Ceramic/Metal Composites with Positive Temperature Dependence of Thermal Conductivity

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Abstract. Most materials show decreasing thermal conductivity with increasing temperature, but an opposite temperature dependence of thermal conductivity is required for some industrial applications. The present work was conducted with a motivation to develop composite materials with a positive temperature dependence of thermal conductivity. ZrO2/ stainless steel powders (304L) composite, with 3% stearic acid, was prepared by normal sintering under the protecting of Ar after mixing by mechanical ball milling technique. With the 304L content increasing from 10% to 20%, the thermal conductivity values increased. For all samples, the thermal conductivity in the temperature range of room temperature to 700 °C decreased with temperature below 300 °C, and then began to increase. The increasing thermal conductivity of the composites (within the high temperature range was attributed to the difference of the thermal conductivity and thermal expansion coefficient between ZrO2 ceramic and 304L stainless steel powders. Two simple models were also used to estimate the thermal conductivity of the composites, which were in good agreement with the experiment results.

1. Introduction
Thermal conductivity is an important transport property of materials, and most materials show decreasing thermal conductivity with increasing temperature. Materials are used in different fields according to the characteristic of thermal conductivity, and the famous-known thermal barrier coating (TBC) materials are representative cases. TBC are used to protect and insulate hot-section metal components, can result in significant temperature reduction at the metal surface, thereby the durability and efficiency of the metal component could be improved [1-3]. The most commonly used TBC is Y2O3-stabilized ZrO2 ceramic [4-6]. However, there is a growing demand for higher fuel efficiency and longer durability, providing a great motivation for developing a new material with thermal conductivity controlled to show positive temperature dependence. That is, at low temperature, the new material has lower thermal conductivity, acting as heat insulating material. While at high temperature, it has higher thermal conductivity and the heat will be diffused more quickly.

In this study, a Ceramic/Metal composite was developed, using the difference of the thermal conductivity and thermal expansion coefficient between ceramics and metals. Voids exist in the interior of the composite at low temperature as shown in Figure 1(a). The heat energy could not shed
easily at low temperature because of the lower thermal conductivity of ceramic and the existence of voids. At higher temperature, the voids will be filled up due to the high thermal expansion coefficient of metals, as shown in Figure 1 (b). Accompanied by the disappearing of voids gradually, the thermal conductivity of the composite becomes increased with temperature, which could be also attributed to the high thermal conductivity of metals. This design concept will be then confirmed by the following calculate models and experiment two ways.

Figure 1 Diagrammatic sketch of Ceramic/Metal composite: (a) at low temperature; (b) at high temperature

2. Experiment process

The commercial elemental micro-powders of ZrO$_2$ (3mol. % Y$_2$O$_3$) and stainless steel powders (304L) with near-spherical were used as starting materials. Firstly, the 304L powders with 3% stearic acid were mixed in a stainless steel jar with stainless steel balls at 300 rpm for 24 h in a planetary ball mill, and the process was under the protection of Ar (99.9%) atmosphere to prevent the powders from oxidation. Next, ZrO$_2$ and the 304L powders with stearic acid mixed by hand according to different ratio, and the resultant powders were compacted into disk-shaped sample with ø15 mm in diameter and ~2 mm in thickness, followed by isostatic cool pressing at 200 MPa for 3 min. Then, the samples were sintering at 1100 $^\circ$C for 4 h under the Ar atmosphere. Finally, the samples ZrO$_2$+$x$% 304L ($x=0, 10, 15, 20$) were prepared.

The phase structures of all samples were examined by X-ray diffraction (XRD) using Cu Kα radiation (D/max-2500). The thermal conductivity ($\kappa$) was calculated using the equation $\kappa=\lambda C_p d$, where $\lambda$ is the thermal diffusivity, $C_p$ is the heat capacity, and $d$ is bulk density of the sample. The thermal diffusivity was measured by a laser flash technique (TC-9000, Ulvac-Riko, Japan) in Ar atmosphere in the temperature range from room temperature to 800 $^\circ$C, the heat capacity was measured using differential scanning calorimetry (DSC-60) and the bulk density was obtained by the Archimedes method.

3. Results and discussion

3.1. Thermal conductivity: model analysis

Here, two simple models were used to estimate the thermal conductivity of composite we designed at low and high temperatures, respectively. In the models, the dispersion is assumed as spherical and the volume fraction of pores is not considered.

At low temperatures, the composite is composed of continuous matrix ceramic phase and the discontinuous dispersed metal phase, and the voids exist. Therefore, the effective thermal conductivity of the composite $K_{eff}$ depends on not only the volume fraction of the dispersed phase $V_d$ but also the dispersion size $a$, and the thermal barrier resistance of the voids $h_v$ is also considered, here $h_v=10^8$W.m$^{-2}$.K$^{-1}$ was used [7]. According to the Equation (1) [8]:

$$K_{eff} = \frac{1}{V_d} \left( \frac{K_1}{V_1} + \frac{K_2}{V_2} \right)$$
At higher temperatures, the voids are filled up because of the thermal expansion. And $K_{\text{eff}}$ at higher temperatures is just a function of $V_d$. It can be expressed as Equation (2) [9]:

$$
K_{\text{eff}} = \frac{[2(K_d - K_m - 1)V_d + K_d + 2]}{[1 - (K_d + K_m)V_d + K_d + 2]} + 2
$$  \tag{1}

For spherical dispersion:

$$
\frac{(dT / dx)_{d}}{(dT / dx)_{m}} = \frac{3K_m}{K_d + K_m}
$$  \tag{3}

Substituting Equation (3) into Equation (2) gives:

$$
K_{\text{eff}} = \frac{K_m V_m (dT / dx)_{m} + K_d V_d (dT / dx)_{d}}{V_m (dT / dx)_{m} + V_d (dT / dx)_{d}}
$$

Substituting Equation (3) into Equation (2) gives:

$$
K_{\text{eff}} = \frac{K_m V_m K_d + 2K^2_m V_m + 3K_m K_d V_d}{V_m K_d + 2V_m K_d + 3V_d K_m}
$$  \tag{4}

Where, $K_{\text{eff}}/K_m$; the effective thermal conductivity of the composite/ the matrix / the dispersion; $V_m$, $V_d$: volume fraction of the matrix / the dispersion; $a$: the radium of the spherical dispersion;

| $V_d$ | a ($\mu$m) | $K_{\text{low temperature}}$ | $K_{\text{high temperature}}$ |
|------|-----------|-----------------------------|-----------------------------|
| 20%  | 2         | 4.7                         | 5.6                         |
|      | 1         | 4.2                         | 5.6                         |
|      | 0.5       | 3.7                         | 5.4                         |
|      | 2         | 5.4                         |                             |
| 30%  | 1         | 4.6                         | 7.1                         |
|      | 0.5       | 3.8                         |                             |

The thermal conductivities of the composite with different $V_d$ and $a$ at low and high temperatures are calculated using function (1) and (4), respectively. From the calculating results shown in Table 1, It is found that the Ceramic/Metal composite we designed has low thermal conductivity at low temperatures and higher thermal conductivity at high temperatures as we expect, indicating our design concept is feasible in theoretically. At the same time, the calculated results also indicate that the thermal conductivity of the composite increases with the volume fracture of dispersion $V_d$.

### 3.2. Thermal conductivity: experimental data

The corresponding experiment was also performed to investigate the temperature dependence of the composite. Figure 2 shows the X-ray diffraction patterns of samples ZrO$_2$+x% 304L (x=0, 10, 15, 20) with 3% stearic acid. The patterns show that the main phase of ZrO$_2$ sintered at 1100 °C for 4 h is t-ZrO$_2$, and little m-ZrO$_2$ phase is also found. For the samples with 304L, 304L is also found with the intensive peaks of t-ZrO$_2$ and m-ZrO$_2$. There is no other phase is detected, indicating that no reaction.
occurs between ZrO$_2$ and 304L powders, and the stearic acid is volatilized during sintering process. Volatility of the stearic acid forms the voids in the composites.

Temperature dependence of the thermal diffusivity for all samples is shown in Figure 3(a). The thermal diffusivity of all samples with 304L decreases with temperature and gets the minimum value below 500 °C, then begins to increase. Meanwhile, with the increasing of 304L content, the values increase, and the corresponding temperature decreases from 500 °C to 400 °C. The measured density values of the samples with 10%, 15% and 20% 304L are 3.501, 3.634 and 3.802 g.cm$^{-3}$, respectively and theoretical density value of t-ZrO$_2$ is 5.9 g.cm$^{-3}$. The density of the composites increases with 304L content increasing.

In order to calculate the thermal conductivity of the Ceramic/Metal composite, and investigate the effect of different content of 304L on the thermal conductivity of the composite, the specific heat of ZrO$_2$+x% 304L (x=10, 20) are measured. With temperature increasing, the specific heat of the two samples both decreases firstly, and then increases as shown in Figure 3(b). And ZrO$_2$+10% 304L has relatively high specific heat when the temperature above 200°C.

Temperature dependence of thermal conductivity for ZrO$_2$+x% 304L (x=10, 20) with 3% stearic acid is shown in Figure 4, together with the model analysis results. For comparison, the thermal
conductivity of ZrO₂ from reference [10] is also listed. The thermal conductivity of ZrO₂ is almost independence of temperature, and with temperature increasing, the thermal conductivity of the two composites both decreases below 300 °C, and then increases. And ZrO₂+20% 304L possess a relatively higher thermal conductivity. So it can be concluded that the thermal conductivity of the composite obtained according to our design concept increases with temperature and volume fraction of 304L at higher temperature, which is also consistent well with the model analysis results.

The thermal conductivity of the composite increased with temperature at high temperatures is attributed to the difference of the thermal conductivity and thermal expansion coefficient between ZrO₂ ceramic and 304L stainless steel powders. At low temperatures, the voids originating from the volatilizing of stearic acid in the composite can bring about the lower thermal conductivity of the composite. At higher temperatures, interior structure of the composite will be changed. The voids are filled up and the composite becomes more density, so the thermal conductivity also becomes higher.

Figure 4 Temperature dependence of thermal conductivity for ZrO₂+x% 304L (x=10, 20) with 3% stearic acid and ZrO₂ [10]

4. Conclusion

A composite with positive temperature dependence was designed, according to the difference of thermal conductivity and thermal expansion coefficient between ceramic and metal. ZrO₂/304L composite had been prepared by mechanical mixing and normal sintering, and simple models were also used to estimate the thermal conductivity of composite. Excitingly, both calculated models used here and the experiment results supported our design concept. The thermal conductivity of the composites increased with temperature at higher temperatures, as well as the volume fraction of 304L powders.

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