

Microstructure and its influence on thermal and electrical conductivity of ZrO_2 –Ag composites

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Abstract

The effects of Ag content on the thermal diffusivity and conductivity of the ZrO_2 –Ag composites were investigated. Experimental results showed a significant increase in thermal conductivity at $\text{Ag} \geq \sim 10$ vol.%, which was primarily due to the formation of continuous Ag phase and a direct evidence was confirmed by a precipitous drop in electrical resistivity. The formation of interconnected Ag phase made the thermal conductivity of the ZrO_2 –Ag composites far beyond theoretical expectation.

Keywords: ZrO_2 –Ag composite; Ceramic matrix composite; Thermal conductivity; Electrical resistivity

1. Introduction

Partially stabilized zirconia has long been recognized as a toughened ceramic relying mainly on its tetragonal-to-monoclinic phase transformation [1,2]. Its low thermal conductivity together with excellent corrosion resistance and chemical stability make the zirconia ceramic a leading thermal barrier material [3].

In zirconia, heat is primarily transferred by phonon. Having three kinds of crystal modifications, i.e. cubic, tetragonal, and monoclinic, zirconia exhibits thermal conduction behavior in different ways, such as cubic zirconia, illustrated as a temperature-independent character. Garvie [4] indicated that such a character reflects a defect-dominant mechanism (e.g. lattice vacancy). Hasselman et al. [3] found that each modification has its own contribution to the thermal conductivity and they obtained thermal conductivity of single-phase ZrO_2 by means of Bruggeman's variable dispersion relation [5].

Most two-phase composites contain a residual pore phase that has no contribution to the thermal conductivity of the composite, i.e. $K_{\text{pore}} = 0$. This pore phase is usually not one of the major considerations in numerous composite theories (the pore phase was considered only by serving it as a zero-conductivity inclusion), such as those proposed by Maxwell [6], Hasselman et al. [7], Bruggeman [5], and Hatta et al. [8]. In addition to the pore phase, Hasselman et al. [7] have

taken interfacial resistance (denoted as $1/h$, where h is the heat transfer coefficient) into consideration to account for the thermal conductivity of a two-phase composite and in general, received a good correlation in many composite materials. However, the Hasselman–Johnson expression is usually limited to composite materials with a dilute second phase, e.g. 5% in volume, and will be discussed in detail in forthcoming analysis.

The incorporation of metal inclusion has been known to enhance the fracture toughness of ceramic materials which are inherently brittle in nature [9,10]. Among those literatures, incorporation of metal into zirconia matrix has not yet been investigated until a recent work by Tuan and Liu [11] who has shown that an increase in fracture toughness can be reached by the addition of metal, such as silver. The purpose of this investigation is thus intended to continue the work of Tuan on further analysis of some transporting properties of the zirconia–silver composites. The thermal conductivity of the composite was investigated in terms of microstructural evolution and an expression was proposed by modifying the Hasselman–Johnson theory to predict the composite conductivity by taking the residual pore phase into account. Electrical resistivity of the composite was also measured.

2. Experimental procedures

Reagent-grade ZrO_2 powder (contained 3 mol% Y_2O_3 , Sumitomo Chem. Co. Ltd., Japan) and AgNO_3 powder

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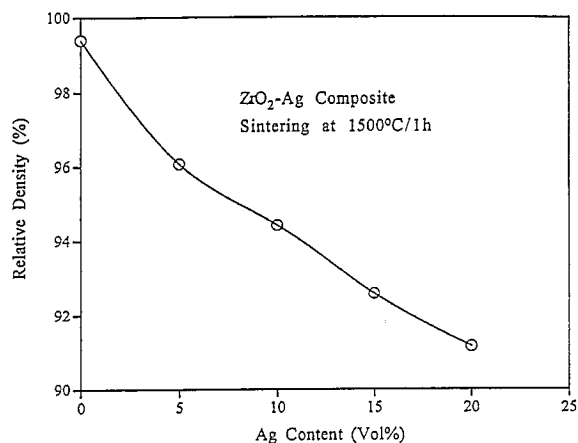


Fig. 1. Relative density of ZrO_2 -Ag composite decreases with Ag content.

(Johnson Matthey Co., UK) were mixed by ball-milling for 2 h. The mixture was reduction-treated in hydrogen atmosphere at 500°C for 3 h, followed by die-pressing under a uniaxial pressure of 50 MPa. The as-pressed compacts were sintered at 1500°C for 1 h in air. Phase distribution of ZrO_2 matrix phase was identified by an X-ray diffractometry before and after machining for subsequent thermal conductivity determination. The density of the composite was determined by a water displacement method. The obtained density was divided by a corresponding theoretical density, which is

defined as 'relative density' in this article. The electrical resistivity of the composite was measured at ambient temperature using a d.c. two-probe technique. Thermal conduction behavior of the composites were measured by a laser-flash technique with specimens in circular disk with dimensions of 10 mm in diameter and ~ 1.6 mm in thickness. The procedure for the measurement and determination of the thermal conductivity has been outlined in detail elsewhere [12].

3. Results and discussion

3.1. Microstructure evolution

The ZrO_2 ceramic with grain size of approximately $0.5\ \mu\text{m}$ was obtained at 1500°C . This temperature was then considered as an optimal sintering temperature pertinent to fabricate the ZrO_2 -Ag composite in this investigation. The relative density of the composites reduced appreciably by further addition of metal-silver as depicted in Fig. 1. This decrease in relative density with increasing content of Ag is probably owing to the evaporation of the residual nitrate which was left during the reduction treatment at 500°C .

The microstructure of the composite showed that, when Ag was above ~ 10 vol.%, the Ag inclusion demonstrated

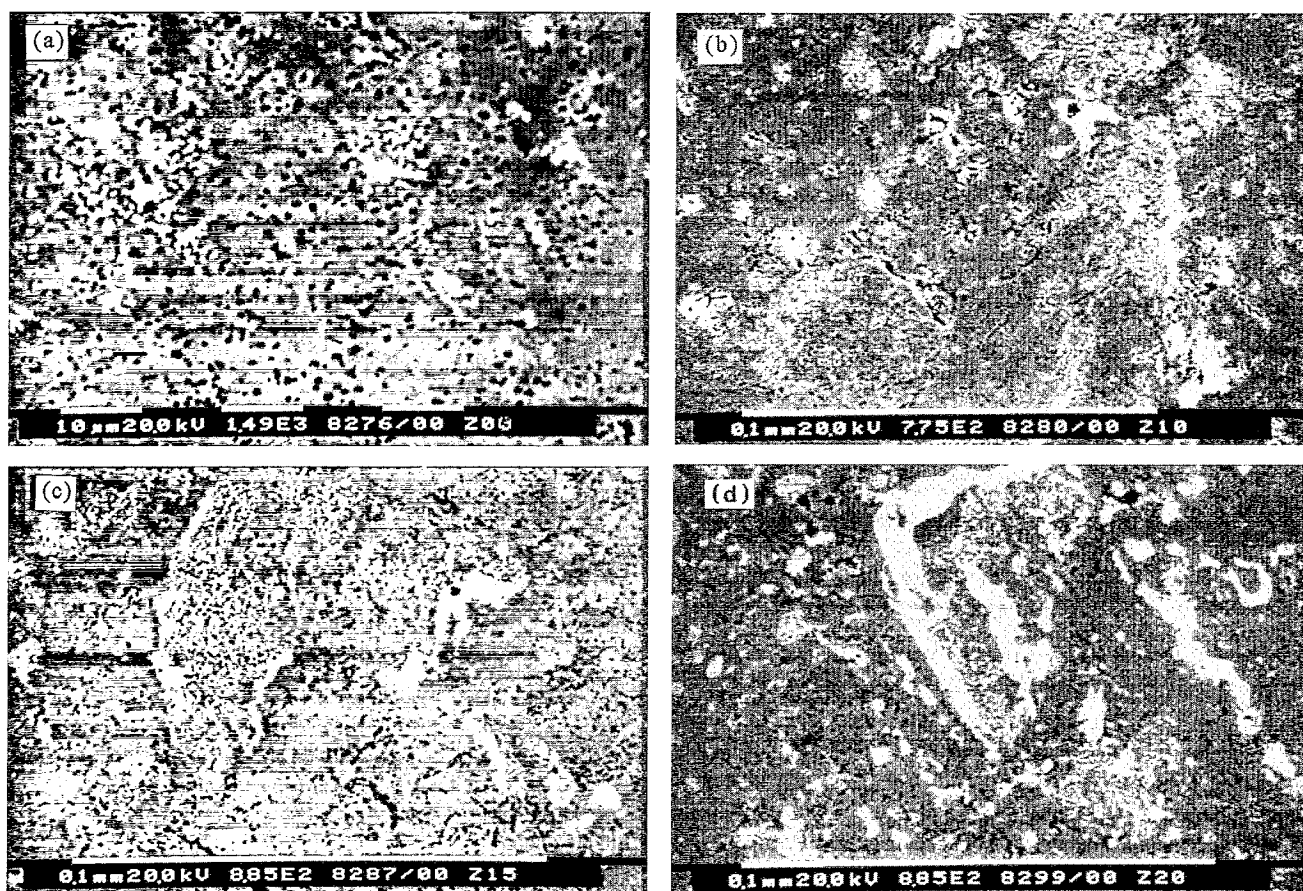


Fig. 2. Backscatter image photos of polished surface of the ZrO_2 -Ag composites with (a) 5%, (b) 10%, (c) 15% and (d) 20% Ag.

bimodal distribution, part of it appeared to percolate into a continuous network and the other part of the Ag phase was distributed sporadically, as shown in Fig. 2(a)–(d) where the bright areas denote the Ag phase and those in gray are the ZrO_2 phase. The wide-spread dark regions are owing to improper sample preparation. The formation of the continuous Ag phase suggested a liquid phase sintering (since Ag has a melting point $\sim 960^\circ\text{C}$) resulting in a slight increase in matrix grain size, i.e. from $\sim 0.5\ \mu\text{m}$ at 0% to $\sim 1\ \mu\text{m}$ at 20% Ag content. No exaggerated ZrO_2 grain growth was found. However, the presence of pore phase together with the elongate or rod-like Ag grains, both which behave as stress risers, deteriorates the mechanical properties, i.e. fracture strength and toughness, of the composite [13].

It is believed that internal microfracture would occur in the composite, as that observed in the Al_2O_3 -Ag system [14], when the size and/or the concentration of Ag inclusion exceeds some critical value. Theoretical calculation according to the analysis of Selsing [15] for the critical inclusion size (R_c) of the composite is approximately $4\sim 5\ \mu\text{m}$ (calculation based on $\Delta T = 500^\circ\text{C}$, $\Delta\alpha = 14.2 \times 10^{-6}\ ^\circ\text{C}$, $E_{\text{Ag}} = 71\ \text{GPa}$, $\nu_{\text{Ag}} = 0.37$, $E_{\text{ZrO}_2} = 240\ \text{GPa}$, $\nu_{\text{ZrO}_2} = 0.337$) which is larger than the measured average value, $3.1\ \mu\text{m}$ (obtained by a linear intercept technique on a polish surface), this result suggests the absence of internal microfracture. However, with further increasing Ag, the inclusion size distribution became much more complicated (Fig. 2(b)–(d)) and the inclusion size can hardly be measured in precision. As a matter of fact, since the critical inclusion size decreases with increasing inclusion content [16,17], it can thus be ascertained that internal microfracture could be present within the composite, particularly when the content of Ag is greater than $\sim 10\%$ because some of the inclusions exhibited a size as large as a few tens of micrometers (Fig. 2).

3.2. Thermal conductivity and electrical resistivity

Polycrystalline zirconia, which is conventionally used as a leading thermal barrier material, possesses three different crystallographic structures, each of them exhibiting different thermal conduction behavior [3]. Prior to machining for thermal conduction measurement, the ZrO_2 has a tetragonal modification regardless of the effect of pore phase. This finding is similar to that observed by Swain et al. [18] who indicated that the ratio of the tetragonal-to-monoclinic phase content decreases strongly with increasing porosity. This observation suggested that the mechanical stresses owing to phase transformation of ZrO_2 is constrained by the surrounding metal phase. However, after machining, the ZrO_2 phase becomes a mixture of tetragonal and monoclinic modifications with proportions varying with inclusion content (Table 1). Therefore, this tetragonal-to-monoclinic phase transformation is primarily stress-induced.

Fig. 3 shows the temperature dependence of the thermal diffusivity of the composites for various Ag contents. The diffusivity increased considerably when Ag approached 10

Table 1

Phase distribution (wt.%) of ZrO_2 in ZrO_2 -Ag composite before and after machining, and after thermal conductivity measurement (where t denotes tetragonal and m is monoclinic modification)

Ag Content (vol.%)	Before machining		After machining		After measurement	
	t	m	t	m	t	m
0	100	0	95.87	4.13	85.9	14.1
5	100	0	92.2	7.80	76.9	23.1
10	100	0	81.78	18.22	55.8	44.2
15	100	0	75.2	24.8	39.2	60.8
20	100	0	73.15	26.85	37.9	62.1

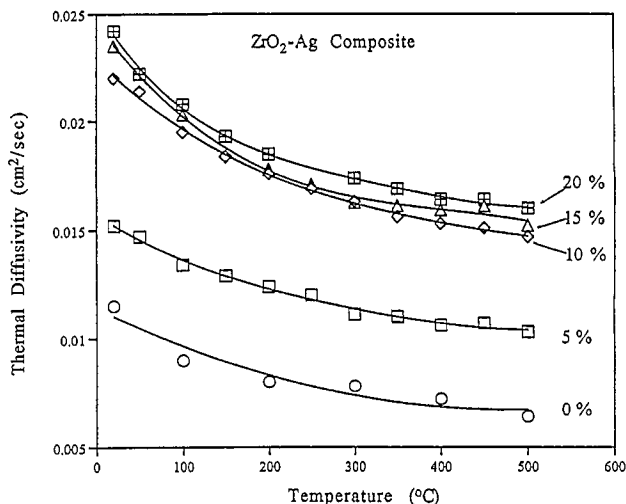


Fig. 3. Temperature-dependence of thermal diffusivity of ZrO_2 -Ag composite.

vol.% and this increase in diffusivity became less pronounced by increasing the Ag further to 20 vol.%. The considerable increase in diffusivity is explainable in terms of microstructure evolution. The Ag phase is likely to interconnect into a continuous network when the content of Ag is larger than $\sim 10\%$. This interconnected Ag network may provide a more efficient way for heat to transport across the composite by electron, and therefore enhances the overall thermal diffusivity/conductivity of the composite. Figs. 4 and 5 show the thermal conductivity and electrical resistivity of the composite, respectively. The precipitous drop in resistivity at ~ 10 vol.% Ag provided further evidence of the formation of a continuous Ag network, similar to that observed by Aharoni in a metal/polymer composite [19].

Hasselman and Johnson [7] modified Maxwell's well-known formula by taking the interfacial resistance factor ($1/h$) into account and gave:

$$K_c = K_m \frac{\frac{K_d}{K_m}(1 + 2\nu_d) + 2\left(\frac{K_d}{ha} + 1\right)(1 - \nu_d)}{\frac{K_d}{K_m}(1 - \nu_d) + \left(\frac{K_d}{ha} + 1\right)(2 + \nu_d)} \quad (1)$$

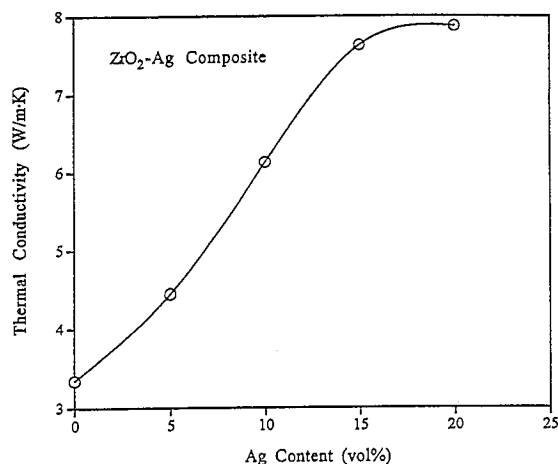


Fig. 4. Thermal conductivity of ZrO_2 -Ag composite as a function of Ag volume fraction.

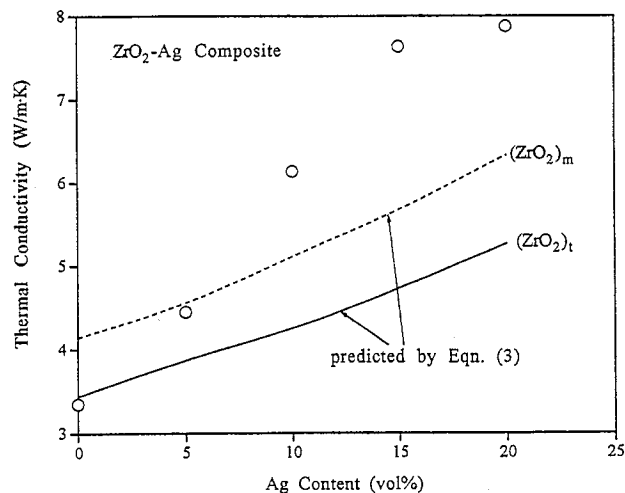


Fig. 6. Theoretical prediction of thermal conductivity of ZrO_2 -Ag composite with an upper bound curve, $(\text{ZrO}_2)_m$, and a lower bound curve, $(\text{ZrO}_2)_t$, in comparison with the measured values (open circle).

volume fraction without causing considerable error in quantitative estimation.

$$K_c = K_m \frac{2(1-v_p)}{2+v_p} \frac{\frac{K_d}{K_m}(1+2v_d) + 2\left(\frac{K_d}{ha} + 1\right)(1-v_d)}{\frac{K_d}{K_m}(1-v_d) + \left(\frac{K_d}{ha} + 1\right)(2+v_d)} \quad (3)$$

To illustrate the validity of Eq. (3), a number of parameters, particularly the conductivity of ZrO_2 , have to be determined. Since the matrix phase is a mixture of both crystal modifications, i.e. tetragonal and monoclinic, an upper bound is assumed to be of pure monoclinic phase with conductivity of $4.2 \text{ W m}^{-1} \text{ K}^{-1}$ and a lower bound is tetragonal ZrO_2 having a conductivity of $3.5 \text{ W m}^{-1} \text{ K}^{-1}$, for Y_2O_3 -containing ZrO_2 [3]. By substituting $K_d = 410 \text{ W m}^{-1} \text{ K}^{-1}$ for metal-silver and the volume fraction of the pore phase (v_p) and inclusion phase (v_d) into Eq. (3), Fig. 6 shows the resulting curves of both bounds and the measured conductivity values of the composite (open circle). As illustrated, the measured conductivities agree well with those predicted by Eq. (3) when $\text{Ag} \leq 5 \text{ vol.}\%$, suggesting the validity of Eq. (3). However, significant enhancement by 20–50% in composite conductivity as compared with those predicted values from both bounds was observed when $\text{Ag} \geq 10\%$. Since the porosity for the composites with $\text{Ag} \geq 10\%$ is in the range of about 5–8 vol.%, such large deviation in between the measured and predicted values at $\text{Ag} \geq 10\%$ cannot simply be considered to be a major handicap of the predictability of Eq. (3), and in fact is primarily ascribed to the microstructural evolution, i.e. formation of a continuous silver phase (see Fig. 5 for further verification), a microstructure that is beyond the scope of the validity of Maxwell's hypothesis.

4. Conclusions

The thermal conductivity and electrical resistivity of ZrO_2 -Ag composites demonstrate a strong dependence on micro-

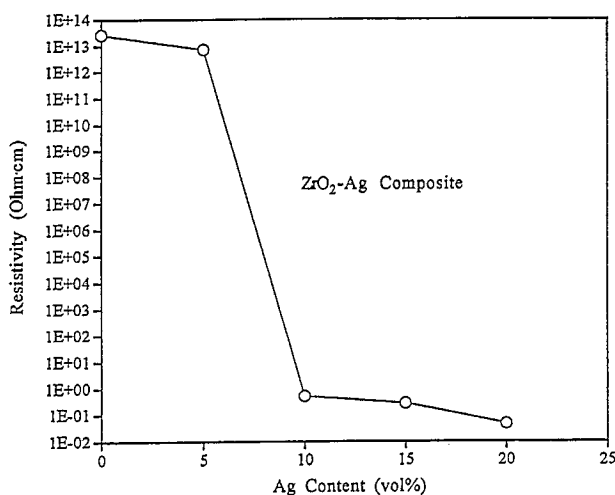


Fig. 5. Resistivity as a function of Ag volume fraction measured at room temperature.

where K is thermal conductivity, a is inclusion size, v is the volume fraction of inclusion phase, and the subscripts m , d , and c denote matrix, inclusion and composite phases, respectively. Strictly speaking, Eq. (1) is valid only for dilute inclusion phase, e.g. 5% in volume. In practice, pore phase is the most frequently observed inclusion in composite materials and is frequently a strong barrier to thermal conduction. If one considered that materials contain a minor second-phase inclusion having a zero conductivity, i.e. pore phase, Eq. (1) becomes:

$$(K_m)_p = K_m \frac{2(1-v_p)}{2+v_p} \quad (2)$$

where $(K_m)_p$ represents the conductivity of matrix phase containing v_p volume fraction of residual pore phase. By plugging Eq. (1) into Eq. (2), a modified expression of Eq. (3) results, which demonstrates both the second phase and the residual pore phase on influencing the composite conductivity. Such an incorporation between Eqs. (1) and (2) is hypothesized to be logically allowable for small porosity

structure of the composite. A modified expression was proposed, based on the Hasselman–Johnson theory, by considering the residual pore phase to predict the thermal conductivity of the composite; however, the prediction failed when the Ag content was greater than about 5 vol.%. Such an unpredictable thermal conductivity was assumed to be caused by the formation of a continuous metal–Ag network, as further evidenced by the electrical resistivity test.

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