 mm thick aluminium foil before the tests. 35 kW/m² heat flux which represents the middle size fire scenario was exposed horizontally to the sample. All tests were performed for three times and the data was reported as the average values. Temperatures, mass loss, smoke and CO generation were recorded with the special software simultaneously in 1 s increment. HRR and THR were calculated from the measurements.

3. Results and Discussion

The heat release rate (HRR), total heat released (THR), time to ignition (TTI) and peak heat release rate (PHRR) are important parameters in cone calorimeter tests to compare fire resistance of different materials [16]. The HRR and the THR curves of PUR and PUR+15TALC foams at the heat flux of 35 kW/m² are shown in Figures 1 and 2, respectively. Both PUR and PUR+15TALC foams showed similar characteristics of thermally thick charring (residue forming) samples in which an initial increase in HRR appears until an efficient char layer is formed and then the char layer thickens resulting in a decrease in HRR.
Although TALC addition did not significantly affect the ignition behaviour of the foam (time to ignition), PHRR and burning of the foam in 75 s, it slowed down flame propagation and the HRR values of TALC filled foam were lower than those of neat PUR during rest of the time. It is thought that talc served to form a stronger char layer which can partially hinder the
decomposition of the material and reduces the heat release rate. In addition, talc addition decreased the amount of combustible materials. Meanwhile, it was determined that there was 19% reduction in the THR with TALC addition.

Figure 3 and 4 shows smoke and CO generations of PUR and PUR/TALC foams, respectively. Smoke and CO are the major cause of poisoning during fires [16]. Smoke and CO generated during fires are strongly affected by material and fire properties [17].

![Figure 3 Smoke generations of PUR and PUR/TALC foams](image-url)
It can be clearly seen from Figures 3 and 4, talc addition did not significantly decrease the peak value of smoke, but peak value of CO decreased with talc addition. The reduction may be explained with the fuel lean conditions in the certain periods and low combustible materials by reducing the amount of raw materials as the amount of filler.

Figure 5 shows the NO emissions of PUR and PUR/TALC foams. As it can be seen from the figure, talc addition did not significantly affect the NO emissions of the foams during 400 s. The maximum NO emissions of the foams were lower than 20 ppm.
4. Conclusions

The effects of 15 wt % TALC addition on fire behaviours of the rigid polyurethane foams were investigated by using the cone calorimeter tests. The experimental results indicated that 15 % TALC addition resulted in lower HRR and THR. Although smoke and NO generation were not affected with TALC addition, CO emission of the foam filled with talc was lower than those of neat foam. It can be concluded that talc may be incorporated in the rigid polyurethane foam up to 15 wt % to reduce the production costs without negative effects in terms of fire resistance and generation of dangerous emissions.

5. References


15. ISO 5660-1: Reaction to fire tests heat release, smoke production and mass loss rate, part 1: heat release rate (cone calorimeter method), 2002.


Acknowledgments

The authors would like to thank Pamukkale University for supporting this study under Project Contract No. 2014FBE026. Also, the authors would like to thank The Scientific and Technological Research Council of Turkey (TUBITAK) for providing the cone calorimeter and some materials under Project Contract No. 108T246.
EFFECT OF TiO₂ AND Cr₂O₃ ON PROPERTIES OF CaO-Na₂O-SiO₂ GLASSES

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2 Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), Sorbonne Universités, UPMC Université Paris 06, CNRS UMR 7590, Museum National d’Histoire Naturelle, IRD UMR 206, 4 place Jussieu, F-75005 Paris, France

Abstract: The aim of this work is to study the effect of TiO₂ and Cr₂O₃ in low additions on the optical, color and thermo mechanical properties of soda-lime-silica glasses. Several compositions were developed and characterized. The results show a decrease of thermal expansion coefficients and an increase of glass transition temperatures with increasing both oxides content TiO₂ and Cr₂O₃ in glasses. Optical properties determined by UV-Visible spectroscopy reveal that the glass absorptions decrease with increasing TiO₂ content. In another hand, three new absorption bands around 350, 445 and 650 nm characteristic of Cr³⁺ and Cr⁶⁺ ions were also appeared in Cr₂O₃ doped glasses spectra. CIE L* a* b* parameters showed that TiO₂ doped glasses were colorless and a slight improved clarity with the TiO₂ additions was detected. However a pronounced greenish color and a significant increase in Cr₂O₃ doped glasses b* parameter values is noticed, despite the low Cr₂O₃ amount added. Electron paramagnetic resonance spectroscopy showed that the amount of ferric ions change with the addition of TiO₂ and Cr₂O₃. Fe³⁺ clusters and Cr³⁺ ions were also revealed.

Keywords: Soda-lime-silica glass, TiO₂, Cr₂O₃, Thermal expansion, Mechanical properties.

1. Introduction

Soda-lime-silica glasses are easily synthesizable, very homogeneous and the most important oxide glasses with a wide range of applications as flat glass, new electrical devices and biomaterials. This importance result from the material properties such as high stability towards crystallization, high potential for fiber drawing, refractive index and thermal expansion coefficient control by composition variations [1].

The addition of transition metal oxides even in small amounts plays an important role in improving the silicate glass properties such as optical absorption and fluorescence [2]. Therefore, great importance was devoted to these transition metal ions glass. In the last decades, applications of these special glasses are realized in various areas such as in the field of optical and colored glasses[3, 4, 5] as well as in advanced technologies such as lasers, solar energy converters and a number of electronic devices [6].

One of the most known transition metal oxides affecting the glasses properties is TiO₂. It is also one of the most encountered impurities in the glass raw materials. Usually, colorless soda-lime glasses are obtained with TiO₂ content lower than 0.05% in weight percent, while higher content generates yellowish colored glasses [6]. According to some authors [7, 8], TiO₂ addition
oxide glasses, generally contributes to their structure stabilization and their properties improvement, for example, chemical durability, mechanical properties, electrical conductivity, etc. Even small amount of TiO$_2$ additions in the glass composition produce an increase in the refractive index and the density of the obtained glasses [9]. According to Gwinn et al. and Alberto et al. [10, 11], the iron red-ox equilibrium is also affected by the titanium oxide presence, a phenomenon which also influence the glass coloration. Regarding the thermal behavior, a decrease of the thermal expansion coefficient is observed with increasing TiO$_2$ concentration [5, 9, 12]. Several other properties such as softening temperature, Elastic modulus, Vickers hardness and viscosity depend on the TiO$_2$ content [13, 14].

Chromium is also a major example of the transition metals that confers interesting optical and electrical properties to the glasses, making them thus intended for various applications [15]. Chromium ions dissolved even in small amounts colored glasses. They also have a strong influence on optical transmission and on insulation degree of glasses [16]. Beyond the green coloration that it permits to bring to the industrial glasses (under Cr$^{3+}$ state), chromium offers important perspectives in the domain of the telecommunications (materials for amplification) and lasers, consequences of its luminescence properties [15,17]. Chromium doped glasses properties are the result of the multiplicity of its red-ox states. Chromium with its electronic configuration 3d$^5$4S$^1$, on its external layer, has an oxidization degree capable to go from 0 to + VI. Nearly all degrees of oxidization are present in the glasses. Nevertheless, the III degrees and VI are the most current in silicate glasses [15, 17]. Chromium ions in their oxidation state Cr$^{3+}$ act as network modifier ions with CrO$_6$ as a structural unit. While under their Cr$^{6+}$ form, they act as network former ions with CrO$_4^{2-}$ like structural units [16].

In this study, five soda-lime silica glasses V$_0$, V$_T1$, V$_T2$, V$_C1$ and V$_C2$ were elaborated. V$_0$ corresponds to the glass obtained without TiO$_2$ and Cr$_2$O$_3$ addition, V$_T1$ and V$_C1$ correspond to the glasses doped with 0.1 wt % of TiO$_2$ and Cr$_2$O$_3$ respectively and V$_T2$ and V$_C2$ correspond to the glasses doped with 0.2 wt % of TiO$_2$ and Cr$_2$O$_3$ respectively. The effect of TiO$_2$ and Cr$_2$O$_3$ in low amount additions on the optical, thermal and color properties of soda-lime glass were studied.

2 Experimental

2.1 Materials

The basic glasses composition is summarized in table 1.

<table>
<thead>
<tr>
<th>Components</th>
<th>Sand</th>
<th>CaCO$_3$</th>
<th>Na$_2$CO$_3$</th>
<th>Na$_2$SO$_4$</th>
<th>MgCa(CO$_3$)$_2$</th>
<th>TiO$_2$ or Cr$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proportion</td>
<td>61.29-x</td>
<td>14.36</td>
<td>19.85</td>
<td>0.5</td>
<td>4</td>
<td>x = 0, 0.1 , 0.2</td>
</tr>
</tbody>
</table>

Table1: Proportion of raw materials in the samples (wt %)
Mixture of 100 g of raw materials (Algerian sand, Na$_2$CO$_3$, CaCO$_3$, and Na$_2$SO$_4$, dolomite and TiO$_2$ or Cr$_2$O$_3$) is placed in a platinum crucible in an electric furnace for a step of calcining at 1400 °C during 4 hours and a melting-refining step at 1560 °C for 2 hours. The liquid is then poured in a stainless steel mold at ambient temperature, allowing a rapid cooling to room temperature and finally annealed at 560 °C for a period of 30 min.

After glass elaboration, a mechanical preparation step is performed: cutting into test tubes, polishing (P400, P600, P1200, P2500, P40000 and with cerium oxide) and grinding until 63 µm. The experimental procedure of the obtained materials is presented in figure 1.

2.2 Sand and glasses characterization

The chemical composition of S$_1$ Sand (Table 2) was carried out by X-ray fluorescence (Panalytical Perl’X 3). The samples were prepared in the pellets form: 8 g of crushed sand with 4.5 ml of a compacted Elvacite resin.

The electron paramagnetic resonance spectra of sand and glasses had been recorded using a Bruker ESP 300 spectrometer, X-band (9.85 GHz) at room temperature (22 °C). About 100 mg of the samples powder were inserted into a pure silica capillary (surprasil). The spectra typically cover the range 0 – 0.4T. They were normalized by the gain and the sample weight. The unit used for the magnetic field is Gauss (1G is equal to 10$^{-4}$ T). The dilatometric measurements were made by a horizontal dilatometer dual road model DIL402, Netzsch with a heating rate of 1 °C / min. The samples were in a prism form [18].

The glass optical absorption spectra were carried out with a double beam Perkin-Elmer 1050 spectrometer in transmission mode. It scans a range of wavelengths between 300 and 4000 nm. The samples were previously polished with Cerium oxide.

The color measurements of the samples were obtained using an X-Rite spectrometer, model 962 S / N 000967 (USA), X-Rite ink formulation software Pinter Pro 5.11 operating with D65 light source, camera viewing angle 10°. The measurements were repeated three times for each composition and medium value was taken.
3. Results and Discussion

3.1 Sand characterization

3.1.1 Chemical composition

As summarized in table 2, $S_T$ is mostly composed by 98 wt % of SiO$_2$. However, TiO$_2$ is present in very low amount (0.07 wt %). $S_T$ does not contain clay fractions since its Loss On Ignition is very low (L.O.I = 0.022 wt %).

Table 2: Chemical composition of $S_T$ Sand.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>Na$_2$O</th>
<th>MgO</th>
<th>P$_2$O$_5$</th>
<th>L.O.I</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt (%)</td>
<td>98.2±0.01</td>
<td>0.88±0.03</td>
<td>0.34±0.04</td>
<td>0.20±0.02</td>
<td>0.12±0.01</td>
<td>0.07±0.004</td>
<td>0.05±0.01</td>
<td>0.05±0.01</td>
<td>0.038±0.003</td>
<td>0.022</td>
</tr>
</tbody>
</table>

Figure 1: Diagram of the experimental procedure of the obtained glasses
3.1.2 Sand EPR study

As shown in figure 2, the EPR spectrum of $S_T$ sand measured at 25 °C, contains an intense predominant resonance line centered at $g \sim 2.53$ (278 mT). Other resonances signals at $g \sim 4.34$, $g \sim 3.48$, $g \sim 2.41$, $g \sim 1.99$ are also obtained. These signals are attributed to Fe$^{3+}$ free and clusters ions present in $S_T$ Sand as impurities [19, 20].

3.2 Physical characteristics and properties of the glasses

3.2.1 Dilatometric analysis

The curves representing the expansion behavior of the glasses $V_0$, $V_{T1}$, $V_{T2}$, $V_{C1}$ and $V_{C2}$ are shown in Figure 3. The inflexion point of these curves corresponds to the glass transition temperature $T_g$, the maximum point is the dilatometric point $T_d$ while the thermal expansion coefficient $\alpha$ is also determined from these experimental curves.

A decrease of thermal expansion coefficient according to the TiO$_2$ and Cr$_2$O$_3$ addition is noticed (Table 3). This decrease is also proportional to the added amount and it is more observed with TiO$_2$ addition ($8.2 \pm 0.2$ and $8.8 \pm 0.2$ $10^{-6}$ °C$^{-1}$ for $V_{T1}$ and $V_{C1}$ respectively). Increasing TiO$_2$ and Cr$_2$O$_3$ added amount generate transition temperature increasing. This $T_g$ increase is more noticed with Cr$_2$O$_3$ addition ($574 \pm 2$ and $580 \pm 2$ °C for $V_{T1}$ and $V_{C1}$ respectively). This behavior suggests glass network reinforcing therefore its polymerization.
A reduction followed by an increase of the dilatometric softening temperature is noticed with the addition of 0.1 wt% and 0.2 wt% of TiO$_2$ or Cr$_2$O$_3$ respectively. The thermal expansion coefficient decreases (Table 3) with TiO$_2$ and Cr$_2$O$_3$ addition due to the fact that the glass thermal expansion is controlled by the thermal vibrations amplitude asymmetry of the bonds in the glass. This vibration asymmetry decreases as the rigidity of the glass network increases [4, 5, 21]. Similar results of TiO$_2$ doped glasses were found by Meechoowas et al. [9].

The glass transition temperatures increase with TiO$_2$ addition, this leads to some structural changes in the glass network. Hence, the increase of Tg glasses containing low TiO$_2$ can also be attributed to the strengthening of the glass network by titanium addition [22]. Similar results were also observed by Meechoowas et al. [9]. The strengthening of the glass network after adding small Cr$_2$O$_3$ amount is also to consider. Chromium ion can act as network former ion, under its Cr$^{6+}$ form with CrO$_4^{2-}$ as structural units [16].

Table 3: Thermal expansion coefficients, Tg, Td of the samples

<table>
<thead>
<tr>
<th>Glasses</th>
<th>Tg (°C)</th>
<th>Td (°C)</th>
<th>α (50-350°C) (10$^{-6}$ °C$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_0$</td>
<td>573 ±2</td>
<td>629 ±2</td>
<td>8.9 ±0.2</td>
</tr>
<tr>
<td>V$_{Ti}$</td>
<td>574 ±2</td>
<td>612 ±2</td>
<td>8.2 ±0.2</td>
</tr>
<tr>
<td>V$_{Ti2}$</td>
<td>585 ±2</td>
<td>628 ±2</td>
<td>8.3 ±0.2</td>
</tr>
<tr>
<td>V$_{C1}$</td>
<td>580±2</td>
<td>621±2</td>
<td>8.8±0.2</td>
</tr>
<tr>
<td>V$_{C2}$</td>
<td>587±2</td>
<td>625±2</td>
<td>8.5±0.2</td>
</tr>
</tbody>
</table>

Table 3: Thermal expansion coefficients, Tg, Td of the samples
3.2.2 UV-visible – IR studies

As it is shown in figure 4-a, the three samples exhibit ordinary glasses absorbance values. Addition of TiO$_2$ decreases slightly this absorption. However V$_{T1}$ absorption is the most decreased compared to V$_0$ and V$_{T2}$ absorptions. The glasses containing titanium dioxide optical absorption spectra show strong ultraviolet cutoff at approximately 310 nm, thus showing an infinite ultraviolet absorption and a zero emission. Similar results were obtained by Kumar [21]. However characteristic absorption bands of the Ti$^{3+}$ ions at 480-510 nm, 570 and 680 nm are not detected. These results are expected as under ordinary melting conditions, it is difficult to obtain reduced Ti$^{3+}$ ions in soda-lime silicate glasses [3]. However the appearance of a small peak around 380 nm, characteristic of Fe$^{3+}$ ions, following the TiO$_2$ addition is noticed. According to the studies of the iron doped glasses by Rus et al. [23] and Kukkadapu et al. [24], ferric ions present absorption bands in the range 325-450 nm and 350-500 nm respectively.

According to the figure 4-b, Chromium oxide addition causes the appearance of three new absorption bands around 350, 445 and 650 nm in V$_{C1}$ and V$_{C2}$ compositions spectra. The two bands observed at 445 and 630 nm are attributed to Cr$^{3+}$ ions present especially in a distorted octahedral coordination, while the band centered at 350 nm is attributed to Cr$^{6+}$ ions [25].

In fact, the two bands located at 350 and 445 nm in the spectrum of the V$_{C2}$ composition with 0.2 wt % Cr$_2$O$_3$ are more intense in comparison with that of the V$_{C1}$ composition with 0.1 wt % Cr$_2$O$_3$, while one located at 650 nm has the same intensity in the spectra of the two compositions. The intensity of Cr$^{6+}$ ions characteristic band is greater compared with those of Cr$^{3+}$ ions. In alkali silicate glasses, Cr$^{6+}$ ions proportion is predominantly than that of Cr$^{3+}$ ion as it is reported by M.A Marzouk et al. [26].

3.2.3 Color properties

According to table 4, the basic glass V$_0$ is the most chromatic (C* = 2.59), comparatively with V$_{T1}$ and V$_{T2}$. By adding small amount of TiO$_2$ (0.1 wt %), chromaticity decreases to become 2.51. By increasing the TiO$_2$ content up 0.2 wt %, the glass becomes more chromatic. The TiO$_2$ addition increases the b* parameter to the yellow color. However, a* parameter values are very influenced by the interference between Fe$^{2+}$/Fe$^{3+}$ and Ti$^{3+}$/Ti$^{4+}$ [27]. Its negative values indicate a slight green color which is attributed to the ferric ions. TiO$_2$ addition brings a slight improvement in the glasses clarity represented by the L* parameter, from 88.4 then 89.4 and 88.7 for V$_0$, V$_{T1}$ and V$_{T2}$ respectively.

However, improvement in glasses clarity and light transmission noticed by TiO$_2$ addition are due to its influence on Fe$^{3+}$/Fe$^{2+}$ ions equilibrium in the glass. Several studies have demonstrated the influence of the titanium presence in the melt on this red - ox equilibrium [10, 11].
Figure 4: a. UV-Visible spectra of V₀, V_T₁, and V_T₂ glasses, b. UV-Visible spectra of V₀, V_T₁, V_T₂, V_C₁, and V_C₂ glasses.

Table 4: L *, a *, b * color parameters of the samples

<table>
<thead>
<tr>
<th></th>
<th>V₀</th>
<th>V_T₁</th>
<th>V_T₂</th>
<th>V_C₁</th>
<th>V_C₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>88.4</td>
<td>89.4</td>
<td>88.7</td>
<td>76.1</td>
<td>73.2</td>
</tr>
<tr>
<td>a*</td>
<td>-2.5</td>
<td>-2.3</td>
<td>-2.6</td>
<td>-18.1</td>
<td>-18.3</td>
</tr>
<tr>
<td>b*</td>
<td>0.7</td>
<td>1</td>
<td>1.1</td>
<td>25.3</td>
<td>32.5</td>
</tr>
</tbody>
</table>

According to Alberto et al. [11], there is interaction between titanium and the melt which favors oxidation of Fe²⁺ to Fe³⁺. This oxidation phenomenon can be explained by considering the presence of direct structural interactions between Fe and Ti: possibility of Iron-Titanate (Fe₂TiO₄) complex formation in analogy to that of Aluminum-Titanate. The effect of Ti on the anionic structure of the silicate melt is also envisaged. Based on the Mossbauer analysis results, Alberto et al. [11] proposed formation of Fe²⁺-O-Ti bonds with Ti⁴⁺ and no bridging oxygen linked with Fe²⁺. Knowing that Ti⁴⁺ is substantially larger than Si⁴⁺, Fe²⁺-O polyhedra have a greater tendency to distortion when bonded to Ti⁴⁺ rather than to Si⁴⁺. This distortion destabilizes the Fe²⁺-O polyhedra and favors ferrous ion oxidation.

Considering Cr₂O₃ addition (table 4), the a* and b* parameters values are very influenced by this addition. In fact, Cr₂O₃ addition increases the value of a* parameter from -2.6 (without addition) to -18.1 and -18.3 for V₀, V_C₁ and V_C₂ samples respectively. These negative values are relative to the green color due to Cr³⁺ ions presence in the two last compositions [15]. On the other hand, the presence and the amount of Cr⁶⁺ ions in the glass influence the b* parameter. Positive values of the latter are the result of a yellowish coloration characteristic of the Cr⁶⁺ ions [15, 17, 26]. Increasing Cr₂O₃ addition induces the predominant formation of Cr⁶⁺ ions when
glasses are melt at 1560°C. This phenomena increases their characteristic absorption band intensity namely 350 nm [25]. However this predominance is also noticeable in the variation observed in the parameters b* values compared with those of a*(1.1, 25.3 and 32.5 for V0, Vc1 and Vc2 samples respectively) [26].

3.2.4 EPR of the obtained glasses

As shown in figure 5, the EPR spectra exhibit an asymmetric signal at g~4.3 (160 mT), accompanied by two weaker features g~8 (85 mT) and g~2 (354 mT). These signals are typically observed for free ferric ions Fe³⁺ distributed in the glassy matrix originate from their paramagnetic transitions in rhombic and axially distorted sites for the lines centered at g~4.3 and g~8 respectively and Fe³⁺ ions clusters: clusters that interact through a dipole or a super coupling magnetic exchange for the line centered at g~2 [23, 28, 29]. These results confirm presence of a significant amount of paramagnetic Fe³⁺ impurities in the raw materials: sand. It is clear that TiO₂ addition did not cause Ti³⁺ ions formation which are typically associated with a resonance peak with factor g~1.94 (350 mT) [30,31].

On the other hand, Vc1 and Vc2 EPR spectra exhibit a broad asymmetric band centered on g~5. It is related to the isolated Cr³⁺ in strongly- distorted octahedral sites of the glass network. A weak resonance signal corresponding to g~2 is also exhibit; it belongs to the isolated Cr³⁺ centers at the axially-distorted octahedral sites [15,32,33]. It also shows an intense and broad line centered on 60 mT (g~13). This signal may be caused by a ferromagnetic resonance due to traces of metallic Fe [29].

According to the EPR spectra, TiO₂ and Cr₂O₃ addition makes changes in the intensities of the resonance signals corresponding to g~8 , g~4.3 and g~13 in comparison with those of the V0 glasses.

Addition of 0.1 and 0.2 wt% of TiO₂ generates increasing intensity of the peak at g~4.3 and g~8. Thus, similar behavior is observed by the authors of [23] in their study of glasses containing Fe₂O₃. Their results were found for iron levels higher than 10 mol %, while in our compositions, iron is only a sand impurity with a concentration which not exceeding 0.12 wt% by weight.

![Figure 5: EPR spectra of V0, VT1, VT2, Vc1 and Vc2 glasses.](image-url)
Therefore, suggestions that titanium addition promoted ferrous ions oxidation to ferric ions [11]. The EPR observations of glasses containing TiO₂ low amounts are in agreement with the UV-Visible spectroscopy results and support the hypothesis of Fe³⁺ ions formation after TiO₂ addition. This explains the changes observed on glass network structure and studies properties. In comparison with V₀ sample EPR spectrum, Cr₂O₃ addition generates also increasing intensity of the peak at g ~ 4.3.

4. Conclusion

Adding small amount of TiO₂ in soda-lime-silica glasses has led to an improved transparency; light transmission, and thermal shock resistance. While Cr₂O₃ addition induced their green coloring (a* increases from 2.5 to -18.1 and b* from 0.7 to 32.5 for V₀ and V_C₂ respectively) and also lowering their thermal expansion coefficients: α (50-350 °C) is decreased from 8.9 10⁻⁶ to 8.3 10⁻⁶ and 8.5 10⁻⁶ °C⁻¹ for V₀, V_T₂ and V_C₂ respectively.

The melt physical characteristics as transition temperature which are also important in an industrial setting (refining, glass forming) are influenced by the addition of TiO₂ and Cr₂O₃ even at low contents. However, glass transition temperature is increased from 573 to 585 °C to 587°C with addition of 0.2 wt % of TiO₂ and of Cr₂O₃ respectively.

Improvements noticed with low TiO₂ addition are the result of some structural changes. These are attributed to the oxidation of Fe²⁺ to Fe³⁺ ions and Fe³⁺ clusters formation promoted by titanium oxide addition according to the glasses EPR analysis and UV-Visible Spectroscopy. Cr³⁺ and Fe³⁺ free ions formation with low Cr₂O₃ additions are also revealed by EPR and UV-Visible spectroscopy.

5. References


M.A. Marzouk, F.H. ElBatal, A.M. Abdelghany, Ultraviolet and infrared absorption spectra of Cr₂O₃ doped-sodium metaphosphate, lead metaphosphate and zinc metaphosphate glasses and effects of gamma irradiation: a comparative study, *Spectrochimica acta. Part A, Molecular and biomolecular


THERMAL SHOCK RESISTANCE OF MULLITE OBTAINED FROM KAOLIN AND TRI-HYDRATED ALUMINA

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Abstract: In this work, the thermal shock behavior of mullite prepared locally under different conditions was investigated. The initial powders used are 60% of trihydrate alumina (Gibbsite) and 40% of Kaolin. The shaping was obtained by uniaxial pressing under three pressures (70, 80 and 100) MPa. After debinding at 600°C, pre-cooked samples were sintered at 1600°C for 1h. Differential thermal analysis coupled with thermogravimetric analysis, conducted on the mixture kaolin-alumina, revealed different microstructural transformations and reactions were occurring during heating. The spectra X-ray diffraction showed the presence of mullite. A water-quenching technique was used for thermal shock tests. The specimens were heated at different temperatures (100 - 500°C), and held at each temperature for 10 min. Then, the heated specimens were dropped by free fall into a water bath, which was maintained at 25°C with a thermostat. The residual strengths of the quenched specimens were determined in a three-point bending test. The results showed that the critical temperature difference ΔTc depends on pressure density and porosity of the samples.

Keywords: Kaolin, Mullite, thermal shock, strength

1 Introduction

Mullite (3Al2O3·2SiO2) is a very important ceramic material. It is used in both areas of traditional and advanced ceramics because it’s the only stable crystalline phase in the alumino-silicate diagram system. It has very interesting properties [1]: low expansion coefficient, high refractoriness, excellent creep resistance, low thermal conductivity and good chemical and thermal stability. Its weakness is its sensitivity to thermal shock. Mullite can be synthesized by a specific heat treatment of natural raw materials (Kaolin, Sillimanite, Halloysite). For example, beyond 1000°C, kaolinite transforms into mullite with a vitreous phase. The enrichment of Kaolin by alumina after sintering leads to the formation of mullite [2].
In the past four decades, extensive studies have been devoted to the understanding and improvement of the thermal shock behavior of ceramics [3-6].

The traditional approach to evaluating the thermal shock resistance of ceramics is based on quenching the sample from an elevated temperature into a quenching medium and relating the maximum tensile stress magnitude to the fracture strength of the material. Neglecting the heat transfer and size effects, the maximum thermal stress generated in a sample subjected to rapid cooling at its external surfaces is given by:

$$\sigma = \frac{E \alpha \Delta T}{1-\nu}$$  \hspace{1cm} (1)

Where $E$ is Young’s modulus, $\alpha$ is the coefficient of thermal expansion, $\nu$ is Poisson’s ratio, and $\Delta T$ is the temperature difference between the quench medium and the component prior to quenching [7].

Rearranging equation (1), we obtain an expression for $\Delta T_C$:

$$\Delta T_C = \frac{\sigma_{th}(1-\nu)}{\alpha E} = R$$  \hspace{1cm} (2)

$R$ is a thermal shock resistance parameter indicating the maximum allowable temperature difference to which a specimen can be subjected without the initiation of fracture under severe transient thermal condition.

In the present work, we have fabricated, in different conditions, Mullite from the mixture of Algerian kaolin of Djebel Debbagh (DD2) and a commercial tri-hydrated alumina. Thereafter, we investigated its resistance to hard thermal shock (quenching in water). Furthermore, the effect of experimental conditions on mechanical and physical properties was studied in relation to the thermal shock resistance.

2 Experimental Methods

2.1- Used materials

2.1.1- Kaolin

The kaolin used was from Djebel Debbagh, located in the north-east of Algeria. Its chemical composition is[8]: 34% Al$_2$O$_3$, 47% SiO$_2$, 14% loss on ignition, 5% other minor constituents). At 1000°C, a primary mullite phase starts to form from the spinel phase. A cristobalite phase starts to forms through the transformation of silica at 1100°C. After this temperature the transformation of the spinel phase to the primary mullite was completed. At 1400°C, the cristobalite starts to dissolve in the mullite matrix. After this temperature (1600°C) only one phase was observed (Figure 1). The curve of DTA (Figure 2) shows a pronounced
endothermic peak, at 500°C characterizing the transformation of the kaolinite to meta-kaolinite. A second exothermic peak appears at 900°C caused by the crystallization of the meta-kaolinite to mullite. Beyond 1400°C, cristobalite is transformed into the amorphous phase.

Figure 1: X-ray diffraction patterns of Kaolin (DD2) treated at different temperatures.

Figure 2: DTA curve of Kaolin DD2 [8].

2.1.2 Tri-hydrated Alumina (Gibbsite)

This is a type of commercial trihydrated Alumina (gibbsite, Al(OH)₃) with pinkish white color. It’s containing (chemical composition) is: 62.97% Al₂O₃, 2.75% SiO₂, 0.64% F, 0.24% Na₂O, 0.13% CaO, 0.06% Fe₂O₃, 0.06% Ti₂O, 0.05% K₂O and 33% of structural water [9]. Dehydration behavior of gibbsite was shown in the DTA and TG thermograms in (Figure 3) which show three pronounced endothermic peaks. The first one was observed at 230°C, characterizing the partial transformation of gibbsite to boehmite and the second one at around 300°C characterizing the complete transformation of gibbsite to boehmite. The third one at
around 500°C corresponds to the transformation of boehmite to transition alumina (γ-alumina).

The TG curve shows three steps of weight loss corresponding to the three endothermic peaks in DTA. The main dehydration corresponds to releasing of structure water at 300°C [10-11]. The transformations of coarse particles of gibbsite consume a significant energy (heat flow ~ 40 µV). The XRD results shown in (Figure 4) agree well with the ones previously mentioned.

![Figure 3: Thermal analysis, DTA and TG curves of trihydrated Alumina [9].](image)

![Figure 4: X-ray diffraction patterns of trihydrated Alumina treated at different temperatures [9].](image)

2.2 Sample preparation and thermal shock testing
The mixture of 60% of Kaolin and 40% of gibbsite was milled by the planetary ball for 5 hours. After drying and disagglomeration by mortar to obtain micronized powder, prismatic specimens were fabricated by uniaxial compaction at a pressure ranging from 70 to 100 MPa. After prebaking slowly to 600°C, the sintering was performed at 1600°C for 2 hours. Thereafter, the samples were rectified by diamond grinding wheel to the dimensions (38x7x6) mm$^3$.

The thermal shock test (Figure 5) involves heating the sample at an initial temperature of shock ranging from 100°C to 500°C after a 20 minute of hold time at this temperature. The specimen was abruptly cooled in a water bath at room temperature. After drying, the sample is visually inspected and thermal shock damage was determined in a 3-point-bend test at room temperature using a tester with a crosshead speed of 0.2 mm/min.

![Thermal shock test apparatus.](image)

### Figure 5: Thermal shock test apparatus.

### 3. Results and Discussion

#### 3.1- Microstructural characterization

Phase transformations were highlighted by several experimental techniques: diffraction X-ray analysis and scanning electron microscopy. We notice the formation of two types of Mullite. The first one (primary mullite) is caused by the transformation of meta-kaolinite and the second (secondary mullite) results of the reaction between Alumina and excess silica present in the starting kaolin. The XRD results shown in (Fig. 6) revealed the existence of two phases the mullite, but also the α-alumina. This latter, unreacted with silica, it results from the transformation of gibbsite above 1200°C [12].
Figure 7 shows SEM photograph of the mixture (DD2 + Gibbsite) sintered, at 1600°C for 2 hours, in which elongated needles characterizing mullite crystals are distributed through a matrix of rounded and small crystals characterizing Alumina.

The total porosity was measured by two methods, the method of Arthur and the method of volumes by integrating in the calculation the value of the absolute density \(3.1366 \text{ g/cm}^3\) of the compound so obtained by Helium Pycnometer. Its evolution is shown in Figure 8. This parameter decreases versus to the compaction pressure, from a maximum value of 26% for the pressure of 70 MPa to 17.46% for the pressure of 100 MPa. This behavior is explained by the densification of the samples and the shrinkage during sintering. In contrast, the mechanical strength, according to the compaction pressure, increases progressively as the compacting pressure increases (Figure 9). The flexural strength rises from a value of 90 MPa for a pressure of 70 MPa to a value of 130 MPa, for the pressure of 100 MPa, this very significant improvement results from the densification of the sample.

![X-ray diffraction pattern of the mixture (DD2 + Gibbsite) sintered at 1600°C for 2h.](image)

Figure 6: X-ray diffraction pattern of the mixture (DD2 + Gibbsite) sintered at 1600°C for 2h.
Figure 7: SEM micrograph of the mixture (DD2 + Gibbsite) sintered at 1600°C for 2h.

Figure 8: Total porosity as a function of compaction pressure.

Figure 9: Flexural strength, according to compaction pressure.
3.2-Thermal shock results

The results of the thermal shock tests are given for the three sets of pressures in figure 10. The maximum difference $\Delta T_c (\Delta T_c \approx 372^\circ C)$ is obtained for specimens pressed with both (80 and 70) MPa. However $\Delta T_c$ found for samples compacted with 100 MPa is less ($\Delta T_c \approx 272^\circ C$). An increasing of pressure leads to a significant increasing of flexural strength, which decreases with increasing porosity. On the other hand, an increase of total porosity leads to an increase in critical temperature difference (figure 11). Anyway it is rather difficult to predict the thermal shock behavior on the basis of only porosity and thus density [13-14].

![Figure 10: Flexural strength according to quenching-temperature difference.](image)

![Figure 11: Quenching-temperature difference as a function of total porosity.](image)
4. Conclusions

A water-quenching technique was used to evaluate the thermal shock behavior of compacts component prepared from proportions of 40% Algerian kaolin and 60% Alumina trihydrate. The DRX shows that these proportions do not lead to a total multilisation of the fired mixture, other proportions should be explored. This mix show good mechanical properties.

The critical temperature difference for crack initiation was found to depend strongly on the ratio of fracture strength. Samples compacted with 100 MPa pressure have a higher starting resistance, paradoxically they are less resistant to thermal shock (lower ΔTc) and their own degradation when shift to the critical state is more pronounced. This result is in coherence with the analysis made by Glandus [15] on the behavior of ceramic materials resistant to crack initiation and damage caused by crack propagation under thermal shock.

5. References


ANALYSIS OF HEAT-SPREADING CAPABILITY OF ENCAPSULATED ANNEALED PYROLYTIC GRAPHITE CORES

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2 Université Paris Ouest, Laboratoire Thermique Interfaces Environnement (LTIE), EA 4415, 50 rue de Sèvres, 92410 Ville d’Avray – France

Abstract: The capability to efficiently transfer the heat away from high-powered electronic devices is a ceaseless challenge. More than ever, the aluminium or copper heat spreaders seem less suitable for maintaining the component sensitive temperature below manufacturer operating limits. Technology-push high-conductivity materials, such as Thermal Annealed Pyrolytic Graphite is an attractive alternative to conventional solid conduction without the gravity dependence of a heat-pipe solution. Despite, the ultrahigh performance rising of APG core, close to 4 times of copper one, is restricted to in-plane thermal conductivities which can be 200 times higher than its through-the-thickness conductivity. So a lower cross-plane thermal conductivity or a higher interlayer thermal resistance than anticipated would compromise APG-based material as efficient heat spreaders. In order to analyse the sensitivity of these parameters on the effective thermal performances, an analytical model for predicting the temperature distribution over an APG flat-plate was developed. Its relevance was compared to numerical simulations as well as experiments for a set of boundary conditions.

Keywords: Annealed Pyrolytic Graphite (APG), Analytical Model

1. Introduction

Annealed Pyrolytic Graphite is typically sandwiched inside a pair of Aluminum sheets in order to cc

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Having an in-plane thermal conductivity of 1200-1700W.m\(^{-1}\).K\(^{-1}\), the Thermal Pyrolytic Graphite (TPG) family seems to be the next paradigm for solving endless needs for more efficient electronic cooling system. The achieved thermal property is the result of a highly ordered state of its crystal structure in well-aligned graphene planes.

If that process allows superb in-plane conduction property, the resulting layered microstructure has in contrast a very low through-the-thickness thermal conductivity, acting as a heat barrier. Consequently the behaviour of this advanced material technology is poorly known as well as the sensitivity of the design parameters on the effective thermal performances.

For exploring that new cooling concept, a test vehicle has been developed and a set of thermal characterizations performed. Then, a modelling approach made to better discern the respective influence of its constitutive parts.

**Thermal vehicle under investigation**

The present investigation focuses on a test vehicle dedicated to the characterization of the effective thermal conductivity of a TPG heat spreader on a concrete application case. The stack-up of 3 layers consists in a thick TPG core of 2mm, which is sandwiched by two external Aluminium plates of 0.6mm. The flat-plate length \((L_b)\), width \((W_b)\) and thickness \((H_b)\) are fixed at 119.4mm, 42mm and 3.2mm, respectively.

A set of temperature probes was placed at five \(x\)-axis locations in the free source-region \([1]\) of the sample as shown Figure 15.

**Figure 15:** Measurements of \(x\)-axis in-plane thermal conductivity

As mentioned, TPG heat spreader has higher in-plane heat transfer capabilities than conventional cooling solution. To define its in-plane heat transfer capability a performance metric is proposed.
Assuming adiabatic external wall conditions, the in-plane thermal conductivity can be approximated from the one-dimensional steady-state Fourier equation. The probe temperatures, monitored at the points 1 and 5, enable to calculate the slope and then to deduct the value of x-axis effective thermal conductivity. This practical method can be checked on similar bar built in Aluminium or Copper, as reported Table 4.

Table 4: Thermal conductivity evaluation from external temperature probes

<table>
<thead>
<tr>
<th>Material reference</th>
<th>6061</th>
<th>6082</th>
<th>6060</th>
<th>C11000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model value</td>
<td>160</td>
<td>180</td>
<td>206</td>
<td>390</td>
</tr>
<tr>
<td>Effective Thermal</td>
<td>159.1</td>
<td>179</td>
<td>204.9</td>
<td>387.9</td>
</tr>
<tr>
<td>Divergence</td>
<td>0.53%</td>
<td>0.53%</td>
<td>0.53%</td>
<td>0.53%</td>
</tr>
</tbody>
</table>

The quality of the results indicates that a metallic bar could be used to calibrate the test bench performances and limits before running the experiment on a TPG structure.

Two industrial samples were tested in laboratory environment conditions. Table 5 provides the measured external temperature profiles of the upper surface of both samples.

Table 5: Experimental temperature measurements

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Temperature (°C)</th>
<th>Slope keff (K.m⁻¹) (W.m⁻¹.K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Xc(mm)</td>
<td>P1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>P1</td>
<td>16.53</td>
</tr>
<tr>
<td></td>
<td>P2</td>
<td>53.3</td>
</tr>
<tr>
<td></td>
<td>P3</td>
<td>159.2</td>
</tr>
<tr>
<td></td>
<td>keff</td>
<td>4.03</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Temperature (°C)</td>
<td>Slope keff (K.m⁻¹) (W.m⁻¹.K⁻¹)</td>
</tr>
<tr>
<td></td>
<td>Xc(mm)</td>
<td>P1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>P1</td>
<td>16.13</td>
</tr>
<tr>
<td></td>
<td>P2</td>
<td>53.3</td>
</tr>
<tr>
<td></td>
<td>P3</td>
<td>139.5</td>
</tr>
<tr>
<td></td>
<td>keff</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Those results demonstrate that a very promising x-axis effective thermal conductivity can be actually achieved using an APG material.

Thermal Modelling assessment

In order to help the designers to early analyse thermal behaviour of that kind of heat-spreader, an analytical model was derived. This one proposes a practical way to address the design of three-layer structures, embedding an anisotropic core material, submitted to multiple sources mounted on its external surfaces and cooling pads. Based on academic approaches [2-9], a set of solutions for a fast calculation of the temperature profile of a set of N constitutive cross-plane layers was established.
The current approach focuses on the impact of the interlayer thermal resistance on the behaviour of external heating sources cooled by conduction [10-11]. Moreover, to better investigate the cooling efficiency, the way the heat is drained throughout the cold-wall frame can be simulated using three-dimensional representation.

**Description of analytical formulation**

The present analyses the case of a simple bar, a stack-up three layers, submitted at one extremity to a heating source and at the opposite one cooled by an infinite heat-sink.

The generalized heat transfer equation in steady-state regime is governed by the equation (1):

\[
k_i \frac{\partial^2 \theta_i(x,y,z)}{\partial x^2} + k_j \frac{\partial^2 \theta_j(x,y,z)}{\partial y^2} + k_z \frac{\partial^2 \theta_k(x,y,z)}{\partial z^2} = 0 \quad (\text{for } 1 \leq i \leq 3)
\]

(1)

Where \( \theta_i(x,y,z) = T_i(x,y,z) - T_\infty \) is the temperature difference between a local spot and the cooling reference and \( k_x, k_y \) and \( k_z \) are axis thermal conductivities of the core layer.

The flat-plate overall length \( (L_b) \), width \( (W_b) \) and thickness \( (H_b) \) are depicted in Figure 16.

![Figure 16: Definition of the geometric parameters of the analytical model](image)

The heating source and the cold-wall area are located at the bottom and upper surfaces of the bar. The lateral sides of the three-layer structure are supposed to be adiabatic:

\[
k_i \frac{\partial \theta_i(x,y,z)}{\partial x} \bigg|_{x=0,Lb} = k_j \frac{\partial \theta_j(x,y,z)}{\partial y} \bigg|_{y=0,Wb} = 0 \quad (\text{for } 1 \leq i \leq 3)
\]

(2)

The top and rear surfaces are respectively submitted to specific uniform heat transfer coefficients \( \bar{h} \) and \( h \). A heating source characterized by its uniform heat flow rate \( q_s \) is mounted on external surfaces of the board.
A specific set of boundary conditions is applied on each of these surfaces.

- For a heating source \( j \) located on top surface:

\[
-k_3 \frac{\partial \theta_3(x,y,z)}{\partial z} \bigg|_{z=H_b} = \frac{\tilde{h}}{k_3} \theta_3(x,y,H_b) - q_{S_j}(x,y) \bigg|_{z=H_b} \quad \text{and} \quad -k_3 \frac{\partial \theta_3(x,y,z)}{\partial z} \bigg|_{z=0} = -\frac{h}{k_3} \theta_3(x,y,0) \tag{3}
\]

- For a heating source \( j \) located on bottom surface:

\[
-k_1 \frac{\partial \theta_1(x,y,z)}{\partial z} \bigg|_{z=0} = -\frac{h}{k_1} \theta_1(x,y,0) + q_{S_j}(x,y) \bigg|_{z=0} \quad \text{and} \quad -k_3 \frac{\partial \theta_3(x,y,z)}{\partial z} \bigg|_{z=H_b} = \frac{\tilde{h}}{k_3} \theta_3(x,y,H_b) \tag{4}
\]

As a new boundary condition, the imperfect contact between two layers \( i \) and \( i+1 \) takes into account the temperature discontinuity (5), as well as the heat flux conservation.

\[
-k_i \frac{\partial \theta_i(x,y,z)}{\partial z} \bigg|_{z=z_i} = \frac{1}{R_{li}} \left[ \theta_i(x,y,z) \bigg|_{z=z_i} - \theta_{i+1}(x,y,z) \bigg|_{z=z_i} \right]
\]

\[
k_{i+1} \frac{\partial \theta_{i+1}(x,y,z)}{\partial z} \bigg|_{z=z_i} - k_i \frac{\partial \theta_i(x,y,z)}{\partial z} \bigg|_{z=z_i} = 0 \tag{5}
\]

**Derived through-thickness expressions**

Using the method of the separation of the variables and the superposition principle, the 3D temperature distribution is calculated by:

\[
\theta(x,y,z) = 4 \cdot \sum_{j=1}^{N_S} \sum_{m=0}^{M_j} \sum_{n=0}^{N_j} A_{m,j} \cdot B_{n,j} \cdot \cos \left( \frac{m \pi}{L_i} \cdot x \right) \cdot \cos \left( \frac{n \pi}{W_i} \cdot y \right) \cdot \omega_{m,n}(z) \bigg|_{z_{cj}} \tag{6}
\]

And the area-mean temperature, for an arbitrary source \( k \), has the form:

\[
\bar{\theta}_k = 4 \cdot \sum_{j=1}^{N_S} \sum_{m=0}^{M_j} \sum_{n=0}^{N_j} A_{m,j} \cdot B_{n,j} \cdot \bar{A}_{m,k} \cdot B_{n,k} \cdot \omega_{m,n}(z_{cj}) \bigg|_{z_{cj}} \tag{7}
\]
The five temperature probes are modelled as circular inactive sources.

The expressions of Fourier coefficients $A_{m,j}, B_{n,j}$ according with source shapes and the definition of the z-axis thermal profile $(\omega_{m,n}(z)|_{z=0})$ depending on source positions are given in [8].

**Calculation corner**

The following analytical and numerical calculations were performed using respectively Mathcad® version 15.0 and Icepak® V17.0. The respective results are defined in the various tables by the subscript AM, for Analytical Model calculation and the subscript NM, for Numerical Model computation. The specific error metrics named $\Delta T$ and $\bar{\Delta T}$ are used to qualify the model agreement, as reported in (8). The numerical results are considered as the reference value.

$$\Delta T = \frac{T_{AM} - T_{NM}}{T_{NM} - T_{\infty}} \quad \text{or} \quad \bar{\Delta T} = \frac{T_{AM} - T_{NM}}{T_{NM} - T_{\infty}}$$

(8)

**Validation of three-dimensional analytical model**

Commonly TPG in-plane thermal conductivity is reported to be 4 times higher than copper and 8 times higher than aluminium but there is little information about the cross-plane value [12-14]. So for the studied case, the in-plane thermal conductivity is supposed 200 times higher than its through-the-thickness conductivity. Moreover three values of aluminium thermal conductivity are weighed.

The values of the thermal conductivity at room temperature are assumed to be equal to:

- Flat-plate: $k_{6061}=160\text{W.m}^{-1}\text{.K}^{-1}, k_{6082}=180\text{W.m}^{-1}\text{.K}^{-1}, k_{6060}=206\text{W.m}^{-1}\text{.K}^{-1}$
- Core layer: $k_{xy}=1600\text{W.m}^{-1}\text{.K}^{-1}, k_z=8\text{W.m}^{-1}\text{.K}^{-1}$

The heat-spreader behaviour is analysed when a fixed temperature of 20°C is applied on the cold-wall area which has a length of 10mm ($L_{CW}$) and a width of 42mm ($W_{CW}$). The $y_C$ centre is located at half heat-spreader width and its $x_C$ centre position is 5mm. The cold-wall area is located on the top surface ($z_3=H_b$) and divided in 6 equivalent sub-surfaces.
A wedge imperfect contact is simulated considering a thermal resistance ($R_{ICW}$) of 2.5K.cm².W⁻¹.

The heating square-source has a length of 32mm and the coordinate of its centre is (103.4, 21, 0).

Table 6 confirms the pertinence of an analytical approach to examine the influence of the two thermal interlayer resistances as well as the contact thermal resistance at card-edge interface on the thermal behaviour of a high-conductivity-core heat-spreader.

### Table 6: Comparison of the central temperature of numerical and analytical models

<table>
<thead>
<tr>
<th></th>
<th>$T_{CW1}$</th>
<th>$T_{CW2}$</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>$T_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_c$(mm)</td>
<td>2.5</td>
<td>7.5</td>
<td>22</td>
<td>41</td>
<td>64</td>
<td>83</td>
<td>104</td>
<td>103.4</td>
</tr>
<tr>
<td>$Y_c$(mm)</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>$Z_c$(mm)</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>0</td>
</tr>
</tbody>
</table>

The analytical and numerical average temperatures of the source are respectively 53.0°C and 52.9°C.

The comparison of its predictions to numerical results shows a good agreement, the divergences are lower than 1% for all checked external temperatures, our purpose.

**Comparison of Heat-spreading efficiency**

For assessing the benefit of TPG heat-spreaders as a new alternative to conventional solid conduction, this latter has been compared to equivalent bars made of copper or aluminium. Further, the comparison highlights the influence of the interlayer thermal resistances on the APG heat spreading performances, as shown Figure 17.

The figure reveals that the performance of high-conductivity-core heat-spreader is mainly depending on the interlayer thermal resistance. Thus, a value equal to 10K.cm².W⁻¹ allows a higher heat transfer than solid conduction given by aluminium bar and will be better than a copper bar if a value below 4.5K.cm².W⁻¹ can be obtained.
A thermal resistance of 0.01K.cm².W⁻¹ permits a thermal gradient reduction of 30°C in comparison of the 10K.cm².W⁻¹ resistance case.

In spite of low cross-plane conductivity, acting as an insulator, the composite structure appears to be an efficient lightweight cooling solution. Nevertheless the building process of TPG heat-spreaders must master the solid-solid contact phenomena with the aim to guarantee a thermal resistance as low as possible.

**Effective thermal conductivity evolution**

Figure 18 shows the resulting curve that describes the evolution of the x-axis effective thermal conductivity of the studied heat-spreaders depending on the interlayer thermal resistance.

The x-axis thermal conductivity of the heat-spreaders multi-layered structure varies from 1035W.m⁻¹.K⁻¹ to 620W.m⁻¹.K⁻¹ (right Y-axis) in line with $R_{IL}$ range.

However, when $R_{IL}$ values are significant, for instance above 5K.cm².W⁻¹, the assumption of the one-dimensional steady-state Fourier equation proves to be deficient.
In fact, the upper \((z=H_b)\) and lower \((z=0)\) temperatures of the zone free of sources may not be assumed equivalent, as highlighted in Table 7.

Nevertheless, those results corroborate the efficiency of TPG solution to drain efficiently the heat away from the source and its cooling potential for a large range of applications [15].

Table 7 : Comparison of the upper and lower center temperatures of the zone free of sources

<table>
<thead>
<tr>
<th>(R_{IL}) (K.cm².W(^{-1}))</th>
<th>(Z_c) (mm)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>3.2</td>
<td>35.68 38.18 40.78 42.80</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>36.37 38.27 40.84 43.23</td>
</tr>
<tr>
<td>(10)</td>
<td>3.2</td>
<td>47.64 54.18 57.42 59.35</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>53.59 55.27 58.11 63.08</td>
</tr>
</tbody>
</table>

Concept of Lumped Modeling for faster analysis

It is generally assumed that multi-layered structure can be represented by one homogenous layer having an orthotropic thermal conductivity and similar overall dimensions. This assumption has the immediate benefit to permit shorter computation time. However, its influence on temperature prediction is often unknown, in particular for small sources.

Figure 19 describes the practical concept of a “Lumped Modeling” (LM) for the heat-spreader layer layout which is usually applied to multi-layered electronic board.

![Figure 19: Order reduction of heat-spreader structure](image)

The LM effective thermal conductivities in-plane (x-y directions) and cross-plane (z direction) are calculated according to (8):
\[ ke_{xy} = \frac{\sum_{i=1}^{n} t_i \cdot K_{xy,i}}{\sum_{i=1}^{n} t_i} \quad \text{and} \quad ke_z = \frac{\sum_{i=1}^{n} t_i \cdot \left(\sum_{i=1}^{n} K_{z,i} + \sum R_{il}\right)}{\sum_{i=1}^{n} t_i} \] (9)

For the studied case, the deducted in-plane and cross-plane values for the LM model are respectively 1060W.m\(^{-1}\).K\(^{-1}\) \((ke_{xy})\) and = 4.224W.m\(^{-1}\).K\(^{-1}\) \((ke_z)\).

Table 8 shows the pertinence of analytical model in the case of mono-layer model. A good agreement of temperature profile between the analytical calculations and numerical computations is achieved.

<table>
<thead>
<tr>
<th>P_{s}=16W @ T_{CW}=20°C</th>
<th>ke_{xy}=13597W.m(^{-1}).K(^{-1}); ke_{z}=4.224W.m(^{-1}).K(^{-1});</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_{CW1} T_{CW2}</td>
<td>P1 P2 P3 P4 P5</td>
</tr>
<tr>
<td>Xc(mm)</td>
<td>2.5 7.5 22 41 64 83 104 103.4</td>
</tr>
<tr>
<td>Yc(mm)</td>
<td>21 21 21 21 21 21 21 21</td>
</tr>
<tr>
<td>Zc(mm)</td>
<td>3.2 3.2 3.2 3.2 3.2 3.2 3.2 0</td>
</tr>
<tr>
<td>T_{AM}(°C)</td>
<td>24.4 25.0 35.3 38.4 41.0 42.9 44.1 48.3</td>
</tr>
<tr>
<td>T_{NM}(°C)</td>
<td>24.5 25.0 35.4 38.4 41.1 42.9 44.2 48.4</td>
</tr>
</tbody>
</table>

However, it can be observed that the LM approach returns a significant under-evaluation of source temperature. An error of 14% on the source temperature is observed. So, the conventional approximation based on a single layer model having effective anisotropic thermal conductivities can be very tricky.

It is clear that the use of the lumped modelling approach to characterize the high thermal performances of a TPG-core structure is not recommended.

**Conclusions**

The current work demonstrates that the in-plane thermal conductivity of Annealed Pyrolytic Graphite is among the highest of any conduction material commonly used in electronic cooling. The analysed case reveals that an effective thermal conductivity twice higher than
copper can be expected for thick APG sheet. However, bad thermal coupling with the embedding metallic structure implies that interlayer contacts and external interfaces must be mastered to guarantee an efficient heat transfer. To lead a fast investigation, an analytical steady-state solution to the heat transfer equation was updated. This one considers the phenomenon of imperfect thermal contacts between the metallic layers and embedded APG core. This approach is a practical tool to early quantify sensitive parameters to select the right design concept or investigate quickly potential thermal issues, such as the critical interlayer thermal resistance. The presented model shows a high accuracy level between analytically derived results and numerical simulations when various thermal interlayer contact resistance scenarios are considered. Further, a method dedicated to the characterization of the effective thermal conductivity of an APG heat-spreaders is proposed. Thus the deducted analytical solution allows to calculate the temperature distribution of the heat-spreaders external surfaces, to compare it with experiment results, in order to quantify a realistic set of thermal contact resistance values.

Reference


EFFECT OF WEAR ON MICROHARDNESS CHANGES OF ALLOY STEELS RUBBING ON X200Cr13 STEEL UNDER DRY CONDITIONS

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Abstract

Microstructure evolution and mechanical properties of alloy steels rubbing on X200Cr13 steel under dry conditions were investigated. Tests were carried out at 2N applied force; they were performed in the aim to characterize together the worn surface and the depth affected by the wear. These measures justify a possible structural surface and/or in depth hardening. Hardness tests are taken at two locations over a length of 5 mm. The microhardness values were taken over a distance of 5 mm at the centre of the sample and 5 mm at the edge of the worn surface under both normal forces, 4 and 8 N. In spite of the fluctuating values of microhardness, we note that the microhardness in the centre of the samples is much higher than that of the edge. The difference between the two zones is of the order of 100 HV. The worn surface at 8 N is greater than the worn surface at 4 N. In this case, the increase in normal force causes an increase of 160 HV to 200 HV in the same areas.

Keywords: Microhardness, microstructure, normal force, wear

1. Introduction

To characterize the metals and plastics hardness, it is generally used bouncing testing or penetration. These tests have the advantage of being simpler to produce and give reproducible results. There are a wide variety of possible hardness tests; they are widely used in quality control to compare and to estimate the strength or stiffness of materials. Microhardness tests are carried out under very low loads; they allow much localized measurements (about 100 .µm²). Using a microdurometer, it is able to determine the hardness of a given phase in a multiphase sample or that of a very fragile and thin sample. The determination of the microhardness provides non-dispersed results accompanied by not coarse uncertainties over conventional methods to determine the hardness of materials [1]. These micro hardness testing can solve many problems such as the hardness measurement of thin layers, evaluation of local hardening, exploration of multiphase alloys, etc. [2-4]. We must certainly take into account the phenomena influencing the measurements of microhardness which require certain operating precautions such as: The print must be sufficiently clear to allow an accurate
reading, which requires a good surface condition of the test piece. The slight growth of hardness up to 1kg load shows the need to specify the charge under which the measurement was made to obtain comparable results. Take into consideration the maximum load to be applied so that the hardness of the metal support does not intervene in the actions [5-7]. The difference in microhardness between the centre and the edge of the piece is probably due to the difference in metal stress conditions; metal plastic flow at the edge; highest increase in the centre temperature and the microhardness is influenced by the evolution of the normal force [4, 8].

2. Study of the microhardness changes

2.1 Surface microhardness

These tests were carried out at 2N applied force; they were performed in the aim to characterize together the worn surface and the depth affected by the wear. These measures justify a possible structural surface and/or in depth hardening. Hardness tests are taken at locations shown in Figure 1 over a length of 5 mm.

Figure 2 shows the microhardness values over a distance of 5 mm at the centre of the sample and 5 mm at the edge of the worn surface under both normal forces, 4 and 8 N. Table 1 shows the average microhardness of the worn surface of the two zones.

![Optical observation of plane sample worn at P=4 N, v=0.63 m/s](image1)

![Optical observation of plane sample worn at P=8 N, v=0.63m/s](image2)

<table>
<thead>
<tr>
<th>Optical observation of plane sample worn at P=4 N, v=0.63 m/s</th>
<th>Optical observation of plane sample worn at P=8 N, v=0.63m/s</th>
</tr>
</thead>
</table>

**Figure 1: Optical observation of the samples contact surfaces plane after the test**

The hatched areas indicate areas of hardness measurement (edge and middle)
In spite of the fluctuating values of microhardness, we note that the microhardness in the centre of the samples is much higher than that of the edge. The difference between the two zones is of the order of 100 HV. The worn surface at 8 N is greater than the worn surface at 4 N. In this case, the increase in normal force causes an increase of 160 HV to 200 HV in the same areas.

The difference in microhardness between the centre and the edge is probably due to the difference in metal stress conditions: metal plastic flow at the edge; highest increase in the centre temperature. The effect of the normal force on the microhardness of the worn surface is very marked (Table 4). This shows that the increase of the normal force increases the surface material hardening and this could explain why the wear does not increase proportionally to the applied normal force (Fig. 1).

### Table 1: Average value microhardness on edge and middle of surface worn samples

<table>
<thead>
<tr>
<th>Zone</th>
<th>edge</th>
<th>Middle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$HV$, 4 N</td>
<td>363.53</td>
<td>438.57</td>
</tr>
<tr>
<td>$HV$, 8 N</td>
<td>518.7</td>
<td>646.21</td>
</tr>
</tbody>
</table>
2.2 In depth microhardness

The study of microhardness in depth measurements were performed in three areas located at different depths ($Z_1, Z_2, Z_3$), respectively to approximately 50, 100 and 500 µm, at the heart of healthy material, called reference zone where the hardness is uniform and identical to that of the material before test.

Table 2 shows the average microhardness corresponding to each zone, for both normal forces. Figure 4 presents the values of microhardness below the worn surface. It is observed that the microhardness at 50 microns is much greater than that of the other two zones: we observe that the value of microhardness increases by 30 % for the load equal to 4 N and by 55 % more for 8 N. The microhardness of zones 2 and 3 are very similar. Figure 5 shows that the microhardness drops significantly when going from surface to the heart of the material. This indicates that the depth of the damaged layer is small and does not exceed 100 µm. It is likely that the depth of the affected layer increases with the normal force, but these measures do not confirm it.

Table 2: Average value of microhardness in various zones

<table>
<thead>
<tr>
<th>Zone</th>
<th>$Z_1$</th>
<th>$Z_2$</th>
<th>$Z_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$HV$ at $P=4$ N</td>
<td>229</td>
<td>179</td>
<td>176</td>
</tr>
<tr>
<td>$HV$ at $P=8$ N</td>
<td>281</td>
<td>180</td>
<td>177</td>
</tr>
</tbody>
</table>

Figure 4: Depth microhardness of plane samples polished and cut in three areas for: $P=4$ and $8N$

Figure 5: Average depth microhardness of plane samples polished and cut for: $P=4$ and $8N$
2.3 Micrographic observations of planar samples after cutting and polishing

Metallographic observations were performed on the transverse profiles of samples obtained by cutting perpendicular to the velocity direction. Figure 6 shows the polished cross-section, not etched, of worn samples respectively under 4 and 8 N. Two results are highlighted:

- Worn surface profile appears fairly smooth at 4 N while for that at of 8 N shows marked irregularity. This shows that the more the normal force is important the more surface damage is significant.
- The appearance of burrs at the edges of the contact points out to a plastic deformation. These burrs are the accumulation of plastic deformation: (Ratcheting phenomenon) [9, 10]. The thickness of the burrs increase greatly with the normal force.

The wear observed is thus probably the result of an abrasion induced by hard particles and by the sample surface plastic flow.

Figure 7 shows the micrographs taken on polished and etched sections of the surface layer and the heart. These micrographs show that the damaged layer during testing is very thin. Below this layer, the granular structure resembling the structure of the heart is preserved. The damaged layer has a thickness of about 5 µm for the normal force of 8 N while the one corresponding to 4 N is so thin that its observation at this scale is very difficult. This confirms the results obtained by microhardness. The Scanning Electron Microscopy (SEM) observation of debris collected from the sample at 8 N shows various shapes of debris, debris very jagged, products probably of abrasion; sheets probably produced by the extrusion of peripheral butts by plastic deformation (Fig. 8).
Figure 6: Micrographic cross sections of only polished samples
<table>
<thead>
<tr>
<th>Surface layer</th>
<th>Heart (reference state)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.jpg" alt="Image" /></td>
<td><img src="image2.jpg" alt="Image" /></td>
</tr>
</tbody>
</table>

**Planar contact – 4 N, v=0.63 m/s**

| ![Image](image3.jpg) | ![Image](image4.jpg) |

**Planar contact – 8 N, v=0.63 m/s**

**Figure 7:** Micrographics of polished and etched samples sections

1: layer damaged, 2 healthy material (in heart)

**Figure 8:** SEM observation of worn sample debris at 8 N and 0.63 m/s:

1 layer, 2 abrasion debris
Conclusion

The principal results in this work can be summarized as follows;

The values of HV for two normal forces have been measured in three areas located at different depths (Z₁, Z₂, Z₃), respectively to approximately 50, 100 and 500 µm. It was found that the values of microhardness increase with increasing of the normal forces, 30 % for the load equal to 4 N and by 55 % more for 8 N. The areas affected by the wear does not exceed 100 µm in depth as the microhardness of both zones Z₂ and Z₃ are similar and smaller than zone1 affected by wear. The damaged layer has a thickness of about 5 µm for the normal force of 8 N while the one corresponding to 4 N is so thin that its observation at this scale is very difficult. This confirms the results obtained by microhardness.

References


CHARACTERIZATION OF THE THERMAL CONTACT PARAMETERS IN AN AIRPLANE BRAKING SYSTEM USING INVERSE METHODS

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Abstract: In this paper, we present a simultaneous estimation of the heat flux generated by friction and the thermal contact resistance under a real airplane braking conditions using an inverse method. The estimation is performed considering an assumption of 1D transient model and multiple interfaces. In order to validate this assumption, 1-D direct model is developed and compared to an analytical quadrupolar model. This model takes into account of a non perfect description of the thermal contact (i.e. two functions to estimate: Heat generated heat flux, Thermal contact resistance for each interface). Then, a numerical study of the sensitivities of the problem is presented. An analysis of the feasibility of the estimation of the parameters is conducted. In a second time, an estimation using numerical data is performed using the current mechanic assumptions on the generated heat flux

Keywords: Estimation of thermal contact parameters, airplane braking, inverse methods

1. Introduction

Modern civil planes are prone to take-off and land several times a day. The companies’ willingness to reduce turnaround time (TAT) and to reduce the weight of the brake, leads to very high loads and temperature in carbon disks. If the temperature estimation or measurement seems natural, friction heat flux at disk contacts is not well defined. Then 3D models robustness and accuracy are non-optimal, since the causes of heat fields are not perfectly determined. The aim of this study is to prove the usefulness of inverse method, in order to characterize in-landing boundary conditions at carbon disk surfaces. Among all the type of inverse heat conduction problem (IHCP), we are interested here in the identification of an unknown heat flux boundary condition. Indeed several studies have been carried out by the past, and shown the possibilities to solve ill-posed problems with inverse algorithms. Inverse heat conduction problem is highly ill-posed, to the extent that any small input modification results in a pronounced modification of the solution, as shown in several works [3][4][5]. In order to solve the inverse problem, a simple direct model has to be developed. Indeed, The Finite Difference Method (FDM) and Finite Elements Method (FEM) have been chosen most of the time, for their implementation easiness. However, their mesh-dependent characteristics require a lot of computation and effort. Their use in a model inversion process is therefore not appropriated because of the increase of computation
times. Therefore, watchfulness is required with computation time, and the 1-D model presented in this paper is developed in order to solve the inverse problem.

2. Thermal direct model of the brake

2.1 Presentation

We propose to develop a simple thermal 1-D model of the breaking period. The breaking system is presented in Fig. 1. It’s composed from nine carbon discs including five stators and four rotors.

![Figure 1: Airplane breaking system/ Representation of the studied 1D system](image)

2.2 Modeling of the system

At each interface stator/rotor, the thermal contact is supposed non perfect. Bardon [1] proposed an expression to describe the interfacial heat exchange. This approach introduces two contact parameters in addition of the generated heat flux: the sliding thermal contact resistance, the intrinsic heat partition coefficient, both are dependents on the thermal constriction resistances. An equivalent expression has been proposed by Tseng [2] to study heat transfer for rolling systems. The authors assume that the heat flux generated by friction is equally partitioned between the two solids (i.e. the intrinsic heat partition coefficient is equal to 0.5). This is the assumption that will be used in this study. During the braking, the heat propagation is supposed to be 1D in all the system, in the transverse direction to the discs as it is shown in Fig. 1. $k^{th}$ rotor is noted $R_k$, $k^{th}$ stator $S_k$ and the $k^{th}$ sliding interface $I_k$.

Carbon discs can then be considered as simple successive rings, with non perfect thermal contact model between each disk. Boundary conditions are set at first, with Fourier conditions at
extremes left and right boundaries. The heat equation can be established for our one-dimensional problem as follow (in \(z\) direction):

\[
\begin{aligned}
\frac{1}{a} \frac{\partial T}{\partial t} &= \frac{\partial^2 T}{\partial z^2}, \\
-\lambda \frac{\partial T}{\partial z} &\bigg|_{z=0} = h_1 (T - T_0), \\
-\lambda \frac{\partial T}{\partial z} &\bigg|_{z=L} = h_2 (T - T_0), \\
T(z, t = 0) &= T_0
\end{aligned}
\]

\(\varphi_k(t) = \alpha_k \varphi_{gk}(t) + \frac{T_{cl}(t) - T_{cr}(t)}{R_{YSC}} \) on each interface \(I_k\)

\(\varphi_k(t)\) is the heat flux entering in the left disc, \(R_{YSC}\) the thermal contact resistance, \(\varphi_{gk}(t)\) the generated heat flux, \(T_{cl}(t)\) and \(T_{cr}(t)\) are respectively the contact temperatures on left and right at the interface \(k\) between a rotor and a stator at the time \(t\). The local heat partition coefficient \(\alpha_k\) is supposed to be equal to 0.5 for all interfaces [17]. The time evolution of the generated heat flux \(\varphi_k(t)\) will be discussed in part 3.1. Using a Finite Difference Method, an implicit matrix system is obtained on the temperature of each node of spatial discretization. The system resolution can be done with the matrix inversion with conjugate gradient method. In order to reduce computation time to its minimum, the tri-diagonal matrix is reduced to a bi-diagonal matrix thanks to the Thomas algorithm [21].

2.3 Results of the direct model

The results are very satisfying, provided that the discretization in time and space are fine enough. The Fig.2 shows the time evolution of the temperature in the middle of stators. The numerical solution (N) is compared to an analytical quadrupolar model (A). The error between the numerical and exact solution, confirm the validity of the modeling, as we compare temperatures monitored at the center of each disks throughout the braking time. Although analytical solution can be faster than numerical ones, FDM modeling is chosen for its simplicity of use and modification. Hence, several phenomena such as radiation or convection are rather simple to add in any numeric simulation, but can be very complex in analytic models. Here we provide a numeric model of the brake, during braking conditions which gives very satisfying results. Although this model is not analytic, we managed to obtain a very short simulation time with good precision thanks to good coding logic. To conclude, this model can be used as a direct function in an inverse algorithm, since it doesn’t take much calculation power and provide a very good accuracy compared to the exact solution.
Figure 2 Spatial Time evolution of the temperature in the center of each disk calculated with 1-D numeric model and 1-D quadrupolar model

3. Sensitivity Analysis

3.1 Parameterization of the problem

The aim of this part is to demonstrate the feasibility of identifying thermal contact parameters: $\varphi_k(t)$ and $R_{TSC_k}$, $\alpha_k$ being supposed to be equal to 0.5. First of all, the assumption of constant sliding thermal resistance $R_{TSC_i}$ is done. The impact of this assumption will be negligible on identification results. Then, the rotational speed of the discs decreases during the braking period from the maximum velocity to zero. Then, in the same way, the generated heat flux will decrease from a maximum to zero. But at the initial time, there is no friction. Therefore, it is necessary to wait some time to reach its maximum value. In order to take into account these observations, it is proposed to model the temporal evolution of the generated heat flux by two straight lines: the first one rising to $\varphi_{max}$ on $t_{max}$, the second one decreasing to zero at the end of the braking period.

The time evolution for each friction interface in the breaking system is presented in Fig. 3. As we have shown in part 2.1, the braking system consists of eight friction interfaces. Considering these elements, the thermal problem could be defined with twenty parameters (three parameters for each interface on (2)):

$$\beta = \begin{bmatrix} \varphi_{max_1}, \varphi_{max_2}, \ldots, \varphi_{max_8}, t_{max_1}, t_{max_2}, \ldots, t_{max_8}, R_{TSC_1}, \ldots, R_{TSC_8} \end{bmatrix}^T \quad (11)$$

Figure 3 Time evolution of the generated heat flux in one interface
3.2 Minimization criterion

The data are simulated from the 1-D Direct Model using the values of parameters given in Table 1. The measurements are generated in the center of each disk in order to simulate the real configuration where the thermocouples are placed in the middle of the stators and rotors. Indeed, currently, the sensors are located in the middle of the discs for technical constraints on the experimental device. In a first approach, convection boundary conditions are imposed on the first and last stators. The convection coefficient is supposed to be constant and we take \( h_1 = h_2 = 100 \text{W/m}^2\text{K} \). The ambient and initial temperature are the same: \( T_0 = 293\text{K} \).

Table 1: Thermal parameters used for the direct generation of the simulated data.

<table>
<thead>
<tr>
<th></th>
<th>I1</th>
<th>I2</th>
<th>I3</th>
<th>I4</th>
<th>I5</th>
<th>I6</th>
<th>I7</th>
<th>I8</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varphi_{\text{max}} ) [W/m(^2)K(^{-1})]</td>
<td>599600</td>
<td>569200</td>
<td>535600</td>
<td>522800</td>
<td>489200</td>
<td>460400</td>
<td>426800</td>
<td>398000</td>
</tr>
<tr>
<td>( t_{\text{max}} ) [s]</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>( R_{\text{TSC}} ) [m(^2)KW(^{-1})]</td>
<td>5e-05</td>
<td>1e-04</td>
<td>1e-04</td>
<td>1e-04</td>
<td>1e-04</td>
<td>1e-04</td>
<td>1e-04</td>
<td>1e-04</td>
</tr>
</tbody>
</table>

In this first approach, different values of \( \varphi_{\text{max}} \) and \( t_{\text{max}} \) for each interface are used in the generation of the data with the 1-D model. Then, one value for \( R_{\text{TSC}} \) on the first sliding surface is different from the others in order to validate the identification procedure. The estimation of \( \beta \) is performed by minimizing the square of the difference between measured data (or simulated data) and calculated temperatures by the direct problem [22] [26] [27]. The functional of the least-square method is given by (12).

\[
J(\beta) = \sum_{i=1}^{i=N} \sum_{j=1}^{j=M} (T_j^i - T_j')^2
\]  

(12)

Where \( T_j^i \) is the measured temperature at time \( t_j \) and abscissa \( x_i \) and \( T_j' \) is the calculated temperature at the same time and abscissa. The problem is non linear to the parameters and we use a Gauss Newton Method in a first time to identify the parameter vector \( \beta \). The identification procedure provides accurate results, i.e. the identified values are identical to the values used in the direct model to generate the measurements.
3.3 Analysis of the reduced sensitivities

Then, the measurements are noised with a Gaussian standard deviation of +/- 0.25K. An discrepancy (ε) appears this time on the estimate $\hat{\beta}$, namely on the values of the sliding contact resistance (Table 2).

Table 2: Estimated Thermal parameters using the noised simulated data.

<table>
<thead>
<tr>
<th></th>
<th>I1</th>
<th>I2</th>
<th>I3</th>
<th>I4</th>
<th>I5</th>
<th>I6</th>
<th>I7</th>
<th>I8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_{\text{min}}$ [$Wm^{-2}K^{-1}$]</td>
<td>599567</td>
<td>569228</td>
<td>535475</td>
<td>522837</td>
<td>488651</td>
<td>461852</td>
<td>425815</td>
<td>398340</td>
</tr>
<tr>
<td>$t_{\text{min}}$ [s]</td>
<td>1.000</td>
<td>2.002</td>
<td>3.008</td>
<td>3.999</td>
<td>5.013</td>
<td>5.968</td>
<td>7.020</td>
<td>7.994</td>
</tr>
<tr>
<td>$R_{\text{TSC}}$ [$m^2KW^{-1}$]</td>
<td>5.25e-05</td>
<td>2.02e-04</td>
<td>0.00016</td>
<td>8.77e-05</td>
<td>8.33e-05</td>
<td>8.80e-05</td>
<td>0.000117</td>
<td>0.000144</td>
</tr>
<tr>
<td>$\varepsilon_{\text{rel}}$</td>
<td>5%</td>
<td>102%</td>
<td>61%</td>
<td>-12%</td>
<td>-17%</td>
<td>-12%</td>
<td>17%</td>
<td>44%</td>
</tr>
</tbody>
</table>

In order to limit the error on the estimation of $R_{\text{TSC}}$, we could introduce a term of penalization in the identification procedure, but in fact we show that the sensitivity to this parameter is very low. The reduced sensitivities calculated for the values of parameters given in Table 1 are plotted in Fig. 4.

In order to illustrate the impact of the sliding contact resistance on the model, the calculation of temperature for different sliding thermal contact resistances from $R_{\text{SC}} = 10^{-n}m^2KW^{-1}$ with
\( n = 3, 4, 5, 6, 7 \) is performed. We can denote that the maximum difference of temperature created by the thermal contact resistance is about \( 0.7K \). The reference for the sliding contact resistance taking into account for the calculation of this variation is \( R_{sc} = 10^{-3} m^2KW^{-1} \). This value of \( 0.7K \) has to be compared to the average in time of the evolution of temperature in each stator and rotor. In fact, it represent only \( 0.2\% \) of this variation of temperature.

### 3.4 Position of the sensors

The inverse method is performed with the temperatures in the center of each solid because of the experimental feasibility of the measurements. We study now the impact of the location of sensors on the set up. Indeed, the sensitivities are higher when the measures will be close to the sliding interfaces. The reduced sensitivity to the maximum heat flux is presented in Fig. 5 for different positions from the interface for the second sensor (i.e. the thermocouple in the first rotor). The center of the disc corresponds to a distance of 9mm. In fact, Fig. 4 presents simultaneously the reduced sensitivities to all parameters for this position sensor. We note from Fig.5 that at 6 seconds, the sensitivity on the sensor located four millimeters of the interface is three times higher than the sensitivity of the sensor in the center of disk. If the sensor is too close to the friction surface, its signal will be extremely noisy due to local fluctuations in generated heat flux. The 2D/3D effect will have a significant impact on the identification. Taking these considerations into account, a sensor located at 3-4 mm from the interface will be the best compromise between a high sensitivity and the respect of the simplifying assumptions.

With the same approach, the sensitivity to the time of the maximum heat flux is shown in Fig. 6. In the same way, the sensors have to be near the interface in order to obtain the highest sensitivity in time. Finally, as we have shown previously, the reduced sensitivity to the sliding contact resistance is very low even if the sensor is located at 1mm of the sliding surface (Fig.6). The value of 0.4K at 1mm will be very low compared to the variation of temperature at this
location. From these observations, we propose to identify only the heat flux. The error on the estimate due to the value of $R_{SC}$ will be insignificant.

![Figure 6 Reduced sensitivities on the time of the maximum heat flux and on the sliding contact resistance](image)

4. Results of estimation procedure from numerical data

For the study, we impose the value of $R_{SC} = 10^{-4} m^2KW^{-1}$. The impact of this assumption on the estimation of the generated heat flux is low. In order to validate the inverse procedure, we propose to use numerical data representing the sensor measurements of the experimental set up. The problem is that we don’t know the boundary conditions of the system. Indeed, the convection coefficients are unknown and it’s difficult to measure the surface temperatures of the first and last stator. That’s why in the numerical model of the inverse method, we use the temperature of the sensor in the middle of the first and the last stator as a boundary condition of the set up. We generate data with convection conditions but in the inverse procedure, we use two of sensors simulations as the boundary condition (first and last stators’ sensors). Then, the minimization of the least square is done on the temperatures of the seven remaining sensors. As we present in the sensitivity analysis part, the parameters vector is: $$\beta = [\varphi_{max}, \varphi_{max}, \cdots, t_{max}, t_{max}, \cdots t_{max}]^T.$$ This representation is not optimum for the estimation. Indeed, the identification of the parameters $t_{max}$ is complex. Indeed, identification procedure from non noisy data generates an error on the estimated $t_{max}$ more over 100%. That’s why another approach is proposed. Rather than identifying a time for the maximum of the heat flux, we propose to estimate a linear heat flux on step times. We use a parameterization of the generated heat flux as it is shown in Fig.7.
Figure 7 Parameterization of the function of the heat flux for each sliding interface

The choice of the increment in time $\Delta t = t_i - t_{i-1}$ is based on the study of the residues obtained by the first method. Indeed, if $\Delta t$ is too small, it will be difficult to identify $\varphi_i$. In fact, the heat flux must have sufficiently varied over a time increment in order to identify the different values of the function. We use this parameterization for the identification of the heat flux in the case where the data are generated taking into account the initial form of the heat flux with the values of $\varphi_{\text{max}}$ given in Table 1, all the $t_{\text{max}} = 1s$. The different times where the values of the heat flux are identified are $t = [0, 0.5, 1, 2, 4, 6, 12, 16]s$. For $t = 0s$ and $t = 16s$, we impose that $\varphi_i = 0$ for all the interface. The inverse procedure used in this estimation is different than what we presented in part 3.2. Indeed, it’s important to constrain the solution in the real positive space. A trust-region method [23], [24], [25] is applied with constrained heat flux: $\varphi_i \geq 0$. Indeed, the minimization procedure could converge to negative heat fluxes namely in the case where $\Delta t$ is low. This configuration is not physical during the braking period. Then, by using this method, we retrieve the simple form of the heat fluxes used in the generation of the data as shown in Fig.8. Then, when data are not noized, the error on the maximum value of the generated heat flux is acceptable, less than 2%. When data are noised (gaussian noise: +/- 0.25K), the error on the estimation is more important, about 20%. Then in order to minimize this error, data could be filtered and the estimation procedure regularized. These solutions could be used on the real data. Then, as we shown in part 3.4, the sensitivity is higher for the sensor near the sliding surface. We use now in the identification procedure, the simulated data at the center of each disc but also the sensor at 1mm of the sliding surface. This time, if the data are noisy (Gaussian noise of +/-0.25K), the maximum error on the estimated generated heat flux is less than 2%.
5. Conclusion

In this article, we present the feasibility of the estimation of the generated heat flux in the interfaces of an airplane braking system. A sensitivity analysis is conducted to highlight the difficulty in the simultaneous estimation of the generated heat fluxes and the sliding contact resistances. Indeed, in this system, the level of heat generated flux by friction prevents a quality estimate of the resistance. Besides, the use of sensor data placed near the sliding surfaces is recommended in order to improve the estimation procedure. Then a strategy of parameterization of the heat flux is presented in order to overcome the assumption of a linear variation of this parameter. Indeed, in the real configuration, it will certainly be necessary to overcome a too restrictive form of the generated heat flux.

6. References


TRIBOLOGICAL BEHAVIOURS OF ZA27/GRAPHENE NANOCOMPOSITES

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3 Department of Metallurgical and Materials Engineering, Engineering Faculty, Karadeniz Technical University, Trabzon, Turkey, ferdemir@ktu.edu.tr
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Abstract: In this study, ZA27/Graphene nanocomposites the samples were fabricated by powder metallurgy technique. ZA27/Graphene nanocomposites with combined % reinforcement of , 0.125%, 0.25%, 0.5%, 1%, 2% and 3% with equal weight % of Gr, Mechanical milling was carried out at the durations of 15 min for mixing of composite powders. The abrasive wear behaviour of nanocomposites were investigated using ball on disc wear test at different loadings of 2 and 10 N. The microstructures of these composites were characterized by a scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) The worn surfaces were analyzed by SEM Results of the wear tests revealed that the wear rate and wear resistance of nanocomposites decreased with an increase in the Gr content. The best wear resistance was obtained at 3 wt % Gr nanoparticle reinforced nanocomposites.

Keywords: ZA27, Gr, Nanocomposite, Wear, Tribology

1. Introduction

Research on attention is concerned with Zinc–aluminum alloys (ZA alloys) that is promising material for tribological applications. At this moment, commercially available ZA alloys have become the alternative material to aluminum cast alloys and bronzes. The ZA alloys have a good castability and unique combination of properties. The ZA alloys, which serve as the matrix for this class of MMCs, are known for their good combination of physical, mechanical and technological properties. High strength, excellent castability, good machinability, low melting point and good tribological properties, as well as low manufacturing cost are among its notable characteristics. [1-2]

The members of the ZA casting alloys are: ZA8, ZA12, and ZA27. These alloys have many advantages over aluminum-based alloys, namely: high strength, good machining and tribological properties, and low casting temperature. Zn-Al alloy, in particular, has been used in bearings and bushing applications, as a replacement for bronze bearings because of its low cost and equivalent or superior bearing performance. Moreover, ZA-27 alloy has shown higher wear resistance and a tensile strength substantially than that of ordinary cast aluminium alloys. ZA-27 alloy finds wide
acceptance in low speed, high load bearing and bushing applications [3-4] ZA27 alloy, the nominal composition listed in Table 1.

Table 1. Chemical composition of ZA27 alloy (% wt.)

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Cu</th>
<th>Mg</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25,5-28,0</td>
<td>2,0-2,5</td>
<td>0,012-0,020</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

On one hand, it has been considered for a number of commercial applications due to good mechanical properties, machinability and wear properties [5-6]. Aluminum in ZA27 helps to facilitate the salt reaction via aluminothermy reduction in the synthesis process.

In the industrial production it is very important to increase the quantity of quality products and without defects, where the structural morphology can also play an important role in the corrosion behavior of the metallic alloys. Although it is well-known that, as much the quantity as the homogeneity in the distribution of second phases are important parameters that define the level of mechanical resistance of the alloy [7-8-9]

The aim of this study is to investigate the effect of reinforcement content on the wear behaviour for both ZA-27 alloy and ZA27/Graphene nanocomposites.

2. Experiments

A mixture of ZA27, nano Gr powders was used as the starting material. The chemical composition of ZA27 is (in weight percent) of 27.2% Al, 2.01% Cu, 0.02% Mg and balance Zn. The mechanical milling (MM) process was conducted in a planetary ball mill (Retsch PM 200) using tungsten carbide containers and balls at the room temperature. Mechanical milling was carried out at the durations of 15 min for mixing of composite powders. In order to avoid excessive temperature during milling, the process was stopped every 30 min then resumed when the temperature of the bowl had decreased to room temperature. Bowl temperature was measured between 35 and 55 °C with an infrared thermometer. The mixtures of ZA27/Gr powders were loaded into a steel die, cold pressed at 200 MPa and then hot-pressed for 3 h at 450°C at pressure of 500 MPa. Zinc stearate was coated on the inner wall of the mold and surface of the simples as a lubricant. The microstructural characterization of the specimens were prepared by grinding paper from 800,1000 and 1200 grit and metallographically polished with 1 µm alumina. The microstructure of the composites was characterized by means of scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS). The experimental densities for the contact samples were determined using Archimedes method. The hardness values of the samples were measured by the Brinell hardness method, and the mean of at least six readings was recorded at a load of 31.25 kgf.

Wear behavior of the composites was examined by using a ball on disk wear tester. The initial average surface roughness (Ra) of a polished sample was 0.4 µm. A H11 hot-work tool steel ball
with diameter of 10 mm and mirror-like surface was contacted on the surface of disk at either 10 or 20 mm from the disk center under the loads of 2 and 10 N. The disk was concurrently rotated for 48 and 96 min with a rotation speed of 100 rpm at room temperature.

3. Result and discussion

3.1. Porosity and hardness

Figure 1 shows the porosities of ZA27 alloy and composites. A important increase of the porosity content of the composite from 0.16% to 1.26 % with reinforcements of Gr content of 0.125% wt. was obtained. Moreover, 3wt% Gr reinforced composites has lower density than ZA 27 alloy. The density decreases with increasing reinforcement. As compared to composites, ZA 27-Gr sample has higher density due to its higher densification ability and the less agglomeration. The density of composites decreases with increase in the Gr content. This can be attributed to the effect multiple pressing during the densification process. The increase in the Gr content from 0wt. % to 3wt% result in few decreasing of density of composite, However a significant increase porosity content of 2wt.% Gr reinforced ZA 27 composites was obtained. The results show that higher than 3wt% Gr content adverse effect on the densification of composites during compaction.

![POROSITY](image)

Fig.1 The porosities of ZA 27 alloy and composites.

Figure 2 shows the Brinell hardness values of ZA27 alloy and composites. As the content of Gr increases from 0 to 3 wt.%, the hardness a decrease substantially. A decrease in the hardness value from 125 to 97,91 HB  is observed with reinforcement of Gr into the ZA 27 alloy matrix.
The relatively lower hardness value for ZA27-Gr composite sample are due to agglomeration of reinforcing Gr particles and the higher porosity content. A few extensive plastic deformation in the ZA27Gr composites sample is occurred. So, the lower stresses are developed at the ZA 27-Gr reinforcement interface.

![BRINELL HARDNESS](image)

Fig.2 The hardness value of ZA27 alloy and composites.

3.2. Wear

The effect of the nano Gr content on the wear of the composites are shown in Figs. 3 and 4, respectively. A decrease in the weight loss with increasing Gr content up to 3 wt.% was obtained. This can be attributed to the effect of self-lubricating of nano Gr. Although, ZA 27-3wt.%Gr composite has higher Gr content than other composites, the highest wear rate was examined. This can be attributed to increasing load carrying capacity with increasing reinforcement content but the bonding strength between the ZA 27 alloy matrix and Gr reinforcement materials decreases significantly. As the applied load change from 2 to 10 N, the wear regime of the ZA 27-3wt. %Gr composite not changed. As can be seen in Fig. 6, the wear mechanism includes the abrasion and adhesion mechanisms.
Fig. 3. The weight loss value of ZA 27 alloy composites

Fig. 4. The weight loss value of ZA 27 alloy composites
Fig. 5. The weight loss value of ZA 27 alloy

Fig. 6. SEM micrographs of the worn surfaces of alloy and composites wear tested at 10N (a) ZA 27 alloy, (b) ZA 27–0.125 Gr , (c) ZA 27–0.25wt.% Gr, (d) ZA 27–0.5wt.% Gr, (e) ZA 27–1wt.% Gr, (f) ZA 27–2wt.% Gr, (g) ZA 27–3wt.% Gr
Fig 7 and 8 shows EDS results obtained from worn surfaces of ZA 27/0.125wt.% Gr and ZA 27/3wt.% Gr composites. EDS results showed that as Gr content increase from 0.125 to 3, C peak broading was observed at the same wear load of 10N. It can be seen that the presence of oxygen is clearly visible in the matrix alloys.

Fig.7. EDS of alloy and composites wear tested at 10N ZA 27–0.125wt.% Gr

Fig.8. EDS of alloy and composites wear tested at 10N ZA 27–3wt.% Gr
4. Conclusions

In this work, nano B4C and nano Gr reinforced ZA-based 27 alloy matrix composites were synthesized by hot pressing method. The main conclusions of this study may be summarized as follows:

1- ZA 27 alloy reinforced with Graphene nanoparticles are prepared successfully using hot pressing process

2- The hardness of the ZA-based 27 alloy reached 125 HB in comparison to 97,91 HB of the ZA 27 /Gr composite reinforced with 0,125wt.% of Gr .

3- The effect of Gr content and applied load on the wear behavior of ZA 27 / Gr is analyzed in detail. The weight loss decreases with increasing Gr content while the ZA 27-3wt. %Gr composite has higher wear rate. The SEM images of the worn surfaces of the ZA 27 / Gr indicates wear mechanism has the adhesive and abrasive wear.

References


WEAR INVESTIGATION OF Al2024/SiC COMPOSITES BY RESPONSE SURFACE METHODOLOGY

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²Abdullah Kanka Vocational School of Higher Education, Karadeniz Technical University, Trabzon, Turkey

Abstract: The effect of SiC particles and applied load on the dry sliding wear behavior of Al2024 alloy composites produced by hot pressing method has been investigated. The percentage of reinforcement and was varied from 0% to 60%. The applied load was changed from 10 N to 20 N. The wear behavior of composites was investigated by ball on disc wear tests. Response surface methodology has been used to plan and analyze the experiment. The regression model was developed for wear rate of dry sliding wear. The results concluded that the amount of SiC reinforcement into the Al2024 matrix is the most important parameter and the decreasing of applied load improves the wear rate.

Keywords: Metal matrix composites, Ball-on-disc wear, Response surface methodology.

1. Introduction

Aluminum metal–matrix composites (AMCs) are currently regarded as a group of advanced materials, due to lightweight, high strength, their perfect physical, mechanical and wear properties while a combination of these desirable properties can be hardly achieved by conventional materials. Al2O3, SiC, B4C, WC, and TiB2 are generally used as reinforcing materials in AMCs. [1,2]. Silicon carbide (SiC) continuous network structure ceramics are a very promising material for use in semiconductor processing, nuclear fusion reactors, heat-sink plates, and high temperature thermo mechanical applications because of their excellent chemical and thermal stability, high thermal conductivity, and good mechanical properties [3]. It is known that in order to get the optimum properties of a composite, especially a suitable combination of strength and ductility, a small size and large volume fraction of the reinforcement(s) are required. Nonetheless, there is a challenge of effectively and simultaneously taking advantage of these two requirements, since small reinforcing particulates in MMCs usually tend to be agglomerated and inhomogeneously distributed through the matrix. A problem of Al/SiC composites is that the microstructure is non-uniform distribution of SiC particles. The most significant detrimental property change may be the decrease in ductility and fracture toughness, which is true for all the AMCs and process histories; a major obstacle preventing their extensive use. The mechanism of reinforcement affecting the fracture toughness of AMCs s is not well understood. Several models have been proposed to characterize the relationship between fracture toughness and microstructure [4]. This problem can be overcome by using mechanical milling method, high-pressure torsion, equal channel angular pressing, and accumulative roll-bonding [5-7].
The aim of this research is to use the response surface methodology on the optimization of characteristics. SiC content (%) and load (N) were selected as the parameters and face centered composite design was used to determine the experimental data and to analyze the effect of parameters on the wear rate.

2. Experimental Procedure

Al2024 alloy powders and SiC particles used as raw materials to fabricate the FGMs. The as-atomized Al2024 powders were supplied commercially with the chemical composition (in wt.%) of 4.85 Cu, 1.78 Mg, 0.385 Si, 0.374 Fe, 0.312 Mn, 0.138 Zn, 0.042 Cr, 0.005 Ti and Al (balance). Al2024 alloy powders with an average particle size of 54 µm were used as the matrix materials and SiC powders with an average particle size of 10 µm (Alfa Aesar, Germany) were used as the reinforcement material. Al2024 matrix powders and SiC particles (30, 40, 50, and 60 wt. %) were blended in a planetary ball-mill (Fritsch Gmbh, model “Pulverisette 7 Premium line”) at room temperature using a tungsten carbide bowl and a high argon atmosphere for 2h in order to break up the hard agglomerates. The milling medium was tungsten carbide balls with diameters of 10mm. The ball-to-powder weight ratio and rotational speed were selected to be 5:1 and 400rpm, respectively. The milling atmosphere was argon which was purged into a bowl before milling. Hot pressing at 560 oC and 500MPa in an argon atmosphere was used for preparation of the Al2024/SiC composites.

Wear behavior of the composites was examined by using a ball on disc wear tester. For wear test, the composite samples were ground with a #2000 SiC abrasive paper and further washed in acetone. The initial average surface roughness (Ra) of a polished sample was 0.2 µm. A H11 hot-work tool steel ball with diameter of 10 mm and mirror-like surface was contacted on the surface of disc at either 5 or 10 mm from the disc center under the loads of 10, 15 and 20 N. The disc was concurrently rotated for 10 min with a rotation speed of 0.5 m/s at room temperature. The wear weight losses were measured from the weight differences of specimens before and after the wear tests using a digital scale in an accuracy of 0.0001 g. The wear rates were calculated by converting the mass loss measurements to volume loss by using the respective densities:

\[ W \text{ (mm3mm-1)} = \frac{\text{mass loss (g)}}{[\text{density (g/mm3 x sliding distance (m))}]} \]

[Eq. 1]

The central composite design (CCD) a standard RSM design of experimental technique is used for minimal combinations of independent variables to determine complex response. For two parameters such as SiC content and load each with three levels 13 experiments were used and the specimens were fabricated according to the experiments. Table 1 shows the independent variable set for running the design matrix and their levels.
Table 1. Controlling Parameters involved and their levels.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC content (%)</td>
<td>0  30  60</td>
</tr>
<tr>
<td>Load (N)</td>
<td>10  15  20</td>
</tr>
</tbody>
</table>

3. Results and Discussion

In this study, optimization of the wear properties of Al2024/SiC composites was carried out using the CCD method. Table 2 shows the designed experiments and corresponding results of the CCD method. The wear rate of Al2024 alloy and Al2024/SiC composites changes from 0.02364 mm³/m to 0.11 mm³/m. The mathematical models obtained for determining the effects of the important parameters on the wear rate are indicated by Equations (2):

\[
C_7 = 0.0342 - 0.001855 \text{sic} + 0.00152 \text{load} + 0.000032 \text{sic*sic} \\
+ 0.000105 \text{load*load} - 0.000041 \text{sic*load} \\
\text{(Eq. 2)}
\]

An analysis of variance (ANOVA) of the generated regression models is presented in Tables 3. The related p value for the model is less than 0.05. The low p value indicates the significance of both models at a confidence level greater than 95%. The obtained regression correction coefficient (R²) is 0.989. From Table 3, the SiC content and load with a contribution of 25.8% and 26.7%, respectively are close to unity.

Table 2. Wear rate results based on generated experimental design by CCD.

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>SiC content (%)</th>
<th>Load (N)</th>
<th>C7: Wear rate (mm³/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>10</td>
<td>0.05925</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>10</td>
<td>0.03628</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>20</td>
<td>0.11000</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>20</td>
<td>0.06220</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>15</td>
<td>0.07770</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>15</td>
<td>0.04762</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>10</td>
<td>0.02364</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>20</td>
<td>0.04946</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>15</td>
<td>0.03546</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>15</td>
<td>0.03497</td>
</tr>
<tr>
<td>11</td>
<td>30</td>
<td>15</td>
<td>0.03556</td>
</tr>
<tr>
<td>12</td>
<td>30</td>
<td>15</td>
<td>0.03687</td>
</tr>
<tr>
<td>13</td>
<td>30</td>
<td>15</td>
<td>0.03454</td>
</tr>
</tbody>
</table>
Table 3. ANOVA results for Response Surface Model for specific wear rate.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>5</td>
<td>0.006473</td>
<td>0.001295</td>
<td>126.31</td>
<td>0.000</td>
</tr>
<tr>
<td>sic</td>
<td>1</td>
<td>0.001695</td>
<td>0.001695</td>
<td>165.39</td>
<td>0.000</td>
</tr>
<tr>
<td>load</td>
<td>1</td>
<td>0.001751</td>
<td>0.001751</td>
<td>170.81</td>
<td>0.000</td>
</tr>
<tr>
<td>sic*sic</td>
<td>1</td>
<td>0.002799</td>
<td>0.002799</td>
<td>222.36</td>
<td>0.000</td>
</tr>
<tr>
<td>load*load</td>
<td>1</td>
<td>0.000019</td>
<td>0.000019</td>
<td>1.84</td>
<td>0.217</td>
</tr>
<tr>
<td>sic*load</td>
<td>1</td>
<td>0.000154</td>
<td>0.000154</td>
<td>15.04</td>
<td>0.006</td>
</tr>
<tr>
<td>Error</td>
<td>7</td>
<td>0.000072</td>
<td>0.000010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>12</td>
<td>0.006545</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ R^2 = 98.90\% \]

As the reinforcement content increases, load carrying capacity of metal matris composite increases, but the weaker bonds can also form between the reinforcement and matrix materials. The distribution of reinforcement material can also determine to wear behaviour of composite. Fig. indicates the effect of the SiC content (%) and the load (L) on the wear rate (mm3 /m). The surface and contour curves showed that the value of the wear rate was minimized when the mean values of the SİC and the lowest values of load were used. A increase in SiC content up to 35.75 wt.% was resulted in decrease with wear rate (fig.1). As compared with composite samples, composite that have 60 wt.% SiC was exhibited lower wear resistance. But , the highest wear rate was observed in Al2024 alloys. This can be attributed to their lower hardness values. As the applied load change from 10 to 20 N, the wear rate of the composite and Al2024 alloy increased significantly and wear mechanism transformed from mild to severe wear regime. For each SiC content, the lowest wear rate was obtained to 10N load.
**Fig.1.** Surface and contour for interaction SiC content and load on the wear rate.

Figs. 2 show the relation between the experiment sets and RSM prediction for specific wear rate of Al2024/SiC composites. The results also show that the experimental and predicted values remain constant at about 1.1%. This means that RSM model predicts accurately, and these models can be used for advance prediction for the purpose of time and cost reduction.
Fig. 2. Experiment sets and RSM prediction on wear rate for Al2024/SiC composites.

Fig. 3 shows that SiC content is 35.75 %, and applied load is 10N. Wear rate can achieve to 0.0196 mm³/m according to the optimized parametric combination.

Fig. 3. Optimum results for minimum wear rate.

4. Conclusions

In this study, the main parameters of SiC content and applied load were analyzed by applying a central composite design as a standard RSM design. The experimental results indicated that the effect of the SiC content and load on the wear rate is similar. The main parameters were optimized as the 35.75 wt. % SiC content and 10N load.
References


CHARACTERIZATION OF POWDER METALLURGY-PROCESSED AZ91 MACHINED CHIPS/NICKEL-COATED GRAPHITE COMPOSITES

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Abstract. In the present paper, the microstructure and mechanical properties of AZ91 Magnesium chips/Nickel-Coated Graphite (NCG) composites obtained by two solid-state recycling processes including cold-pressing followed by hot extrusion were studied. In the experiment, AZ91 Magnesium chips was reinforced with 5, 10, 20 and 40 wt. % of NCG and then compacted at 1600 MPa followed by hot extrusion at 623K at an extrusion ratio of 9:1 in air. The interfaces between NCG particles and AZ91 Mg matrix alloy were very clean. The wear resistance improved with the addition of NCG particles although some reduction in microhardness was observed.

Keywords: AZ91 machined chips; Composites; Nickel-coated graphite; Solid-state recycling; Wear.

1 INTRODUCTION

Magnesium (Mg) alloys are promising materials in the manufacture of automotive parts owing to their lightness, high specific strength, good machinability and high recycling potential [1 - 3]. With the increase of demand, chip and scrap from manufacturing process (die casting and plastic forming process) and product replacement create a big amount of waste which needs recycled [1]. In general, metallic chips and scraps always can be remelted to cast into ingot for subsequent processing. However, the high surface-to-volume ratio of Mg alloy chips leads to melt losses, hazards during transportation, high oxide contents. So, recycling with liquid state approaches may not be efficient to overcome in Mg recycling because of the needs of special protective environment and extra caution. Therefore, there is a growing need for more effective recycling processes for Mg alloy chip and scrap. In recent years, recycling by solid state approaches has been shown to possess a number of technological advantages over the traditional casting processes because its cost is relatively low, also favorable for environment protection. In the solid state recycling, chips and scraps are recycled by consolidation using plastic deformation processes such as cold or hot pressing followed by hot extrusion without melting [1 - 3].
Mg alloys recycled by a solid state recycling technique show excellent mechanical properties [1, 4]. However, their low resistance to wear under insufficient liquid lubrication and their severe seizure under boundary lubrication conditions are the weak points for their superior tribological properties [3]. In order to cover the deficiencies in tribological properties of Mg alloy, efforts have been made to develop self-lubricating composites due to their promising advanced properties [5, 6]. Mg-graphite (Gr) self-lubricating composites are preferred because the solid lubricant contained in them can be automatically released during the wear process to reduce the wear. Since Gr is known to be non-wetting for metals such as Mg and Al, various coatings have been developed to facilitate incorporation of fibers or particulate graphite in the metal matrices [7, 8]. The effect of nickel (Ni) as reinforcement with the microstructural and mechanical properties of pure Mg has been investigated by Hassan and Gupta [9]. Their work has revealed that the Ni reinforcement may produce a substantial increase in mechanical properties with minimal porosity and defect free Ni/Mg interface. But up to now, study on the AZ91 machined chips reinforced with Nickel-Coated Graphite (NCG) in applications based on their high wear resistance has not been reported from reference. This work reports the development of a composite (AZ91 machined chips and NCG powders), the study of the microstructure of the composites, and explore the effect of NCG particles added on the tribological behavior of the composites.

2 EXPERIMENTAL METHODS

The materials used in this work were AZ91 Mg alloy chips directly coming from the machining process in the industrial manufacture (see figure 1 a). AZ91 machined chips with the size of 220 µm and NCG particles about an average particulate size of 130 µm are used as the main ingredients of composite. NCG particles were mixed with AZ91 Mg chips to produce AZ91 Mg - NCG composites with 0, 5, 10, 20 and 40 wt.% of reinforcement content, hereafter termed as the A0, A5, A10, A20 and A40, respectively. The mixtures were then filled into a 30 mm cylindrical mould in diameter and cold-pressed. Following the cold-press process, hot extrusion was carried out in air at 623K and an extrusion ratio of 9:1 to produce a 10 mm bar in diameter, shown in figure 1 b.
Characteristics of the composites were investigated by microscopic examinations, X-ray diffraction (XRD) analyses, density and microhardness measurements, and dry sliding wear tests. Microstructural surveys of the AZ91 Mg - NCG composites prepared utilizing standard metallographic techniques were inspected with a Scanning Electron Microscope (SEM). Phase analysis of the composites was examined by XRD with CuKα radiation. The density of the composites was determined using a helium-gas-based pycnometer. The microhardness of the composites was measured under 500 g load by a Shimadzu HMV2 hardness tester. The hardness values were determined by taking the average of five successful measurements.

Dry sliding wear performances of the composites were performed on a reciprocating wear tester operating in ball-on-disc configuration at room temperature. In this configuration, an Al₂O₃ ball with a diameter of 10 mm was sliding forward and backward against the composites with a sliding speed of 1.7 cm s⁻¹. Normal load of the test, sliding amplitude (wear track length) of the reciprocating motion and overall sliding distance were 2 N, 10 mm and 50 m, respectively. During the wear tests, the temperature and the relative humidity were maintained as 20±5 °C and 40±5 %, respectively. The friction coefficient force was continuously recorded during the tests. After the wear test, the wear tracks formed on the composites were detected by a surface profilometer (Surftest SJ 400). The wear of the Al₂O₃ balls were evaluated by an Optical Microscope (OM) examination of their contact surfaces. To evaluate wear mechanisms, wear tracks of the composites were further studied using a SEM equipped with an Energy Dispersive Spectroscopy (EDS).

3 RESULTS AND DISCUSSION

The typical macrographs of the composites with different mixture ratios were shown as figure 2. From those figures, it can be seen that the more the content of the NCG particles is, the more the agglomeration along the extrusion direction in banded form is. At the same time, the interface between the AZ91 Mg and NCG particles is clean. It can be seen that the AZ91 Mg chips and NCG particles have good metallurgical bonding interfaces (see figure 3).
Figure 2. Low magnification SEM micrographs of hot extruded (a) A0, (b) A5, (c) A10, (d) A20 and (e) A40 composites.
Figure 3. High magnification SEM micrographs of hot extruded (a) A5, (b) A10, (c) A20 and (d) A40 composites indicating good bond between matrix and reinforcement.

Figure 4 shows the XRD pattern of the unreinforced AZ91 Mg alloy and NCG particle reinforced AZ91 Mg composites. The XRD pattern confirmed the presence of Mg, Gr and Ni in the composites. These results indicate the presence of Mg (in the largest peaks), and the presence of Ni and Gr is indicated by minor peaks. The increase in the intensity of diffraction peaks of Ni and Gr with an increase of NCG reinforcement in the composite is evident. Figure 4 also shows that there is no oxygen reaction in the composites during the hot extrusion process.
Figure 4. The XRD patterns for the prepared AZ91 Mg and AZ91 Mg-NCG composites.

Table 1 shows the density and microhardness results of AZ91 Mg and AZ91 Mg–NCG composites. It is observed that there is an increase in density with increase in NCG reinforcement. This can be attributed to the addition of higher density reinforcements of NCG [10]. The microhardness values remain relatively stable until 5 wt.% of NCG have been added to the AZ91 Mg matrix, above which, the microhardness values start to drop. The incorporation of NCG into the AZ91 Mg matrix has minimal effect on the microhardness of the composites until the threshold of 5 wt.% NCG. Above the threshold, the microhardness starts to decrease due to an increase in the soft NCG clusters in the AZ91 Mg matrix which affects the integrity of the composite.

Table 1. Results of density and microhardness measurements of composites with different weight percentage of NCG.

<table>
<thead>
<tr>
<th>Composites</th>
<th>NCG (wt.%)</th>
<th>Density (g/cm³)</th>
<th>Microhardness (HV0.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>0.0</td>
<td>1.49</td>
<td>65.4</td>
</tr>
<tr>
<td>A5</td>
<td>5.0</td>
<td>1.52</td>
<td>64.8</td>
</tr>
<tr>
<td>A10</td>
<td>10</td>
<td>1.59</td>
<td>58.9</td>
</tr>
<tr>
<td>A20</td>
<td>20</td>
<td>1.68</td>
<td>59.1</td>
</tr>
<tr>
<td>A40</td>
<td>40</td>
<td>1.95</td>
<td>56.1</td>
</tr>
</tbody>
</table>

The wear behavior of the composites is shown in figure 5. It can be clearly seen that the wear rate of the composites is considerably improved by the addition of the reinforcement particles and decreased by increasing NCG weight fraction from 5 to 40 wt.% A strong bond between the NCG reinforcement and AZ91 Mg matrix helps in the load transfer from the latter to the former. Although the soft NCG is a non-load bearing constituent, a strong particle/matrix interface (see figure 3) favors improvement in tribological properties owing to ease of load transfer. The results are in accordance with the previous work by Ramesh et al. [11] on wear behaviour of uncoated and Ni–P coated SiC reinforced Al6061 composites processed by liquid metallurgy route followed by hot extrusion. They have reported that strong
interfacial bond between matrix and reinforcement in case of Ni–P coated SiC reinforced composites contributes significantly to the improved wear resistance by increasing the load transfer efficiency between matrix and reinforcement.

![Graph](image)

**Figure 5.** Effect of NCG content on the wear rate of the composites.

Appearances of the wear tracks developed on the examined composites and their corresponding testing balls were shown in figure 6. The worn surfaces of the composites are covered with white and black lubricating films as a result of Ni and Gr extruded from AZ91 Mg matrix. Meanwhile, A10, A20 and A40 composites imparted the least damage to the Al₂O₃ ball compared to the unreinforced A0 and A5 composite. The reduction in surface damage of Al₂O₃ balls by the addition of NCG can be attributed to the formation the protective tribolayers. As shown in figure 6, the unreinforced A0 and A5 composite develop a hard layer of comminuted Mg oxide particles and the wear scars on the Al₂O₃ ball sliding against the unreinforced A0 and A5 composite are very large. Higher magnification SEM micrograph and corresponding EDS analysis of the bright area (marked A in figure 7 a) and darker layer (marked B in figure 7 a) on worn surface of A20 composite are shown in figure 7. EDS analysis confirmed that the bright area on A20 composite worn surface beside Ni element contained small intensity carbon, oxygen and magnesium peaks (see figure 7 b). In contrast, EDS analysis of the darker area on A20 composite worn surface showed a high intensity carbon peak and small intensity nickel and oxygen peaks (see figure 7 c). The presence of strong carbon peak and weak nickel peak in the darker layer implies the increased smearing of NCG particles at the contact surface while the oxygen element predicates the oxidation reaction.
Figure 6. Low and high magnification SEM micrographs of wear tracks generated on the (a) A0, (b) A5, (c) A10, (d) A20 and (e) A40 composites, and OM images of their corresponding testing balls.
Figure 7. (a) High magnification SEM morphology of wear track generated on the A20 composite, and its EDS analysis of (b) bright area and (c) darker layer on the worn surface of A20 composite.

The effect of NCG addition on friction coefficient is shown in figure 8. Friction coefficient and the fluctuation of the friction coefficient decreases as the percentage of NCG addition increases. Figure 8 shows that the friction coefficient...
of A10, A20 and A40 composites is between 0.17 and 0.22, and that is a lower than those of the unreinforced A0 and A5 composite, of which the friction coefficient is between 0.5 and 0.6. When NCG particulates are added, the reduction in the coefficient of friction is due to the release of NCG particle during their wear process which acted as the solid lubricant. Guo et al., [12] observed a similar behaviour of decrease of friction coefficient with increase in Gr-Ni addition in wear tests performed on Al/SiC/NCG hybrid composites. Moreover, there are some sudden fluctuations in the friction coefficient, particularly in the case of unreinforced A0 and A5 composite (see figure 8). As previously noted, a thin lubricating graphite rich film formed on the worn surface of A5 composite was less stable and had less coverage in comparison with A10, A20 and A40 composites. These fluctuations in the friction coefficient can be due to delamination of weakly bonded and thin film from the worn surface, which leads to leaving behind the fresh surface. This phenomenon was reflected as the jump in the fluctuations at some points in the similar friction plots of the A0 and A5 composite.

Figure 8. Friction coefficients for the AZ91 Mg chips/NCG composites.

4 CONCLUSIONS
From the study reported above, the following conclusions can be drawn:
(i) AZ91 Mg chips – NCG composites have been successfully fabricated using the cold press followed by hot extrusion.
(ii) Results of density measurements show that little heavy composites can be produced with the incorporation of NCG.
(iii) Although addition of NCG particles above the threshold of 5 wt.% NCG leads to a decrease in the microhardness of the composites, there are simultaneous improvements in wear rate and friction coefficient.

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REFERENCES

PHASE EQUILIBRIA IN FLUID MIXTURES EMBEDDED WITH GRAPHENE GENEALOGIC TREE NANOPARTICLES

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Abstract: The importance of thermodynamic and phase behavior of working fluids embedded with nanostructured materials is fundamental to new nanotechnology applications. Considering the extremely large number of different both nanoparticle types and reference fluids, it is obvious that there is need for developing theoretically sound methods of the prompt estimation thermodynamic properties and phase equilibria for emerging working media. The effect of nanoparticles on the critical point shift for classical fluids doped by nanoparticles is examined. Global phase diagrams of two-component fluids with nanoparticles are analyzed. The global phase diagram studies of binary mixtures provide some basic ideas of how the required methods can be developed to visualize the phase behavior of nanofluid blends. The mapping of the global equilibrium surface in the parameter space of the equation of state (EoS) model provides the most comprehensive system of criteria for predicting binary mixture phase behavior. Results of calculations of phase equilibria for some nanofluids are described.

Keywords: phase equilibria, nanofluid mixtures, graphene, carbon nanotube, fullerene

1 Introduction

Nanofluids (NF), i.e. fluids embedded with nanostructured materials, have recently became a subject of growing scientific interest due to reports of greatly enhanced thermal properties [1]. The heat transfer in nanofluids the Thomson Reuters rating agency associates with “Research Nanofluids Fronts 2013” 100 top-ranked specialties in the sciences and social sciences [2]. Key features of NF include thermal conductivity exceeding those of conventional suspensions, a nonlinear relationship between thermophysical properties and concentration for NF containing carbon nanotubes, and a significant increase in critical heat flux in boiling heat transfer. NF phenomena will allow to create a new class of efficient working and bring such benefits like energy efficiency (e.g., improving heat transfer, reducing pumping power), lower operating costs, smaller/ lighter systems (small heat exchangers) and cleaner environment (e.g., reducing heat transfer fluid inventory) [3], [4].
The key values that define thermodynamic and phase behavior of fluids are the critical point for pure substance and critical lines for binary mixtures. The mapping of the global equilibrium surface on the critical parameter space of components provides the most comprehensive system of criteria for predicting the binary mixture phase behavior. These singular properties of nanofluids have not been studied yet. At present time, neither experimental data nor theoretical assessments about changes in the singularities of conventional fluids after nanoparticle doping are available in literature. The presence of nanostructured materials should displace the singularity allocation and change the phase behavior of mixtures due to critical point shift of components.

The principal aim of this work is to study the effect of graphene genealogic tree nanoparticles (carbon nanotubes, fullerenes, and graphene flakes) on the phase behavior of conventional fluids and their mixtures.

This work is organized as follows. In the first part, we study the influence of nanoparticle adding on critical point location in the one-component fluids. We suggest that regular and singular parts of thermodynamic surface of reference fluid and nanofluid with small nanoparticle volume concentration (<5%) are coincided in reduced form. The shift of critical point for CO2 doped with graphene genealogic tree nanoparticles is theoretically predicted. Then, we consider possible changes in the phase behavior of two component fluids under nanoparticle doping. Analysis of phase behavior is based on global phase diagram of binary mixtures. These diagrams are not represented in pressure–temperature variables; instead, they are represented in the space of parameters of an equation of state. For example, in terms of the van der Waals equation of state the constants $a$ and $b$ directly related with the critical parameters of pure components. The critical parameters change for nanofluids leads to a change both combination rules and equation of state parameters for binary mixture. It can shift the position of characteristic point on the global phase diagram and change the type of phase behavior. Some examples of the nanoparticle adding effect on liquid – vapor and liquid – liquid equilibria are given.

2 Phase behaviour of nanofluid mixtures

Critical point identifies thermodynamic behavior of pure substance in wide range of parameters of state. Adding of nanoparticles changes the intermolecular interactions between fluid components embedded with nanostructured materials and shifts phase equilibria in the nanofluids. Here we suggest the fluids with small impurities obey the corresponding state principle.

2.1 Influence of nanoparticle adding on critical point location

It is hypothesized that the regular and singular parts of thermodynamic surface of base fluid and nanofluid with small nanoparticle volume concentration are coincided in reduced form. The compressibility factor ($Z$) of nanofluid is defined via scaled pure reference fluid properties
\[ Z = Z(\rho_{\text{Cnf}}/\rho, T/T_{\text{Cnf}}), \]  

(1)

where critical parameters of nanofluid \((\rho_{\text{Cnf}}, T_{\text{Cnf}})\) are calculated from available equation of state in vicinity of critical point. To estimate the critical parameters of reference fluid – nanoparticles system the fundamental equations of state in reduced form for industrial fluids [9] are used. To compute thermodynamic properties of nanofluids under investigation in the range 0 … 5% volume concentrations of nanoparticles \((np)\) the density of nanofluid \((nf)\) calculated via reference fluid density \((rf)\) by standard relation [5]:

\[ \rho_{nf} = (1-\varphi)\rho_{rf} + \varphi\rho_{np} \]  

(2)

The search algorithm of nanofluid critical parameters is as follows. From the fundamental EoS of given substance the \(p - \rho - T\) data are generated in vicinity of critical point to establish the power law equations [6]

\[ \frac{\rho_{\sigma}}{\rho_c} - 1 = N_1(1 - \frac{T_{\sigma}}{T_c}) \pm N_2(1 - \frac{T_{\sigma}}{T_c})^\beta \]  

(3)

where \(\rho_{\sigma}\) is the saturation density for the liquid or the vapor, kg/m\(^3\); \(T_{\sigma}\) is the temperature along saturation curve, K; \(\rho_c, T_c\) are critical density and temperature; \(N_1, N_2, \beta\) are fitting parameters.

This equation is valid only in the critical region. The critical pressures for each fluid are determined from calculations with the equation of state at the critical temperature and density. It is assumed that equation (3) is valid both reference substance and nanofluids. The application of universality to dissimilar critical points is based on the isomorphism principle, which formulates the conditions for expressing the theoretical scaling fields through physical field variables. The \(N_1, N_2, \beta\) are calculated from the \(\rho - T\) data set for pure substances and then used to estimate nanofluid critical parameters at different nanoparticle concentrations. The algorithm accuracy is checked at limit \(\varphi = 0\) to reproduce the critical point data for pure components. The results of our calculations reproduce the EoS data from [6, 7] within experimental accuracy of density measurements for given substance.

Here we consider as an example the critical point shift for CO\(_2\) embedded with different types of nanoparticles: graphene genealogic tree (CNT (Fig. 1a), fullerenes (Fig. 1b), and graphene flakes (Fig. 1c)) which have bulk density \(\rho_{\text{CNT}} = 1330\ \text{kg/m}^3\), \(\rho_{\text{C60}} = 1650\ \text{kg/m}^3\), \(\rho_{\text{G}} = 2230\ \text{kg/m}^3\), correspondingly.
Thermodynamic behavior for selected fluids near critical point is generated via the fundamental equations of state from [6, 7]. The predicted critical temperature shifts under adding of different nanoparticles are presented in Table 1 and Figs. 2, 3. The growth of volume nanoparticle concentration tends to increase slightly the CO₂ nanofluid critical temperature. Changes that are more significant observed for critical density (Fig. 3).

Table 1: Critical temperature ($\Delta T_c = T_{cnf} - T_{CO2}$) and density ($\Delta \rho_c = \rho_{cnf} - \rho_{CO2}$) shifts in carbon dioxide embedded with different nanoparticles

<table>
<thead>
<tr>
<th>Nanoparticle types</th>
<th>$\Delta \rho_c$, kg/m$^3$ at $\phi = 1%$</th>
<th>$\Delta \rho_c$, kg/m$^3$ at $\phi = 5%$</th>
<th>$\Delta T_c$, K at $\phi = 1%$</th>
<th>$\Delta T_c$, K at $\phi = 5%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>$5.74$</td>
<td>$22.6$</td>
<td>$0.01$</td>
<td>$0.11$</td>
</tr>
<tr>
<td>C$_{60}$</td>
<td>$7.47$</td>
<td>$33.2$</td>
<td>$0.01$</td>
<td>$0.13$</td>
</tr>
<tr>
<td>Graphene</td>
<td>$12.47$</td>
<td>$55.7$</td>
<td>$0.02$</td>
<td>$0.19$</td>
</tr>
</tbody>
</table>
Figure 2 Saturation curve and critical point CO$_2$ shift under graphene genealogic tree nanoparticle doping

Figure 3 Critical density shift for CO$_2$ under graphene genealogic tree nanoparticle doping
2.3 Azeotropy in binary mixtures with nanoparticles

The conditions of azeotropic state are

$$\mu_i^f = \mu_i^s, \quad i = 1, 2, \quad x_i^f = x_i^s$$

Azeotropy in binary fluids can be easily predicted in the framework of global phase diagrams. The corresponding boundary state is called the degenerated critical azeotropic point (CAP) and represents the limit of the critical azeotropy at $x_i \rightarrow 0$ or at $x_i \rightarrow 1$. This results in solving the system of thermodynamic equations for a degenerated critical azeotrope. One may obtain the relationships for azeotropy boundaries from the global phase diagram [shaded A(Azeotropy ) and H (Hetero-azeotropy)] regions in Fig. 4. The above azeotropic borders are straight lines in the $(Z_1, Z_2)$-plane that cross at a single point near the centre for equal sized molecules. It opens the opportunity for obtaining the series of inequalities to separate azeotropic and non-azeotropic regions of the global phase diagram. For the Redlich – Kwong EoS [8] a corresponding relationship was obtained in the analytical form [9]:

$$Z_2 = \mp Z_1 - 0.67 (I \pm Z_1) \left( \frac{1 - Z_4}{I \pm Z_3} - 1 \right).$$

The convenient set of dimensionless parameters for the Redlich-Kwong model is as follows [10]:

$$Z_1 = \frac{d_{22} - d_{11}}{d_{22} + d_{11}},$$

$$Z_2 = \frac{d_{22} - 2d_{12} + d_{11}}{d_{22} + d_{11}},$$

$$Z_3 = \frac{b_{22} - b_{11}}{b_{22} + b_{11}},$$

$$Z_4 = \frac{b_{22} - 2b_{12} + b_{11}}{b_{22} + b_{11}}$$

where

$$d_{ij} = T_{ij}^* \frac{b_{ij}}{b_{ii}b_{jj}}, \quad T_{ij}^* = \left( \frac{\Omega_{ij} \alpha_{ij}}{R \Xi_{ij}} \right)^{3/2}, \quad \Omega_{ii} = \left[ g \left( \frac{1}{2} \frac{1}{3} - 1 \right) \right]^{-1}, \quad \Omega_{ij} = \frac{2}{3} \frac{1}{3} - 1.$$

The combining rules for the binary interaction parameters are
\[ a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j}, \quad b_{ij} = (1 - l_{ij}) \frac{b_i + b_j}{2}. \]

where \( k_{ij} \) and \( l_{ij} \) are fitting coefficients in the Lorentz-Berthelot combining rule \((k_{ij} = l_{ij} = 0)\).

Global phase diagrams of binary fluids represent the boundaries between different types of phase behaviour in a dimensionless parameter space. In a real \( p - T - x \) space, two relatively similar components usually have an uninterrupted critical curve between the two critical points of the pure components.

![Global phase diagram of the Redlich-Kwong model for equal size molecules \((Z_z = 0)\); Notations: tricritical line; azeotropic boundary; the Lorentz – Berthelot combining rule](image)

Here we consider phase behavior of the R1234yf – R161 zeotropic blend and R1234yf – R161 – graphene genealogic tree nanoparticles as most likely azetotropic system that are recognized as low global warming potential (GWP) refrigerant to replace the R134a refrigerant. The equation of state parameter for low-boiling component R1234yf were taken from [11]: \( T_C = 367.85 \text{ K}, \rho_C = 3.382 \text{ MPa} \) and \( \omega = 0.280 \). For the R161 equation of state parameters, corresponding values are as follows: \( T_C = 375.35 \text{ K}, \rho_C = 4.7 \text{ MPa} \) and \( \omega = 0.210 \). The binary interaction parameters were fitted by the Lorentz-Berthelot combination rule \((k_{ij} = l_{ij} = 0)\). The results of phase equilibria calculations for different temperatures in the pressure – composition diagrams demonstrate that the R1234yf doped with the CNT, \( C_{60} \), and graphene nanoparticles, correspondingly increases the critical temperature of pure low-boiling component until 369 K. This shift conduces to transformation from zeotropic state to azetotropic state.
2.4 Influence of nanoparticles on the shift of liquid – liquid equilibria

Influence of nanoparticles on the shift of liquid – liquid equilibria we have studied for the liquid – liquid coexistence curve of the binary fluid nitrobenzene-heptane. Fitting coefficients $k_{ij}$ and $l_{ij}$ have been restored from experimental data Borzenkov, Zhelezny [12]. The RK or other cubic EoS belong to the mean field models that cannot simultaneously describe experimental data near critical point and at low temperatures. Here we preferred the more exact description of near-critical area. Coefficients $k_{ij}$ ($l_{ij}$) are 0.01824 (0.01392) for nitrobenzene-heptane mixture and 0.01794 (0.0148) for nitrobenzene – heptane – TiO₂, correspondingly. Deviations of mean field model from experimental data for binary mixtures of interest are shown in Fig. 5. The changes of coefficients $k_{ij}$ and $l_{ij}$ displace the liquid – liquid coexistence curve of binary mixture and location of upper critical end point (Fig. 5). Experimental data treatment shows that upper critical end point (UCEP) for the liquid – liquid coexistence curve of the binary fluids nitrobenzene – heptane and nitrobenzene – heptane – nanoparticles TiO₂ are as follows: $T_{UCEP} = 292.998$ K, $x_{UCEP} = 0.519$ and $T_{UCEP} = 292.46$ K, $x_{UCEP} = 0.531$, correspondingly. The doping of graphene genealogic tree nanoparticles leads to intermediate values for UCEP (Fig.5).
3. Conclusion

This study is one of the first attempts to establish and demonstrate multiple links existing between the critical point shift in classical fluids and phase equilibria phenomena in mixtures embedded with nanostructured materials. From the very beginning of these efforts, the obtained results serve very useful information for scientists and engineers working in the field of emerging nanotechnology applications. The examples the critical point shift for CO$_2$ with different types of nanoparticle doping: graphene genealogic tree (CNT, fullerenes, and graphene flakes) are given. A wide variety of phase diagrams from analysis of variations in geometry and energy characteristics of mixture components are analyzed via global phase diagrams. As illustration, phase behavior of systems R1234yf – R161 and R1234yf – R161 – nanoparticles that are recognized as low GWP refrigerants has been studied. Computer modeling has shown a possible azeotropy appearance in the zeotropic blend with nanoparticle doping that can pretend to be replacement of conventional refrigerant R134a. Impact of nanoparticles on the shift of liquid – liquid equilibria are discussed for the liquid – liquid coexistence curve of the binary fluids nitrobenzene-heptane and nitrobenzene – heptane – graphene genealogic tree nanoparticles. We have shown that the presence of nanoparticles in a binary critical mixture of two liquids changes the location of upper critical end point. There is no doubt that extension of our knowledge about thermodynamic and phase behavior of nanofluids will lead to the creation of reliable engineering recipes for solving the actual problems of nanotechnologies.
4. References


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THE USAGE OF VIBRATORY STRESS RELIEF METHOD IN WELDING

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Abstract

The residual stresses occur in the part after welding, as a result of the thermal expansions and the metallurgical transformation. Depending on the amplitude and distribution in the material, occurred residual stresses cause distortion in welded work piece or a crack in the welding zone. Therefore, a thermal treatment is usually carried out to decrease the residual stresses after welding process. But nowadays, non-thermal stress relief methods are preferred due to some disadvantages of thermal stress relief methods (heat treatments) such as negative effects on the material and the difficulty in the application for large scale work pieces. In this study, reduction of the residual stresses which occur after welding and cause to decrease in the life cycle of materials, by using a non-thermal method called “vibratory stress relief” and the application of this method to welded parts are investigated.

Keywords: Vibration, Stress relief, Resonant frequency, Residual stress

1. Introduction

Thermal or mechanical methods such as casting, plastic deformation and welding used in production cause residual stresses in parts [1]. The formed residual stresses, depending on their distributions and magnitudes in material, lead to distortion or cracking of manufactured material. Furthermore, the residual stresses can also decrease the corrosion resistances, fatigue strength and toughness of material. Considering the usage of manufactured materials, combining of residual stresses and applied working loads on parts result in deformation or cracking due to the formation of fracture in materials.

Besides these residual stresses can cause crack formation in material or distortion in welded part, they can also remain in weld region without resulting in any macroscopic defect. However, the combination of residual stresses and stress applied by load can cause a fracture in part after the residual stressed part is loaded. The most important danger for welded materials is this situation [2]. The parts which are assumed to have residual stresses were heat treated after welding for decreasing the residual stresses. Thus, the possible fracture formation in parts under load are prevented. In thermal stress relief methods, the consumed energy and cost of process are high and processing time is long. Furthermore, these methods have disadvantages such as application difficulties to large scale parts, being environmentally hazardous and changing of
metallurgical properties and tolerances of surface and dimensions of parts. Besides the disadvantages of thermal stress relief methods, they are used commonly [1, 3].

Thus, non-thermal methods are developed and used to eliminate the disadvantages of thermal methods in recent years. Vibratory stress relief method is one of these methods. Vibratory stress relief method comes into prominence for having useful properties such as low investment cost, easy applicability to parts, enhancement of the mechanical properties of parts [4] and being nonpolluting [1, 3]. In this method, the work pieces are vibrated periodically between two boundary forces and thus, micro plastic deformations form in the work pieces. These micro deformations provide to decrease the residual stresses [5].

In this study, the basic principles of vibratory stress relief method are explained and the usage of this method in welding is emphasized.

2. The Basic Principles of VSR Method

There are two hypotheses that explain the mechanism of vibratory stress relief. One of them is depending on the movement of atoms that constitute the crystal lattice similar with thermal methods. Therefore, sufficient energy is given to atoms to replace new positions by applying low-frequency vibrations to material [6]. According to the other hypothesis, stress relief is clarified with plastic deformation. Thus, the residual stresses and the applied periodic stresses combine and exceed the yield stress of material during the vibrations. This situation cause plastic deformation that decrease residual stresses [6].

When any force is not applied a system, vibrations depending upon own stiffness and mass of system caused only by initial force or movement is called natural frequency. Natural frequency ($f_n$) of a simple mass-spring system is explained in Fig. 1 [7].

$$f_n = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

**Figure 1.** Schematic representation and the natural frequency of single mass-spring system

Resonance is the stimulation applied by a force/vibration that has the same frequency with the natural frequency of a work piece or a system. In resonance condition, the vibration amplitude of the work piece or system increases. Resonance peak occurs when the frequency of applied vibration is same with the natural frequency of work piece. Vibratory stress relief (VSR) process is applied in three different ways. These are resonant-VSR (R-VSR), Sub-resonant VSR (SR-VSR) and Sub-harmonic VSR (SH-VSR). All engineering materials have several natural
frequencies. VSR process at resonance vibrations is the basis of R-VSR. Strains occurred by cycles combines with the residual strains in the material. This situation decreases the residual stresses and provides homogeneous distribution of residual stresses [8]. In SR-VSR, used equipment is same with R-VSR. This method used when the resonant frequencies cannot be reached with the R-VSR system. Thus, sub-resonant frequencies are used for stress relieving in SR-VSR. The method that the sub-resonant frequencies are used called SR-VSR [8]. The optimum results can be derived by spending ten times more process time than which is needed in R-VSR [9]. If both of the resonant and sub-resonant frequencies cannot be obtained, sub-harmonic frequencies would be used. The method which is applied in this way is called SH-VSR. In this method, a system which is different from R-VSR and SR-VSR systems is used to obtain sub-harmonic frequencies. By using this method, the atoms of material are vibrated and these atoms move towards near another place in the crystal lattice. The vibrations are not heard or understood because of the low energy consumption of this method.

The work piece which will be applied VSR is isolated from the external forces and vibrations to reduce and distribute homogeneously the residual stresses in the material. Rubber or foam isolators are usually used for isolation [6, 9]. Stress relief process begins with the controlled vibrations that are applied to the work piece. The vibrations are applied to the work piece with a motor that has changeable eccentric load and adjustable rotational speed (Fig. 2(a)). Furthermore, vibratory stress relief process is applied to plain bars by using electromagnetic vibrators (Fig. 2(b)) [10].

![Vibratory stress relief systems](image)

**Figure 2.** Vibratory stress relief systems; (a) eccentric loaded vibratory stress relief system [1]; (b) Schematic representation of resonant vibration feedback control loop [11]
The system that will be used for vibratory stress relief method has different types depending on the sizes of work pieces. If the size of work piece is large, the vibrator can be mounted directly to the work piece. When the method is applied to the small sized work pieces, the work piece is fastened to an isolated table. Then, the vibrator vibrates to this table [6, 9]. The residual stresses of the small sized work pieces that have not natural frequencies in the range of the natural frequency of the vibrator, can be reduced by using the vibration table. The natural frequency of the whole mass decreases by mounting the small work pieces to table. Thus, the residual stresses of the work piece can be decreased more effectively. An accelerometer is mounted on the work piece or table to determine the natural frequency. The frequency of vibration depends on the size, material and shape of the work piece [6]. The frequencies that are below 100 Hz are usually used in the commercial applications of the VSR process. Resonant frequencies of similar metals are approximately constant since resonance depend on the E/ρ ratio (E: Elastic modulus, ρ: Young modulus) [10].

3. VSR Applications on Welded Parts

Residual stresses that usually cause to form three-dimensional stresses occur during the welding process. Residual stresses can create three-dimensional tensile stresses in heat treated welded parts (especially thick materials). These stresses decrease the dynamic load-carrying capacity and plastic deformation properties. Furthermore, they cause to develop brittle fracture in welded parts. To minimize these risks, it is suggested that the heat treatment (especially stress relief annealing) of welded parts should be done. Besides, heat treatments of welded parts can be done to increase the mechanic strengths, decrease the hydrogen content, prevent the crack formation in the weld region and decrease the hardness of HAZ [12].

The vibratory stress relief method is suggested as an alternative to expensive heat treatment methods in many cases/studies. In one of these studies, Munsi et al. [13], joined the 0,18 % carbon steel flat bars by using MIG welding method. They joined carbon steel flat bars in the form of single pass butt weld. After welding process, three different sample groups were prepared i.e. (a) as-welded, (b) heat treated, (c) vibratory treated. Then, they investigated the fatigue strengths these samples. In their study, welded samples were subjected to VSR process and fatigue test in the same system. The schematic representation of the system that was used by Munsi et al. is shown in Figure 3.

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Figure 3. The schematic representations of (a) Cantilever beam specimen; (b) VSR treatment and fatigue test setup used by Munsi et all. [13]

Munsi et all. applied sinusoidal periodic loads to welded samples with a vibrator that present in the VSR test system. The part which transmits the vibration to samples was designed not to cause an axial force on samples. Stress relieving method was done under ± 365 MPa dynamic stress. The frequency and process length of VSR treatment were chosen 25Hz and 5 min, respectively. The obtained results showed to Munsi et all. that the best fatigue strength results belong to the vibratory stress relieved samples [13]. However, Munsi et all. did not pay enough attention to the natural frequencies of samples in their detailed VSR study.

In an another study, Shankar [6] welded ASTM A-36 steel plates in the form of X butt weld. Welded plate was mounted on the table that was isolated from external forces/vibrations by using blowup rubber isolators. Shankar mounted a DC motor to the back side of table and obtained the required vibrations for stress relieving by using this motor. Figure 4 shows the schematic representation of the system that Shankar used for VSR.
Shankar mounted welded plates to table with bolts for transmitting the vibrations effectively to the welded plates. After Shankar adjusted the resonant frequency by manually, the vibrations were applied to samples for 20 minutes [6].

4. Results

Heat treatments are expensive and are not useful (due to the furnace capacity) for large scaled parts. For large scaled parts, heat treatment of welded area is done locally with an induction system or gas flame. However, these heat treatments decrease the surface and dimensional quality of parts and also, depending on the applied heat amount, change the metallurgical properties. Thus, mechanically stress relief methods are used to decrease the residual stresses of
these type parts. Vibratory stress relief method is one of the mechanically stress relieving methods that is applied to large scaled parts.

This method depends on the stress relieving basis that the vibrations are applied periodically between two limit forces to residual stress occurred work piece after welding. These applied vibrations cause displacement of atoms in the crystal lattice and/or plastic deformation. Thus, the residual stresses decrease. According to the frequencies of applied vibrations, this method is carried out in three different ways: Resonant-VSR (R-VSR), Sub-resonant VSR (SR-VSR), Sub-harmonic VSR (SH-VSR). The most effective stress-relieving method is R-VSR. The frequency of applied vibrations are adjusted to be the same with the natural frequency of work piece to decrease the residual stresses effectively (resonant frequency is obtained). After these applied vibrations, fatigue life is increased and macro defects are prevented such as crack formation.

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