

Toughening alumina with silver and zirconia inclusions

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Abstract

Both silver and zirconia inclusions are added into an alumina matrix, the strength and toughness of the composites are determined. The toughening agents prohibit the grain growth of the matrix, the strength of alumina is, therefore, enhanced. The addition of two toughening agents also enhances the toughness of alumina. The presence of Ag inclusions raises the transformation ability of ZrO_2 ; however, the toughness increase of the Al_2O_3 – ZrO_2 –Ag composites is slightly lower than the sum of the toughness increase of Al_2O_3 – ZrO_2 and of Al_2O_3 –Ag composites. The present study demonstrates that the toughening effects contributed by a transformation toughening agent and a ductile toughening agent can interact with each other; nevertheless, such interaction depends strongly on the microstructure of the composites. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ag; Al_2O_3 ; Composites; Strength; Toughness and toughening; ZrO_2

1. Introduction

The applications of ceramics as engineering components are often limited by their brittleness. To improve the toughness of ceramics is, therefore, a challenging task for most ceramists. The addition of second-phase inclusions that influence the propagation of cracks has been one much-studied approach. Among the second-phase inclusions studied, zirconia particles,^{1,2} silicon carbide whiskers^{3,4} and metallic particles^{5,6} have received great attention. The presence of silicon carbide whiskers can bridge the crack surfaces and/or deflect the crack.⁴ However, the health hazard⁷ induced by exposing to whiskers prohibits their use. The presence of metallic inclusions can also bridge the flaws by the ductile phase in the wake zone behind the crack tip.^{5,6}

The phase transformation of zirconia can induce stresses to prohibit the opening of crack surfaces.^{1,2} The toughness of a zirconia-toughened composite, $K_{IC,c}$, is composed of matrix toughness, $K_{IC,matrix}$, and a toughness enhancement, ΔK_{IC} , attributed to the phase transformation as

$$K_{IC,c} = K_{IC,matrix} + \Delta K_{IC} \quad (1)$$

The phase transformation of zirconia mainly takes place in a region, process zone, near an advancing crack, where the constraint applied by the rigid matrix is diminished. The toughness enhancement is thus a function of zone size as,⁸

$$\Delta K_{IC} = AF_t E_c \varepsilon (r_c)^{1/2} \quad (2)$$

A , F_t , E_c , ε and r_c in the above equation are a stress-related constant, the volume fraction of transformable zirconia, the elastic modulus of composite, the strain induced by phase transformation and the half of maximum width of process zone respectively. The process zone width is proportional to the matrix toughness as⁸

$$r_c = B(K_{IC,matrix}/\sigma_t)^2 \quad (3)$$

B is also a stress-related constant, σ_t the critical stress required for zirconia to transform from t -phase to m -phase. Eqs. (1)–(3) can be combined into one equation as

$$K_{IC,c} = K_{IC,matrix} + C * E_c * F_t * K_{IC,matrix} \quad (4)$$

C is a constant.

The above equation implies that the toughness of a ceramic can be significantly increased by choosing a toughened matrix. The toughened matrix can be a composite; therefore, the toughness of ceramics can be significantly enhanced through the addition of two toughening agents

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simultaneously (one toughening agent has to be t-ZrO₂). Becher and Tieggs provided experimental evidences to demonstrate that the toughness increase of the mullite containing both SiC whiskers and TZP particles can be higher than the sum of the toughness increase of the mullite containing SiC whiskers and of the mullite containing TZP particles.⁹ They claimed that the so-called synergy effect* can be observed for the composites containing two toughening agents. The synergy effect was also found in the works of Claussen and Petzow,¹⁰ Jang et al.,¹¹ Chen and Tuan¹² on alumina matrix composites, and of Hong et al.¹³ on mullite matrix composites. However, the experimental results from other groups showed different results. The results from Claussen and Petzow,¹⁰ Ruh et al.¹⁴ on mullite matrix composite indicated an additive effect; namely, the toughness of the composite containing two toughening agents is the same as the sum of the toughness increase of the composites containing one toughening agent. In any case, these studies all demonstrated that the toughness of ceramics can be enhanced by adding two toughening agents.

A recent study showed that the toughness of alumina can be enhanced by adding both Ag inclusions and TZP agglomerates.¹⁵ However, the toughness increase of the composite is lower than the sum of the toughness increase of the composite containing only Ag and only TZP agglomerates. The shrinkage of TZP agglomerates is prior to the densification of the Al₂O₃ matrix, the Ag melt was thus sucked into the shrinking TZP agglomerates during sintering. In their composites, silver inclusions are therefore embedded in the zirconia agglomerates. The phase transformation of zirconia did take place; however, the transformation stresses are absorbed by the nearby silver particles.¹⁵ Therefore, neither the synergy nor additive effect was observed in their study. The presence of TZP agglomerate affects not only the toughening behaviour² but also the interactions between the toughening agents. In the present study, TZP particles are used instead; furthermore, care was taken to disperse the TZP particles into alumina matrix to avoid the formation of zirconia agglomerates. The mechanical properties of the Al₂O₃-ZrO₂-Ag composites are determined, the toughening behaviour of the composites is investigated.

2. Experimental procedures

Alumina (TM-DR, Taimei Chem. Co. Ltd., Tokyo, Japan), silver oxide (Ag₂O, Johnson Matthey Co.,

U.K.) and zirconia (TZP, ZrO₂ + 3 mol% Y₂O₃, Hanwha Ceramics Co., Australia) powders were ball milled together in ethyl alcohol for 24 h. The grinding media used were zirconia balls. The slurry of the powder mixtures was dried with a rotary evaporator. The dried lumps were crushed and passed through a plastic sieve. Powder compacts with dimensions of 7×6×50 mm were formed by uniaxially pressing at 44 MPa. The sintering was carried out in a box furnace at 1600°C for 1 h in air. Silver inclusions resulted from the decomposition of Ag₂O during the heating stage.⁶ The heating rate and cooling rate were 5°C/min. The Al₂O₃-ZrO₂ and Al₂O₃-Ag specimens, for comparison reason, were also prepared with the same techniques. Some discs, 2.54 cm in diameter, were prepared for the measurement of elastic modulus with an ultrasonic technique.

The sintered specimens were machined longitudinally with a 325 grit resin-bonded diamond wheel at a cutting depth of 5 µm/pass. The final dimensions of the specimens were 3×4×36 mm. The strength of the specimens was determined by 4-point bending at ambient, room-temperature conditions. The upper and lower spans were 10 mm and 30 mm, respectively. The rate of loading was 0.5 mm/min. The fracture toughness was determined by the single-edge-notched-beam (SENB) technique. The notch was generated by cutting with a diamond saw. The width of the notch was around 0.3 mm.

Phase identification of sintered and machined specimens was performed by X-ray diffractometry with CuK_α radiation. The relative phase content of zirconia was estimated by using the method proposed by Evans et al.¹⁷ The final density of the specimens was determined by the Archimedes method. The solubility between the materials used in the present study was low, the relative density of the sintered composites was estimated by using the theoretical density of 3.98 g/cm³ for Al₂O₃, 6.05 g/cm³ for TZP and 10.5 g/cm³ for Ag. Polished surfaces were prepared by grinding and polishing with diamond paste to 6 µm and with silica suspension to 0.05 µm. Silver could vaporize during sintering, the volume fraction of Ag in the specimens after sintering was determined by counting the point fraction on the polished surfaces. The polished specimens were then thermally etched at 1500°C for 0.5 h to reveal the grain boundaries of matrix grains. Microstructural characterization used scanning electron microscopy (SEM). The size of Al₂O₃ grains, ZrO₂ and Ag inclusions was determined by using the line intercept technique. The interconnectivity of Ag inclusions in the alumina matrix was determined by measuring the electrical resistivity at room temperature.

3. Results and discussion

There are only α-Al₂O₃, t-ZrO₂ and Ag observed in the XRD patterns of the sintered composites. No Ag₂O

* The synergy effect is a phenomena that the interactions of two agents so that their combined effect is greater than the sum of their individual effects. In the present study, the sum of two individual toughening effect is always treated as the basis for comparison. However, there is no implication whatsoever that two individual toughening effects can be superimposed together.

or m-ZrO₂ on the surface of the sintered specimens is detected. It indicates that Ag₂O was fully decomposed to result in Ag and no oxidation taken place during sintering in air. The oxidation was not observed for the diffusion of oxygen in the oxide is slow and the decomposition of the unstable oxide is relatively fast.¹⁸ The constraint applied on the zirconia particles near surface is small; there may be some m-ZrO₂ near the surface region. However, the amount of m-ZrO₂ may be too low to be detected by the facility used in the present study.

The volume fraction of Ag in the composites after sintering is shown in Table 1. The final amount of Ag is lower than the added amount due to the high vapor pressure of Ag during sintering. Fig. 1 shows the relative density of the composites as a function of total inclusion content. The density decreases with the increase of inclusion content, indicating that both zirconia and silver inclusions prohibit the densification of alumina matrix. A very small amount of Zr⁴⁺ solute can slow down the densification of Al₂O₃.¹⁹ The wetting of silver melt on alumina is relatively poor,²⁰ the presence of silver melt is, therefore, detrimental to the densification. Nonetheless, the relative density of the composites prepared with the technique used in the present study is higher than 94.5%.

The polished micrographs of the composites containing 15%ZrO₂, 15%Ag and 15%ZrO₂+15%Ag are shown in Fig. 2. In the Al₂O₃/(ZrO₂+Ag) composite, the bright particles are Ag, the gray ones are ZrO₂ [Fig. 2(c)]. The microstructures of the thermally etched specimens are shown in Fig. 3. Many voids as found in Fig. 3(c) and (d), which were left behind by the evaporation of silver

during thermal etching. However, by comparing the polished microstructures (Fig. 2) the locations for Ag inclusions before thermal etching can be identified. The ZrO₂ and Ag inclusions distribute uniformly within the matrix. ZrO₂ agglomerates are hardly observed in the Al₂O₃-15%ZrO₂ composite, Fig. 3(b). It demonstrates that the technique employed in the present study can successfully disperse ZrO₂ particles into the matrix. In the Al₂O₃/(ZrO₂+Ag) composite, many ZrO₂ agglomerates do nevertheless exist [Fig. 2(c)]; furthermore, Ag and ZrO₂ particles tend to attach to each other closely within the matrix. The melting point of silver is 960°C, which is well below the sintering temperature. The wetting of silver melt on zirconia is slightly better than that on alumina (contact angle: 117° vs. 120° at 140°C);^{20,21} silver melt may tend to move toward ZrO₂ particles to form (ZrO₂+Ag) clusters.

Most Ag and ZrO₂ inclusions are situated at the grain boundaries of matrix grains, Fig. 3. The presence of Ag and ZrO₂ inclusions can thus prohibit the grain growth of alumina.^{6,22} Fig. 4 shows the size of alumina grains as a function of total inclusion content. The size of alumina grains decreases with the increase of inclusion content.

Fig. 5 shows the flexural strength of the composites as a function of inclusion content. Each datum shown in the figure is the average value of 4 specimens. One standard deviation of the data is also shown in the figure. Except the composites with high inclusion content and consequently with low density, the strength of the composites increases with the increase of inclusion content. Fig. 6 shows the strength of the composites as a function

Table 1
The relative density, inclusion content, elastic modulus and electrical resistivity of the composites

Composition ^a	Relative density ^b (%)	Silver content ^c (vol.%)	Zirconia content ^c (vol.%)	Elastic modulus (GPa)	Electrical resistivity (Ω-cm)
Al ₂ O ₃	99.7			396	6E13
+ 5%ZrO ₂	99.5		5.0	388	
+ 7.5%ZrO ₂	98.2		7.5	381	
+ 10%ZrO ₂	99.4		10.0	381	
+ 12.5%ZrO ₂	99.4		12.5	375	
+ 15%ZrO ₂	97.5		15.0	360	
+ 5%Ag	99.1	4.7		368	5E12
+ 7.5%Ag	99.6	6.6		354	4E12
+ 10%Ag	99.7	8.1		338	6E12
+ 12.5%Ag	98.0	9.0		321	5E12
+ 15%Ag	97.0	9.0		324	4E12
+ 5%ZrO ₂ + 5%Ag	99.5	4.7	5.0	367	5E12
+ 7.5%ZrO ₂ + 7.5%Ag	99.0	7.0	7.5	336	5E12
+ 10%ZrO ₂ + 10% Ag	97.7	9.1	10.1 ^d	318	4E12
+ 12.5%ZrO ₂ + 12.5%Ag	96.3	10.9	12.7 ^d	295	2E12
+ 15%ZrO ₂ + 15%Ag	94.5	12.2	15.5 ^d	293	2E12

^a Added amount.

^b Average value of 8–10 specimens.

^c After sintering.

^d The higher zirconia content is resulted from the loss of Ag during sintering.

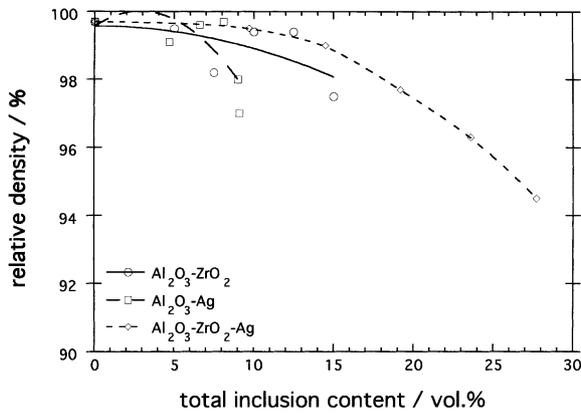
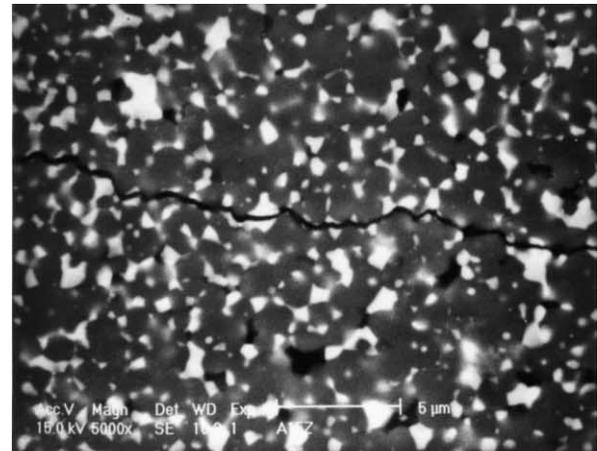


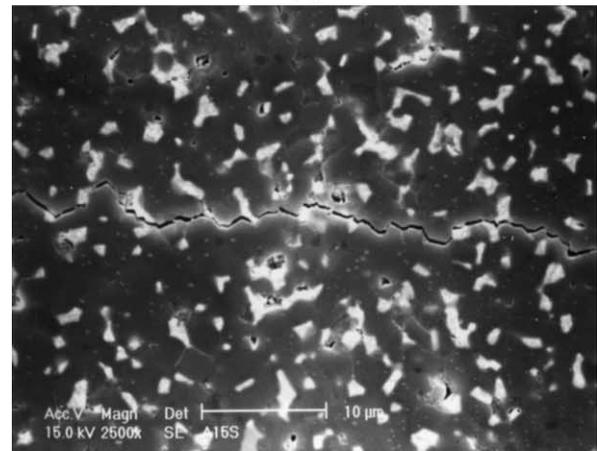
Fig. 1. The relative density of the composites as a function of total inclusion content.

of the grain size of the alumina matrix. The strength of the composites shows a strong dependence on the size of alumina grains. The strength of ceramics is dominated by the size of the critical flaw in the specimen. The size of flaws is larger than the size of grains and usually increases in size with the increase of grain size.²³ The presence of ZrO₂ and Ag inclusions prohibits the grain growth of matrix grains. The microstructure of the composites is thus refined, the strength is consequently enhanced.

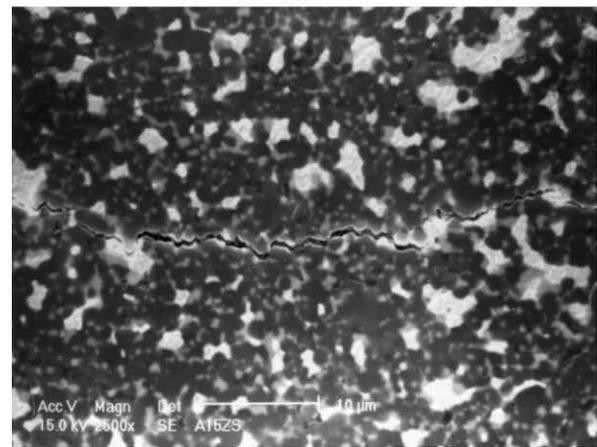
Fig. 7 shows the fracture toughness of composites as a function of total inclusion content. The toughness of alumina is enhanced by adding ZrO₂, Ag and ZrO₂ + Ag inclusions. The size of inclusions increases with the increase of inclusion content, Fig. 8. The Ag and ZrO₂ particles are not easily distinguished from each other in the Al₂O₃-ZrO₂-Ag system; an example is given in Fig. 2(c). Extra care, nonetheless, was taken to determine the size of ZrO₂ and Ag inclusions in the Al₂O₃-ZrO₂-Ag composites. The size of Ag inclusions varies from 0.75 to 2.5 μm; which is either smaller than or equivalent to that of Al₂O₃ grains, Fig. 4. Unlike the metallic fibre-reinforced ceramics,²⁴ the toughness of Al₂O₃-Ag composites exhibits no, at least not noticeable, crack-resistance behaviour.²⁵ It may be due to the size of the metallic inclusions is too small to offer enough bridging stress. The increase of inclusion content increases the possibility for the inclusions to contact each other. The coarsening of inclusions is thus more easy to take place during sintering with the increase of inclusion content. The size of ZrO₂ and Ag inclusions in the Al₂O₃-ZrO₂-Ag composites is larger than those in Al₂O₃-ZrO₂ and Al₂O₃-Ag composites, Fig. 8. It implies that the better wetting between ZrO₂ and Ag melt makes ZrO₂ and Ag inclusions in the Al₂O₃-ZrO₂-Ag composites relatively attractive to each other. The increase of inclusion number increases the possibility of the inclusions to interact with crack; however, the coarsening of the inclusions reduces the number of the inclusions. The toughness of the composites is thus not



(a)



(b)



(c)

Fig. 2. The polished surfaces of the composites containing added (a) 15 vol.% ZrO₂, (b) 15% Ag and (c) 15 vol.%ZrO₂ + 15 vol.%Ag. The crack was introduced by indentation.

enhanced linearly with the increase of the inclusion content.

Fig. 9 shows the amount of monoclinic phase on the fracture surface of the ZrO₂-containing composites. The amount of m-phase increases with the increase of ZrO₂ content. The transformation ability of ZrO₂ inclusions in Al₂O₃ matrix increases with the increase of ZrO₂

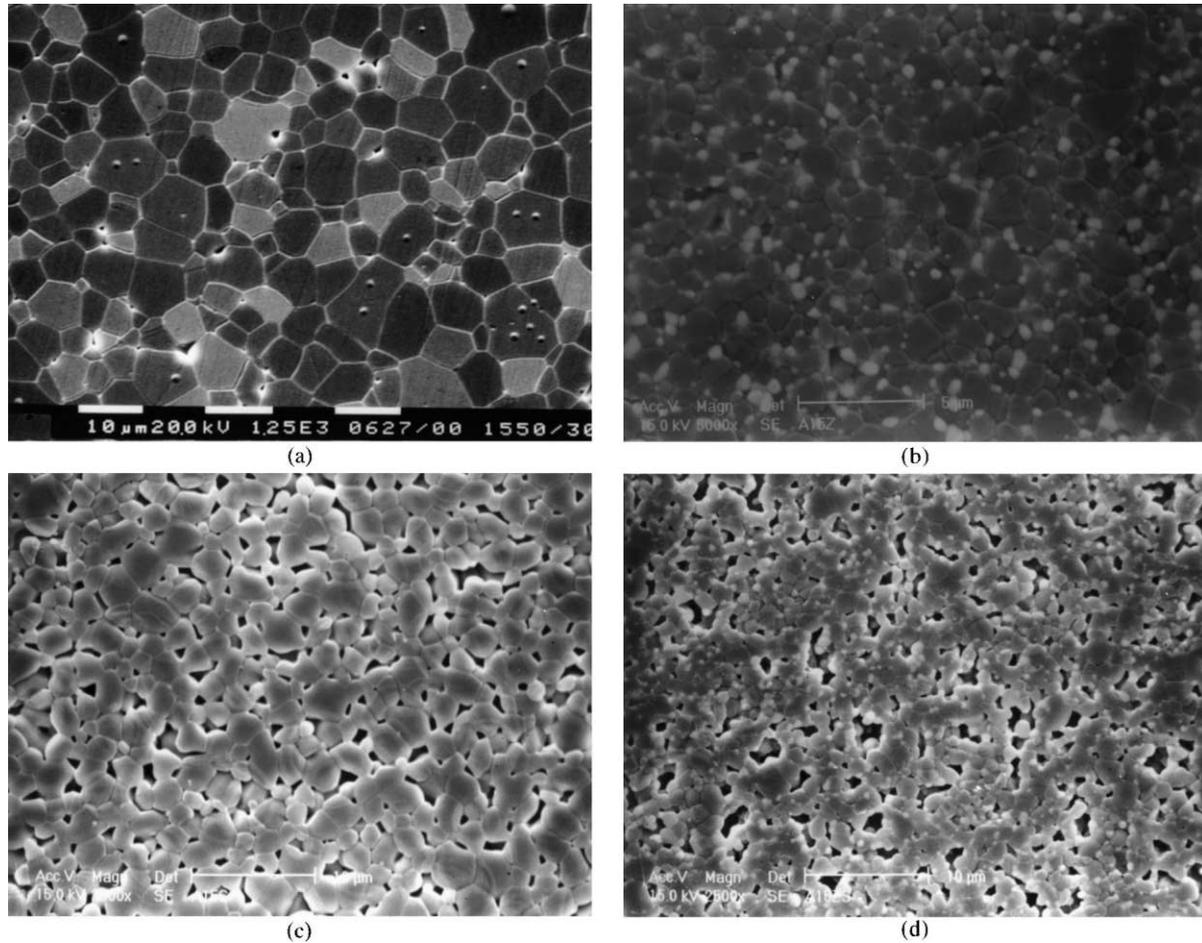


Fig. 3. The polished and thermally etched surfaces of (a) Al_2O_3 and the composites containing added (b) 15 vol.% ZrO_2 , (c) 15% Ag and (d) 15 vol.% ZrO_2 + 15 vol.% Ag.

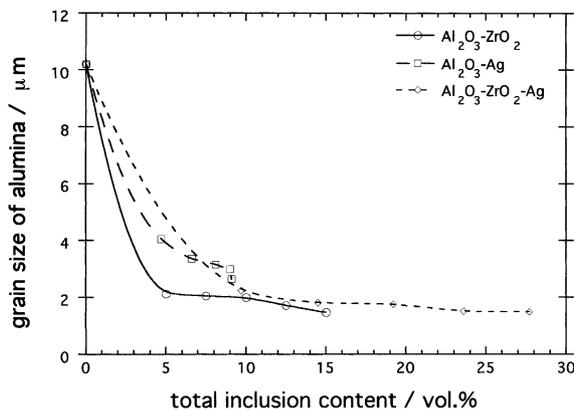


Fig. 4. The grain size of alumina matrix as a function of total inclusion content.

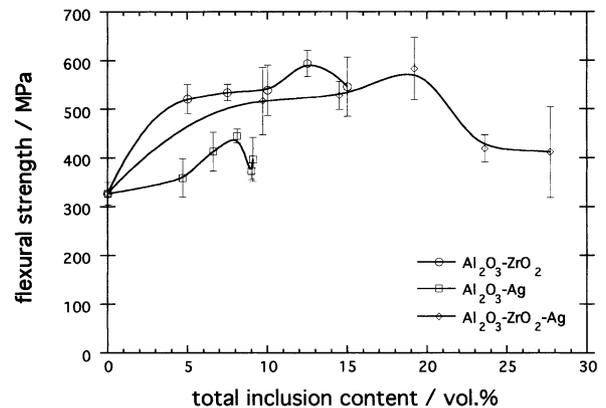


Fig. 5. The flexural strength of composites as a function of total inclusion content.

size^{26,27} and zirconia content.⁸ Furthermore, the stiffness of the matrix decreases with the increase of ZrO_2 content, Table 1, the increase of m-phase with increasing zirconia content in the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ composites can thus relate to the coarsening of ZrO_2 inclusions and to the decrease of elastic modulus. The presence of Ag inclusions also enhances the transformation of ZrO_2 inclusions. The addition of Ag inclusions reduces the

elastic modulus of the matrix, Table 1. The constraint applied on the ZrO_2 particles by the matrix is thus reduced, the transformation of ZrO_2 can take place relatively easier. Fig. 10 shows the toughness increase of the $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Ag}$ composites as a function of total inclusion content. The sum of the toughness increase of the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ and of the $\text{Al}_2\text{O}_3\text{-Ag}$ composites is also shown as the basis for comparison. The toughness

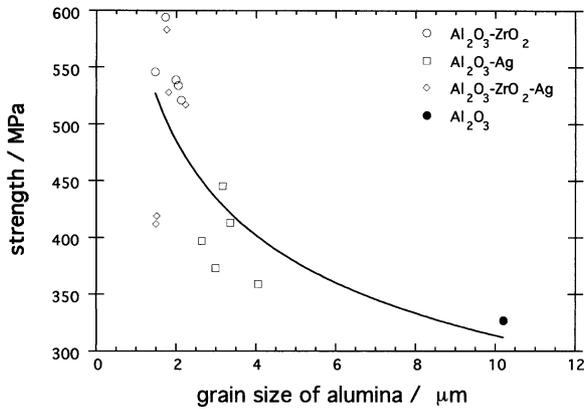


Fig. 6. The flexural strength of composites as a function of grain size of alumina matrix.

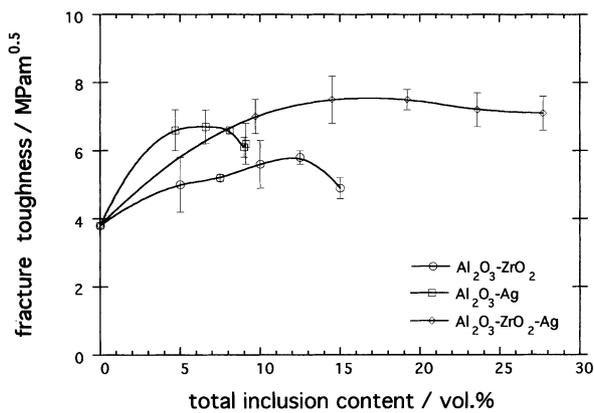


Fig. 7. The fracture toughness of composites as a function of total inclusion content.

increase of the Al₂O₃-ZrO₂-Ag composites is slightly lower than the sum of the toughness increase of the composites containing only one toughening agent.

The Al₂O₃-Ag can be seen as a toughened matrix for the Al₂O₃-ZrO₂-Ag composites. The toughness and elastic modulus of Al₂O₃-Ag composites relative to those of Al₂O₃ is shown in Table 2. The percentage of toughness increase is higher than that of the elastic modulus decrease. The loss of matrix stiffness is smaller than the increase of matrix toughness; Eq. (4) suggests that a synergy effect should be observed. However, the experimental results shown in Fig. 10 contradict to the prediction proposed by Becher and Tiegs.⁹ The theoretical analysis shown in Eqs. (2)–(4) is applicable to the system in which the toughening particles are separated from each other. The attachment of the ZrO₂ and Ag inclusions reduces significantly the number of the inclusions (Fig. 8). Furthermore, the transformation stresses of ZrO₂ particles are absorbed by the nearby soft Ag inclusions, the contribution of transformation toughening is thus diminished. The present study confirms the suggestion made by Tuan and Chen,¹⁶ that the importance of microstructure on the mechanical properties of the composites containing two toughening agents. Furthermore,

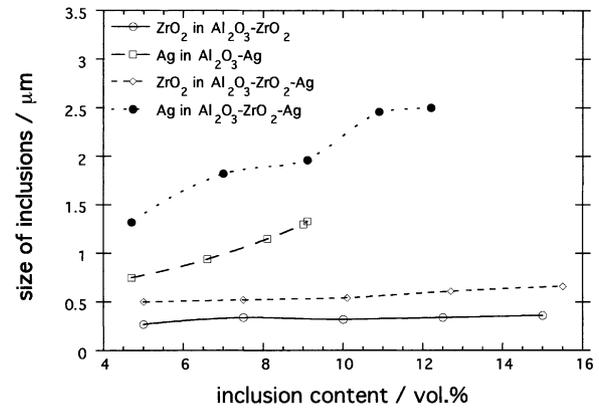


Fig. 8. The size of inclusions as a function of inclusion content.

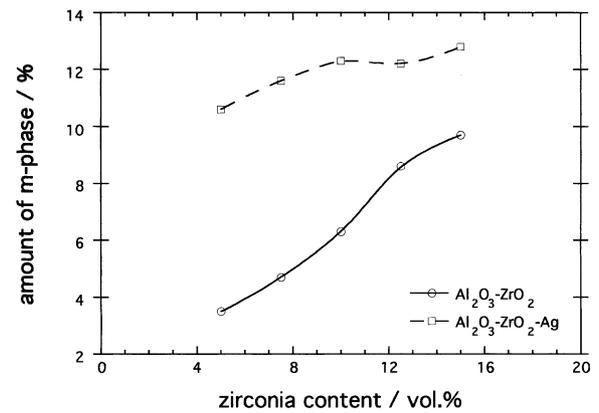


Fig. 9. The amount of monoclinic zirconia on the fracture surface as a function of zirconia content.

Table 2
The toughness ratio and elastic modulus ratio of the specimens

Composition ^a	$\frac{K_{IC, Al_2O_3-Ag}}{K_{IC, Al_2O_3}}$	$\frac{E_{Al_2O_3-Ag}}{E_{Al_2O_3}}$	$\frac{K_{IC, Al_2O_3-ZrO_2-Ag}}{K_{IC, Al_2O_3-ZrO_2}}$
Al ₂ O ₃ + 5% Ag	1.7	0.92	1.4
Al ₂ O ₃ + 7.5% Ag	1.8	0.89	1.4
Al ₂ O ₃ + 10% Ag	1.7	0.85	1.3
Al ₂ O ₃ + 12.5% Ag	1.6	0.81	1.2
Al ₂ O ₃ + 15% Ag	1.6	0.82	1.5

^a Added amount.

the present study indicates that two toughening agents have to be separated from each other in order to activate the synergy effect as demonstrated by a study on Al₂O₃-ZrO₂-Ni composites.¹²

Despite the synergy effect on mechanical properties is not observed for the Al₂O₃-ZrO₂-Ag composites, the composite with both 7.5% ZrO₂ and 7.5% Ag has the highest toughness value in all the compositions investigated in the present study. For the composite, the Ag inclusions are not interconnected to each other, Table 1, demonstrating by a high electrical resistivity. It indicates

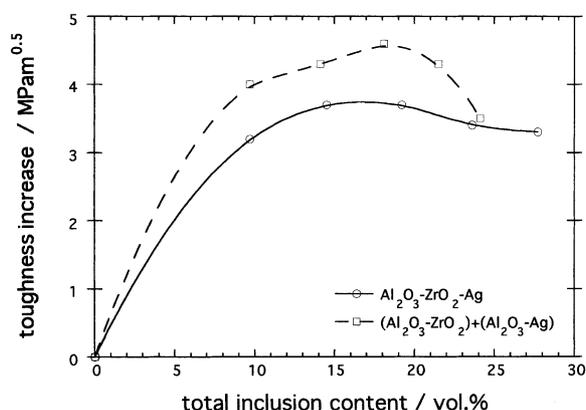


Fig. 10. The toughness increase of the $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Ag}$ composites as a function of total inclusion content. The sum of the toughness increase of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ and of $\text{Al}_2\text{O}_3\text{-Ag}$ composites is also shown for comparison.

that the composite can be applied as an electrical insulator with acceptable mechanical properties.

4. Conclusions

The strength and toughness of Al_2O_3 can be enhanced by adding both ZrO_2 and Ag inclusions. The presence of ZrO_2 and Ag inclusions prohibits the grain growth of Al_2O_3 matrix. The strength of $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Ag}$ composites is thus high for their refined microstructure. More t- ZrO_2 particles transform to m- ZrO_2 in the $\text{Al}_2\text{O}_3\text{-Ag}$ matrix than those in Al_2O_3 matrix. However, the synergy effect on toughening behaviour is not observed. It is mainly due to that ZrO_2 and Ag inclusions in the $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Ag}$ composites are closely attached with each other. The soft Ag inclusions act as cushion to absorb the transformation stresses induced by the phase transformation of nearby ZrO_2 particles.

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