THERMAL DIFFUSIVITY OF ZIRCONIA/IRON COMPOSITES

Muhammad W. Wildan

ABSTRACT

This paper presents thermal diffusivity of zirconia stabilized with 3 mol % yttria (known as 3Y-TZP) matrix composites reinforced with iron powder. Specimens with different iron contents (0%, 10%, and 25%) volume were produced by using pressureless sintering at 1450°C for 4 h in argon. This sintering condition resulted in almost fully dense samples. Thermal diffusivity of the samples was measured using Laser Flash Method (LFM). The results show that the thermal diffusivity of zirconia (3Y-TZP) at room temperature is 0.011 cm²/s and the thermal diffusivity of the composites increases with increasing iron content. However, for each composition, the thermal diffusivity decreases as the temperature increases, because the thermal diffusivity of both the matrix (zirconia) and the reinforcement (iron) decreases with increasing temperature.

Keywords: zirconia, iron, composites, thermal diffusivity

INTRODUCTION

It is well known that ceramic materials generally exhibit excellent properties such as high melting point, good high temperature strength, high Young's modulus, high hardness, good wear and corrosion resistance, relatively low coefficient thermal expansion (CTE) and thermal diffusivity, and low density. Ceramics, however, have limited applications in engineering due to their brittleness and low fracture toughness (Barsoum, 1997). Therefore much research in engineering ceramics is focused on improving mechanical properties such as fracture toughness and strength. In addition, there are two thermal properties that are important in ceramic materials viz. thermal expansion coefficient (CTE) and thermal diffusivity/conductivity. Low CTE and thermal diffusivity/conductivity in ceramics may give advantages and disadvantages. The low thermal conductivity allows ceramics to be used as insulation materials and the low CTE will give no significantly dimensional change when temperature increases or decreases. However, those properties could cause in lowering thermal shock resistance (TSR) of ceramics (Barsoum, 1997).

Incorporating ductile metal as a second phase into ceramic matrix has become a way to overcome such brittleness and increase fracture toughness since the ductile metal inclusion may reduce crack propagation (Geichard, et al. 1998). Generally ceramics and ductile metal have big different value in term of CTE and thermal diffusivity. The effect of the ductile metal reinforcement in ceramics matrix on those thermal properties therefore also needed to investigate. This research aims to investigate the effect of iron particles on thermal diffusivity of zirconia/iron composites. Moreover, this paper also presents the effect of temperature on thermal diffusivity in each composition.

Zirconia is an interesting ceramic material from the point of view of developing ceramic-metal composites because it has good mechanical properties and also its thermal expansion coefficient (10 x 10⁻⁶/°C) is close to that of metals, which enables development of zirconia-matrix composites reinforced with metal and minimizes the thermal stress during fabrication and use of zirconia-metal composites.

Several researchers have reported work in zirconia-metal composites. Works on nickel-zirconia ceramic metal composites used in SOFC (solid oxide fuel cell) have been reported in literature (Hu et al. 1998; Kondo et al., 1999). The increasing applications of zirconia as solid electrolyte and zirconia ceramic-metal composites is anodes in SOFC have opened up research in zirconia reinforced with metal (Midb, 1993). Stainless steel has also been reported as a reinforcement of zirconia ceramic composites (Wenqun et al., 1999). Considerable achievement have been reported by Nawa et al. (1996) regarding the simultaneous improvement of strength and fracture toughness of zirconia (3Y-TZP)/molybdenum nano-composites.

Zirconia and zirconia-containing ceramics are used widely in traditional (abrasives, refractories, foundry sand and floor) and engineering areas (Ruhle, 1997). A comprehensive survey of thermal diffusivity of dense polycrystalline zirconia ceramics has been reported by Hasselman et al. (1987) using a Laser Flash Method. The study included the effect of

1 Ir. Muhammad Wazie Wildan, M.Sc., Ph.D., Department of Mechanical Engineering, Gadjah Mada University

62 MEDIA TEKNIK No.3 Tahun XXVII Edisi Agustus 2005 No ISSN 0216-3012
FUNDAMENTAL

The thermal conductivity of ceramic matrix composites depends on the amount and arrangement of each constituent, and their individual thermal conductivity. Moreover, it is also sensitive to porosity, microcracks, and interfacial contact. From the rule of mixtures in terms of volume fractions, the thermal conductivity of a linear and inverse unidirectional composite can be described by the upper and lower bounds respectively, as follows (Warren, 1993):

a. Linear rule of mixture (upper bound) (Warren, 1993)

\[ k_u = v_m k_m + v_r k_r \]  \hspace{1cm} (1)

b. Inverse rule of mixture (lower bound) (Warren, 1993)

\[ k_l = \frac{v_m + v_r}{k_m k_r} \]  \hspace{1cm} (2)

More specifically, in particulate composites where spherical particles are isolated in a continuous matrix with a good thermal contact, the thermal conductivity of the composites can be approximated calculated using the Eucken model as follows (Kingery et al., 1976):

c. Eucken model (Kingery et al., 1976)

\[ k_e = k_m \left[ \frac{2v_r (1 - Q)}{(2Q + 1)} \right] \left[ \frac{1 - v_r (1 - Q)}{Q + 1} \right] \]  \hspace{1cm} (3)

where \( k \) is thermal conductivity, \( v \) is volume fraction, \( Q = k_m k_c \), \( m, r \) and \( c \) represent the matrix, the reinforcement, and the composite respectively.

Thermal diffusivity of composites can be calculated from the above equations if the heat capacity and density of the composites are known. In this case the heat capacity and density are not dependent on transport phenomena but dependent only on the amounts of each component (Warren, 1993), so they can be estimated simply (Hasselman, 1986 and Warren, 1993) using the following equations:

- Heat capacity \((C_p)\) of a composite:

\[ C_p = v_m C_m + v_r C_r \]  \hspace{1cm} (4)

- Density \((\rho)\) of a composite is:

\[ \rho = v_m \rho_m + v_r \rho_r \]  \hspace{1cm} (5)

The density of a material however, is not a constant value but depends on the temperature, due to thermal expansion. Therefore, the density of each component as a function of temperature should be taken into account. It can be estimated using the assumption that thermal expansion is isotropic, as follows (Hasselman, 1986):

\[ \rho = \rho_0 \left( \frac{1 + 3\alpha(T - T_0)}{\rho_0 \alpha} \right) \]  \hspace{1cm} (6)

where \( \rho \) is the density at temperature \( T \), \( \rho_0 \) is the density at room temperature \( T_0 \) and \( \alpha \) is the linear coefficient of thermal expansion (CTE).

Finally, the thermal diffusivity of the composites can be calculated using the following equation (Hasselman, 1986):

\[ \alpha = \frac{k_e}{\rho_0 C_p} \]  \hspace{1cm} (7)

The above equations will be used to analyze the thermal diffusivity of zirconia/iron composites below. The thermal diffusivity of samples was measured using the Laser Flash Method in argon atmosphere.

METODOLOGY

The materials used in this research are described in Table 1. The zirconia used was zirconia stabilized with 5.4 wt% \( Y_2O_3 \) grade of fine particle size and the metal is of standard reagent grade purity. The shape of iron particles is spherical as shown to Figure 1. Zirconia powder with the appropriate amount of the reinforcements (0%, 10% and 25% volume of iron) was placed into a plastic container and dry-mixed for 2 hours in a turbo-mixing machine. The mixture was then uni-axially compacted in a 15 mm diameter cylindrical steel die using a pressure of 30 MPa to produce green pellets. The samples were then pressureless sintered in a horizontal alumina tube furnace in argon atmosphere at 1450°C for 1 hour with a heating rate of 10°C/minute. The density was measured using Archimedes principle. The
microstructure and distribution of reinforcement particles were observed using optical microscope. Laser flash method (LFM) was used to measure thermal diffusivity. Samples of 15 mm diameter were used for thermal diffusivity measurement from room temperature up to 1000°C in argon atmosphere.

![SEM of iron powder](image)

**Figure 1. SEM of iron powder**

**Table 1. Material properties of zirconia and iron**

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>Particle size (μm)</th>
<th>Parity (%)</th>
<th>Other elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconia</td>
<td>5.90 (mean)</td>
<td>6-8 (mean)</td>
<td>99.0+</td>
<td>C, Si, P, S, B, F, O</td>
</tr>
<tr>
<td>Iron</td>
<td>7.87 (mean)</td>
<td>93.8</td>
<td></td>
<td>Al₂O₃</td>
</tr>
</tbody>
</table>

Note: all materials were produced of Goodfellow, UK.

Figure 2 shows the schematic of the Laser Flash Apparatus (LFA 427) system, which consists of four main components:

- Measuring unit with furnace, laser and infra red detector
- Controller for measuring unit
- Power supply for laser system
- Data acquisition system and computer

**RESULTS AND DISCUSSION**

The density of the composites containing 10% and 25% volume measured using Archimedes principle shows almost fully dense samples (the relative density is greater than 98%). Figures 3 and 4 show optical micrographs of zirconia matrix composites containing 10 vol% iron (Fe) and 25 vol% iron (Fe) respectively, sintered at 1450°C for 1 hour in argon gas. It can be seen in those figures that the density of the samples looks almost fully dense with very little porosity. The iron particles in both figures are also well distributed. Some particles that are close together join and form larger particles. It can be seen in the sample with 25 vol% Fe (Figure 4) that more iron particles are joined together as the distance between particles is smaller. At this condition where the iron particles are small (6 micron in diameter) and the distances between them are small, sintering process not only occurs in the matrix but also occurs in the reinforcement.

![Schematic of LFA 427 system](image)

**Figure 2. A schematic of LFA 427 system**

![Optical micrograph of (10 vol% Fe + zirconia) sintered at 1450°C for 1 hour in argon gas.](image)

**Figure 3. Optical micrograph of (10 vol% Fe + zirconia) sintered at 1450°C for 1 hour in argon gas.**

64 MEDIA TEKNIK No.3 Tahun XXVII Edisi Agustus 2005 No.ISSN 0216-3012
Distribution of particles in composites will influence the thermal diffusivity, because the total value of thermal diffusivity/ conductivity not only depends on the amount of each component but also depends on the degree to which the components are connected (Chiang, et al., 1997).

Figure 5 shows thermal diffusivity of zirconia/iron composites at room temperature as function iron content. The thermal diffusivity of the composites increases since the iron content increases as iron has higher thermal diffusivity (0.23 cm²/s) (Incropera and DeWitt, 1996) than zirconia (0.0197 cm²/s) (from this experiment). The models of thermal diffusivity of composites (linear rule of mixtures, inverse rule of mixtures and Eucken model) and the experimental data are presented. It can be seen in Figure 5 that the experimental data are in a good agreement with the Eucken model (Equation 3). The increase of thermal diffusivity in the composites is not only dependent on the amount of iron, but also dependent on the degree of connectivity between particles. As mentioned in the previous paragraph that the samples are almost fully dense (greater than 99% of theoretical density) and the iron particles are well embedded in the matrix resulting in good thermal contact between matrix and the reinforcement. Moreover from the microstructures (Figures 3 and 4), it can be seen that some iron particles clustered and formed into larger particles. From these, it can be concluded that the increase of thermal diffusivity of zirconia/iron composites which is not linear with increasing iron content is due to the higher degree of connectivity of iron particles at higher iron content. The getting bigger difference between the experimental data and the Eucken model for the composites containing iron more than 15 vol% may also be influenced by that phenomena.

Table 2 shows the thermal diffusivity of zirconia stabilized with 3 mol% yttria (3Y-TZ) as a function of temperature obtained from this experiment.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Thermal Diffusivity (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.01097</td>
</tr>
<tr>
<td>100</td>
<td>0.00796</td>
</tr>
<tr>
<td>300</td>
<td>0.00893</td>
</tr>
<tr>
<td>500</td>
<td>0.00843</td>
</tr>
<tr>
<td>600</td>
<td>0.00782</td>
</tr>
</tbody>
</table>

Figure 6 shows the effects of temperature and iron content on thermal diffusivity of zirconia/iron composites sintered at 1450°C for 1 hour in argon.

MEDIA TEKNIK No.3 Tahun XXVII Edisi Agustus 2005 No.ISSN 6216-3012 65
Figure 6 shows thermal diffusivity of the composites containing 10 vol% and 25 vol% of iron as a function of temperature. The estimation of thermal diffusivity of the composites using Eucken's model is also presented in this Figure. It is clearly seen that thermal diffusivity of both composites decreases with increasing temperature. This behavior is expected because the thermal diffusivity of each constituent also decreases with increasing temperature. From the experimental data, the thermal diffusivity of zirconia decreases from 0.01097 cm²/s at room temperature to 0.00767 cm²/s at 600°C (see Table 2), while the thermal diffusivity of iron decreases from 0.230 cm²/s (at room temperature) to 0.0454 cm²/s (at 700°C) (Incropera and DeWitt, 1996). It is also expected that the composites containing 25 vol% iron have higher thermal diffusivity than that of 10 vol% iron at the temperature range as shown in Figure 6. The experimental results of composites with both iron contents are in good agreement with the model given by Eucken model.

The data required for calculation of Eucken model were taken from the experiment and literature. Data for thermal diffusivity (20°C – 600°C) and thermal expansion coefficient of zirconia (20°C – 1000°C) were available from experiment, while the heat capacity (from 20°C to 600°C) was obtained from data given by Hasselman et al. (1987). The coefficient of thermal expansion (CTE) of zirconia is 10 x 10⁻⁶°C⁻¹ (at 20°C – 1000°C) (Widan, 2000). The data of thermal diffusivity and heat capacity at higher temperature were extrapolated from those available data. The data of iron was taken from literature given by Smithells and Eranding (1976) and Incropera and DeWitt (1996).

CONCLUSION

At room temperature, the thermal diffusivity of zirconia/iron composites increases with increasing iron content due to thermal diffusivity of chromium is greater than that of zirconia. The thermal diffusivity of zirconia/iron composites decreases with increasing temperature due to both thermal diffusivities of zirconia and iron decreases with increasing temperature.

ACKNOWLEDGEMENT

The author would like to thank Professor Alan Hendry and Dr. HJ Edtress for their remarkable help and discussion during this research.

REFERENCES


