Journal of the European Ceramic Society **14** (1994) 37–43

The Interactions between Silver and Zirconia Inclusions and their Effects on the Toughening Behaviour of $Al_2O_3/(Ag+ZrO_2)$ Composites

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(Received 26 July 1993; revised version received 9 December 1993; accepted 20 December 1993)

Abstract

The toughening behaviour of Al_2O_3/Ag, Al_2O_3/ZrO_2 *and* $Al_2O_3/(Ag+ZrO_2)$ *composites has been studied. The toughness increase of the* $Al_2O_3/(Ag+ZrO_2)$ *composites is less than the sum of the toughness increase of the* Al_2O_3/Ag *and of the* Al_2O_3/ZrO_2 *composites. It results from the interactions between silver and zirconia inclusions during sintering. In the present study the interactions between silver and zirconia inclusions are examined carefully. The influence of the interactions on the microstructure development and on the toughening behaviour of the composites is discussed.*

Das Zähigkeitsverhalten von Al_2O_3/Ag, Al_2O_3/ZrO_2 *und* $Al_2O_3/(Ag+ZrO_2)$*-Verbunden wurde untersucht. Die Zunahme der Zähigkeit der* $Al_2O_3/(Ag+ZrO_2)$*-Verbunde ist kleiner als die Zähigkeitszunahme der* Al_2O_3/Ag *und* Al_2O_3/ZrO_2*-Verbunde. Dies ist auf die Wechselwirkung zwischen Silber und Zirkoniumoxideinschlüssen während des Sinterns zurückzuführen. In der vorliegenden Arbeit wurde diese Reaktion sorgfältig untersucht. Der Einfluß der Wechselwirkung auf die Gefügeentwicklung und auf das Zähigkeitsverhalten der Verbunde wird diskutiert.*

Le renforcement de la ténacité de composites Al_2O_3/Ag, Al_2O_3/ZrO_2 *et* $Al_2O_3/(Ag + ZrO_2)$ *a été étudié. L'augmentation de la ténacité de composites* $Al_2O_3/(Ag + ZrO_2)$ *s'avère être inférieure à celle obtenue par l'addition des augmentations de ténacité propres à chacun des composites* Al_2O_3/Ag *et* Al_2O_3/ZrO_2*. Ce fait résulte des interactions entre les inclusions de zircone et d'argent qui ont lieu au cours du frittage. Dans la présente étude, les interactions entre inclusions d'argent et de zircone sont examinées avec attention. L'influence de ces interactions sur le développement de la microstructure et sur le renforcement de la ténacité est discutée.*

Introduction

Since the application of ceramics as engineering components is often limited by their brittleness, extensive research efforts have been directed to improve their toughness. The addition of second-phase inclusions which influence the propagation of cracks has been one much-studied approach. Among the second-phase inclusions studied, zirconia particles and silicon carbide whiskers have received great attention.[1,2] With the addition of zirconia particles or silicon carbide whiskers, not only the toughness of ceramic matrix is enhanced but also the strength is frequently increased.

More than one toughening agent has also been added to improve the toughness of brittle ceramics. A few examples are given in Table 1.[3–6] As systems 2, 3 and 5 in the table show, when both zirconia inclusions and SiC whiskers are added simultaneously to alumina or mullite, the toughness enhancement of the composites may be roughly the same as the sum of the toughness increase of the composites containing a single toughening agent.[3,4,6] For these systems, the zirconia inclusions and SiC whiskers are assumed to interact with crack independently. Therefore, the additive effect as

$$\Delta K_{IC(zirconia+SiC)} = \Delta K_{IC(zirconia)} + \Delta K_{IC(SiC)} \qquad (1)$$

is observed. In the above relationship, $\Delta K_{IC(zirconia+SiC)}$ is the toughness enhancement of the composite containing both zirconia particles and SiC whiskers, $\Delta K_{IC(zirconia)}$ the toughness increase of the composite containing only zirconia inclusions, and $\Delta K_{IC(SiC)}$ the toughness increase of the composite containing only SiC whiskers.

However, the toughness enhancement for the same composite systems may also be higher than the sum of each single toughness increment,[3,5] as examples 1 and 4 in Table 1 show, since the

Journal of the European Ceramic Society 0955-2219/94/$7.00

Table 1. Reported values for the toughness of composites containing two toughening agents.

Number	*Systems*	K_{IC} *(MPam$^{0\cdot5}$)*	ΔK_{IC} *(MPam$^{0\cdot5}$)*	*Reference*
1	Al_2O_3	4·7		
	+ 15% ZrO_2	6·2	1·5	3
	+ 20% SiC_w	8·5	3·8	
	+ 15% ZrO_2 + 20% SiC_w	13·5	8·8	
2	Al_2O_3	4·2		
	+ 15% ZrO_2	6·3	2·1	4
	+ 20% SiC_w	9·1	4·9	
	+ 15% ZrO_2 + 20% SiC_w	12·5	8·3	
3	Mullite	2·8		
	+ 10% ZrO_2	3·5	0·7	3
	+ 20% SiC_w	4·4	1·6	
	+ 10% ZrO_2+ 20% SiC_w	5·4	2·6	
4	Mullite	2·0^a		
	+ 20% ZrO_2	3·6^a	1·6	
	+ 20% SiC_w	4·6^a	2·6	5
	+ 20% ZrO_2 + 20% SiC_w	10·5^a	8·5	
5	Mullite	2·3		
	+ 23% ZrO_2	4·0	1·7	6
	+ 30% SiC_w	4·7	2·4	
	+ 23% ZrO_2 + 36% SiC_w	5·4	3·9	

[a] tested at 800°C

Throughout this paper, the amount of inclusion is expressed in volume content unless otherwise stated.

toughness is affected by the local crack resistance. When the toughness of the matrix is increased by adding one single reinforcement, as the other reinforcement is added, Becher & Tiegs suggest that the toughness is further enhanced due to the higher matrix toughness.[5] They thus propose that the two toughening processes are not independent. The toughness increase of the composite containing two toughening agents is greater than the sum of the two single toughness increments, so

$$\Delta K_{\mathrm{IC(zirconia+SiC)}} > \Delta K_{\mathrm{IC(zirconia)}} + \Delta K_{\mathrm{IC(SiC)}} \qquad (2)$$

Adding two or more reinforcements to brittle ceramics can bring dramatic benefits in toughness. Furthermore, it opens many possibilities to design complex microstructure and to achieve improved mechanical performance.

Recent studies suggest that ceramics can be effectively toughened through the addition of metallic inclusions.[7,8] The toughening enhancement is believed to be contributed by the plastic deformation of the ductile inclusions. Two conditions have to be fulfilled in order for the plastic deformation to be fully exploited; firstly, the crack has to be attracted by the metallic particle; secondly, the metallic particles need to be firmly bonded to the brittle matrix. In the present study, both zirconia and silver inclusions are added to alumina. The toughness of the Al_2O_3/(Ag+ZrO_2) composites at room temperature is determined. The toughening behaviour of the composites is correlated to their microstructures.

2 Experimental

Al_2O_3/Ag, Al_2O_3/ZrO_2 and Al_2O_3/(Ag+ZrO_2) composites were prepared by milling alumina (TM-DR, Taimei Chem. Co. Ltd, Tokyo, Japan) and silver oxide (Ag_2O, Johnson Matthey Co., UK) and/or zirconia (TZ-3YA, Tosoh Co., Tokyo, Japan) in ethyl alcohol for 4 h. The grinding media used was zirconia balls. The particle size distribution of the as-received zirconia powder in ethyl alcohol was measured by a laser particle analyser (Microtrac, Leeds & Northup Co., USA). The particle size of the zirconia powder after ball milling for 4 and 24 h was also determined with the same facility. 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 were formed by uniaxially pressing at 44 MPa. The sintering was performed in air at 1600°C for 1 h. The heating and cooling rates were 5°C/min. The silver inclusions were formed from the decomposition of silver oxide during the heating stage.

In order to investigate the reactions between silver and zirconia, zirconia specimens, 50%Ag/50%ZrO_2 composites and zirconia powder compacts embedded within Al_2O_3/20%Ag powder mixtures were also prepared. The zirconia specimens and 50%Ag/50%ZrO_2 composites were prepared with the same procedures as those for the alumina matrix composites except the cooling rate was varied. Embedded specimens, the zirconia compacts embedded within Al_2O_3/20%Ag powder mixtures, were prepared by die pressing zirconia powder at 44 MPa first. One of the zirconia compacts was sintered at 1600°C for 1 h to densify the compact fully. The other zirconia compact was not sintered. The sintered and unsintered compacts were embedded in the Al_2O_3/20%Ag powder mixtures and cold-isostatically pressed at 250 MPa. The embedded specimens were then sintered at 1600°C for 1 h with heating and cooling rates of 5°C/min.

The sintered composites were machined longitudinally with a 325 grit resin-bonded diamond wheel at cutting depths of 5 μm/pass. The specimens were not chamfered. The final dimensions of the specimens were (3 × 4 × 36) mm^3. The fracture toughness was determined by the single-edge-notched-beam (SENB) technique. The notched beam was fractured with a four-point bending fixture, with upper and lower spans of 10 mm and 30 mm, respectively. The four loading pins were kept in position by rubber bands to avoid undesirable friction constraints. The rate of loading was 0·5 mm/min. The notch of width around 0·45 mm was generated by cutting with a diamond saw.

Phase identification of sintered and machined specimens was performed by X-ray diffractometry with CuK_α radiation. The relative phase content for the dispersed zirconia was determined by using the relationship.[9]

$$F_t = \frac{0{\cdot}6\, I_t\,(111)}{0{\cdot}6\, I_t\,(111) + I_m\,(111)} \times 100\% \qquad (3)$$

where F_t is the weight fraction of tetragonal phase, $I_m(hkl)$ and $I_t(hkl)$ are the integral intensities of the (hkl) peaks of the monoclinic and tetragonal phases respectively. The lattice parameters of zirconia and silver in ZrO_2 and $50\%Ag/50\%ZrO_2$ composites after sintering were also determined. To assure the accuracy of the determination of lattice parameters, a thin layer of silicon powder was applied on the surface of specimens to act as external standard.

The partial pressure of liquid silver at elevated temperature is rather high, for example, the vapour pressure of silver at 1600°C is 10 mmHg.[10] Therefore, the volume fraction of silver is decreased as sintering proceeded. The weight of the specimens was measured before and after sintering and the silver content after sintering was determined from the weight change. The final density of the specimens was determined by water displacement. Before submerging the specimens in water, a wax was applied to the surface to prevent water penetration. The polished surfaces were prepared by grinding and polishing with diamond paste to 6 μm and with silica suspension to 0·05 μm. The size of silver inclusions after sintering was determined by using the linear intercept technique on the micrographs taken from the polished surfaces. The polished specimens were then thermally etched to reveal the grain boundaries of the matrix. The size of the matrix grains was also determined by using the linear intercept technique on micrographs taken from the thermally etched surfaces.

3 Results and Discussion

The X-ray results show that no silver oxide is found as the composites are sintered at 1600°C for one hour. The silver content after sintering, relative density, the size of inclusion and of alumina matrix grain of the composites are shown in Table 2. Since part of the silver is vaporized during sintering, the final silver content is less than the added amount. The relative densities of the composites are quite similar, so the influence of porosity on the determination of toughness can thus be ignored. Typical microstructures for the composites containing silver, zirconia, and silver and zirconia are shown in Fig. 1. A crack is introduced by indentation to reveal the interactions between the inclusions and crack.

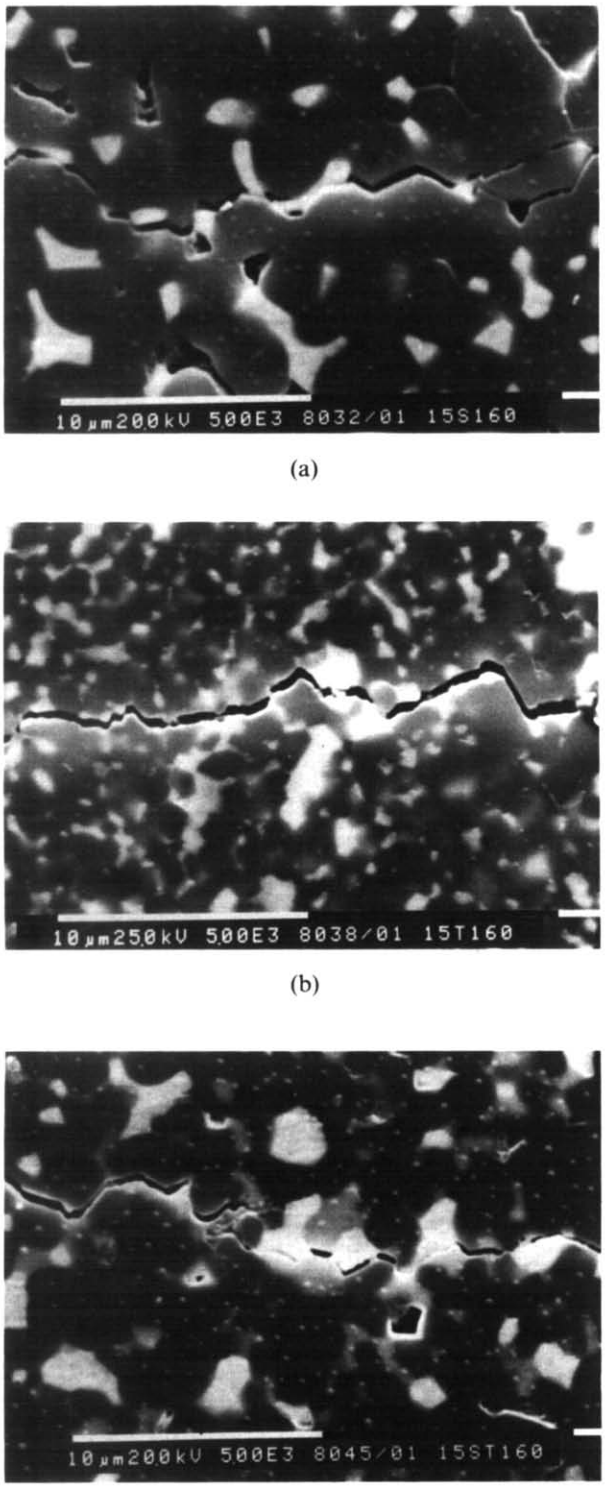
Table 2. The silver content after sintering, the relative density, the size of silver inclusions and of alumina matrix grains, for the composites

Systems	*Silver content after sintering (%)*	*Relative density (%)*	*Inclusion size of silver (μm)*	*Grain size of alumina (μm)*
Al_2O_3	—	98·6	—	10·9
+2·5%Ag[a]	2·5	98·3	1·0	5·3
+5%Ag	4·7	98·5	1·1	4·3
+10%Ag	8·2	98·8	1·4	4·2
+15%Ag	9	97·1	1·5	4·0
$+2{\cdot}5\%ZrO_2$	—	99·0	—	5·0
$+5\%ZrO_2$	—	99·0	—	3·6
$+10\%ZrO_2$	—	99·9	—	2·5
$+15\%ZrO_2$	—	99·5	—	2·1
+2·5%Ag $+2{\cdot}5\%ZrO_2$	2·5	98·7	1·2	4·6
+5%Ag $+5\%ZrO_2$	4·7	98·3	1·6	3·5
+10%Ag $+10\%ZrO_2$	9	98·5	2·2	2·8
+15%Ag $+15\%ZrO_2$	11·8	98·5	2·1	2·6

[a] The value indicates the volume content of added inclusion.

The mean particle size of the as-received zirconia powder is 14 μm. After milling in ethyl alcohol for 4 and 24 h, the mean particle size of the zirconia powder is decreased to 2·1 μm and 2·2 μm, respectively. However, the specific surface area of the zirconia powder reported by the manufacturer is 17 m^2/g, i.e. the size of the primary particles is 0·06 μm. It thus suggests that some zirconia particles are agglomerated after milling. In Fig. 1(a) and (b), the bright particles are silver and zirconia inclusions, respectively. The zirconia agglomerates which survived after the milling and forming processes can be observed in Fig. 1(b). A similar microstructure for the same system has also been reported by Witek & Butler.[11] In the composite shown in Fig. 1(c), 15 vol.% silver and 15 vol.% zirconia inclusions are added before sintering. In the figure, the bright particles are silver inclusions, grey particles are zirconia inclusions and the black matrix is alumina. Some zirconia inclusions are distributed within the alumina matrix; however, some zirconia inclusions are associated with silver inclusions.

The fracture toughness of the composites is shown as a function of added inclusion content in Fig. 2. Each point reported in the figure is the average value of 3 to 5 specimens. The error bars show one standard deviation. The values on the x-axis of Fig. 2 indicate the added silver content or the added zirconia content. For the purpose of comparison, since the amount of silver added is



(a)

(b)

(c)

Fig. 1. The polished surfaces of (a) Al_2O_3/15 vol.% Ag, (b) Al_2O_3/15 vol.% ZrO_2 and (c) Al_2O_3/(15 vol.% Ag + 15 vol.% ZrO_2) composites. The small particles on the surfaces are contamination from the polishing suspension.

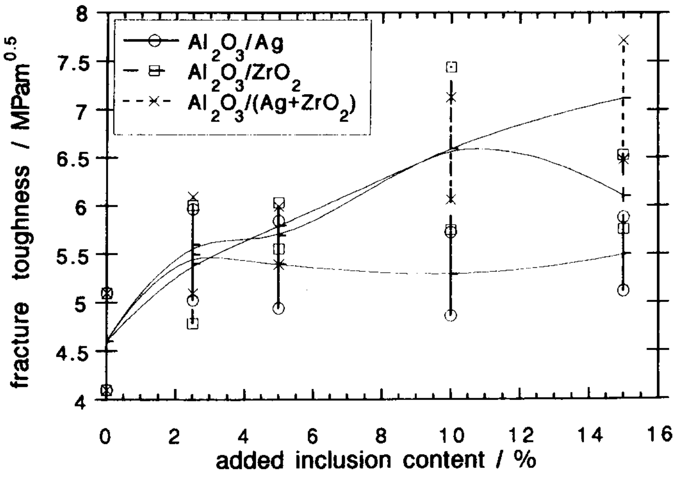


Fig. 2. The fracture toughness of the composites as a function of added inclusion content.

the same as the added amount of zirconia in the composites containing both silver and zirconia inclusions, the total inclusion content added is in fact double the values on the x-axis. The following figure (Fig. 3) is also expressed in the same way.

From Fig. 2, the toughness of Al_2O_3/Ag, Al_2O_3/ZrO_2 and Al_2O_3/(Ag+ZrO_2) composites is higher than that of alumina matrix alone. The composites containing tetragonal zirconia inclusions is believed to be toughened by a transformation toughening mechanism.[1] Because the crack surfaces are bridged by silver inclusions, Fig. 1(a), the toughness enhancement of the composites containing silver inclusions is contributed by the plastic deformation of the silver inclusions. It is the same mechanism which contributes to the toughness enhancement for Al_2O_3/Al[7] and Al_2O_3/Ni[8] composites.

The toughness increase of the Al_2O_3/(Ag+ZrO_2) composites is shown as a function of added inclusion content in Fig. 3. The additive values which are the toughness increase of the Al_2O_3/Ag composites added to that of the Al_2O_3/ZrO_2 composites are also shown for comparison. Since some silver inclusions interact with zirconia agglomerates, Fig. 1(c), the toughness increase of the Al_2O_3/(Ag+ZrO_2) composites is less than the addition of the toughness enhancement contributed by the plastic deformation alone and by the transformation alone. Nevertheless, as more silver and zir-

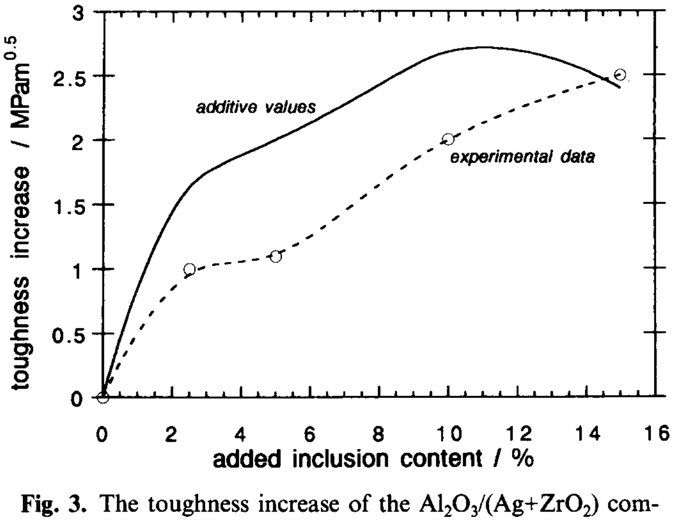


Fig. 3. The toughness increase of the Al_2O_3/(Ag+ZrO_2) composites. The additive of the toughness increase of the Al_2O_3/Ag composites and of the Al_2O_3/ZrO_2 composites is also shown for comparison.

Table 3. The lattice parameters of the silver and the zirconia inclusions in the zirconia specimens and in the 50%ZrO_2/50%Ag composites

	Tetragonal ZrO_2 Lattice Parameter, a	*Tetragonal ZrO_2 Lattice parameter, c*	*Silver Lattice parameter, a*
Reported values	5·094[12]	5·177[12]	4·086[a]
ZrO_2[b]	5·110	5·171	—
ZrO_2/Ag[b]	5·107	5·166	4·091
ZrO_2/Ag[c]	5·127	5·153	4·099

All the samples are sintered at 1600°C for 1 h.

[a] JCPDS card index no. 4-0783.

[b] The cooling rate for the specimens is 5°C/min.

[c] The composite is removed immediately from the furnace after sintering at 1600°C for 1 h.

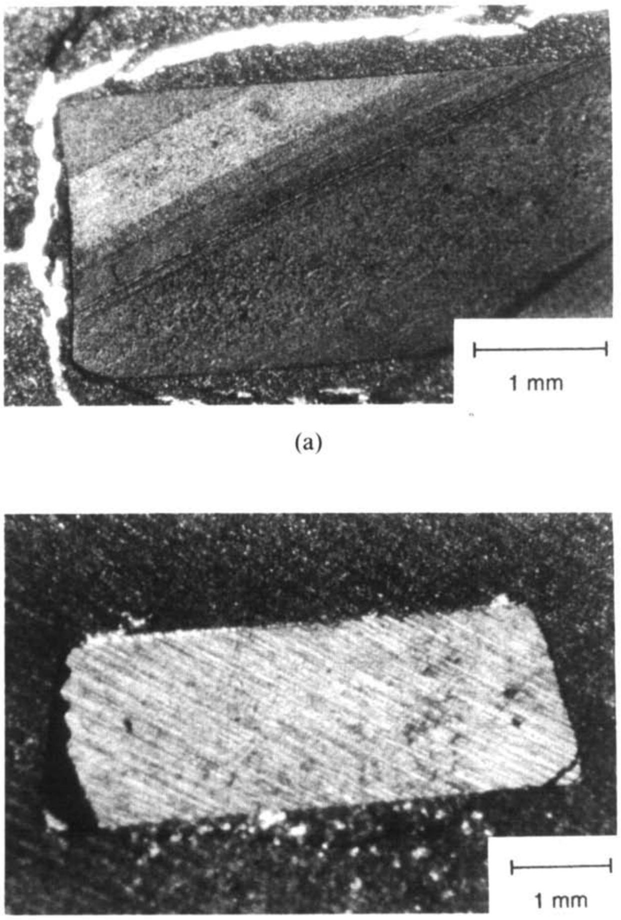
conia inclusions are added, the toughness is significantly enhanced.

There are two possible reasons that the zirconia inclusions and silver inclusions are associated with each other after sintering. These are that:

(1) Solid solution between silver and zirconia is formed at high temperature, silver and zirconia particles are then precipitated out during the cooling stage;
(2) Since silver melts at 961°C, as the zirconia agglomerates are sintered and decrease in size, the silver melt is absorbed by the shrinking agglomerates.

In order to determine whether the solid solution between silver and zirconia is formed at high temperature or not, the lattice parameters of the zirconia and of the silver in the zirconia specimen and in the 50%Ag/50%ZrO_2 composites are determined, see Table 3. The samples are cooled with two different cooling rates. One cooling rate employed is 5°C/min, the other is roughly 100°C/min in the range of 1600°C to 1500°C and 35°C/min in the range of 1500°C to 600°C. The difference between the lattice parameters of zirconia in ZrO_2 and in ZrO_2/Ag composites is below 0·4%. The difference between the lattice parameter of silver in ZrO_2/Ag composites and the reported value is less than 0·2%. These values are very small. This implies that the solubility of silver in zirconia or zirconia in silver is very limited.

As far as the second possible reason is concerned, the microstructure of the zirconia embedded specimens is observed. In Fig. 4(a), an unsintered zirconia is embedded in Al_2O_3/20%Ag powder mixtures at the beginning. As the embedded specimen is sintered at 1600°C for 1 h, a layer of silver can be observed to form near the zirconia compact. When a sintered zirconia pellet is embedded in Al_2O_3/20%Ag powder mixtures, Fig. 4(b), only a small amount of silver appeared near the surface of the zirconia. Due to the silver layer appearing only on the surface of the unsintered zirconia pellet, it thus suggests that liquid silver is absorbed by the shrinking zirconia agglomerates during sintering.



(a)

(b)

Fig. 4. The cross-sections of the embedded specimens. (a) An unsintered zirconia compact and (b) a sintered zirconia compact are located at the centre of the Al_2O_3/20%Ag powder mixtures before sintering.

It is interesting to investigate the transformation ability of zirconia inclusions within the composites. The extent of martensitic transformation of the composites is qualitatively estimated by examining the change in the relative phase distribution of zirconia before and after grinding using a resin-bonded diamond wheel (325 grit). The specimens are mounted together and ground at the same time. The residual tetragonal-phase content in the composites before and after grinding is shown as a function of zirconia content in Fig. 5. The zirconia in the composites is 100% tetragonal phase after sintering. About 10% tetragonal zirconia is transformed to monoclinic as the Al_2O_3/ZrO_2 composites are ground with the diamond wheel. As silver inclusions are added, more tetragonal zirconia inclusions are transformed to the monoclinic phase. Since zirconia inclusions tend to be attached to soft silver inclusions, the constraint applied on the zirconia is thus reduced. Therefore, more zirconia

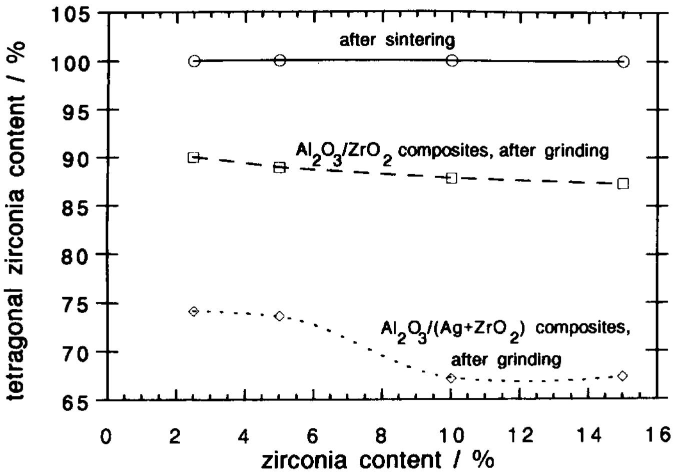


Fig. 5. The tetragonal phase content for the zirconia-containing composites before and after grinding.

particles can be transformed.

Even though more zirconia inclusions are transformed in the $Al_2O_3/(Ag+ZrO_2)$ composites, the toughness increase of the composites is not higher than the additive of two individual toughness increments. For the composites containing only silver inclusions, the toughness is enhanced by the plastic deformation of silver inclusions. For the composite containing zirconia inclusions, due to the transformation of zirconia particles, the propagation of the crack is suppressed. Due to the stress field around the transformed zirconia inclusions, the crack is deviated away from the zirconia particles. For composites containing (zirconia+silver) inclusions, even though the zirconia particles are easily transformed, since the crack is deviated away from the inclusions, the plastic deformation of the silver inclusions is not able to be fully utilized. By the same argument, the silver could absorb the induced stress from the phase transformation of tetragonal zirconia, so reducing opposition to the advancing crack tip. The plastic deformation and transformation toughening tend to compensate each other to some extent; therefore, the toughness of the $Al_2O_3/(Ag+ZrO_2)$ composites is less than the values proposed by the additive effect. The present system demonstrates the importance of microstructure on the toughening behaviour. It also implies that the difference between the reported values in Table 1 may be related to microstructural variation.

4 Conclusions

The toughening behaviour and microstructure development of $Al_2O_3/(Ag+ZrO_2)$ composites is investigated in the present study. The toughening behaviour of Al_2O_3/Ag and Al_2O_3/ZrO_2 composites is also studied for comparison purposes.

Either the plastic deformation of silver inclusions or transformation of tetragonal zirconia inclusions can enhance the toughness of alumina. As silver and zirconia are added together into the alumina matrix, the silver melt is absorbed by the shrinking zirconia agglomerates during sintering. The silver inclusions are thus attached to the zirconia agglomerates. For the $Al_2O_3/(Ag+ZrO_2)$ composites, due to the interaction between the silver and zirconia inclusions, the two toughening mechanisms are not independent of each other. The constraint applied on the zirconia by the soft silver is relatively small, tetragonal zirconia particles are much more easily transformed but at the expense of the contribution of plastic deformation of the silver inclusions to the toughness enhancement. Furthermore, the transformation stress of the zirconia inclusions is absorbed by the surrounding soft silver, the suppression applied on the advancing crack by the zirconia inclusions is thus decreased. Therefore, the toughness increase of the $Al_2O_3/(Ag+ZrO_2)$ composites is less than the additive of the toughness increase of the Al_2O_3/Ag composites and of the Al_2O_3/ZrO_2 composites.

Acknowledgment

Valuable comments from Prof. R. J. Brook, Oxford University, are gratefully acknowledged.

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