Journal of the European Ceramic Society **16** (1996) 583–586
© 1996 Elsevier Science Limited
Printed in Great Britain. All rights reserved
0955-2219/96/$15.00
0955-2219(95)00166-2

The Corrosion Behaviour of Al_2O_3 Toughened by Ag Particles

W. H. Tuan & W. B. Chou

Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 10764

(Received 7 June 1994; revised version received 16 August 1995; accepted 27 August 1995)

Abstract

The strength and toughness of alumina can be enhanced by adding silver inclusions. In the present study, the corrosion behaviour of such Al_2O_3/Ag composites in nitric acid is investigated. The strength of the composites containing 2·5 vol% silver is not affected after the corrosion test. However, the weight loss of the composites containing 10 vol% silver is increased with increasing corrosion time. The strength and the toughness of the composites after corrosion are significantly degraded. For example, the strength of the composites containing 10 vol% silver is decreased by 50% and the toughness by 30%, when the composites are soaked in nitric acid for 1000 h.

1 Introduction

Ceramics are superior for their chemical stability and therefore are frequently used in hostile environments. However, the application of ceramics as structural components has been limited by their brittleness. Recent studies suggest that the toughness of alumina can be significantly enhanced by adding silver inclusions.[1–3] A key question then arises concerning the ability of such composites to resist corrosion, since initial failure will expose the metal reinforcement to the environment. In the present study, the corrosion behaviour of silver-toughened alumina in nitric acid is investigated as a model system representing extreme conditions. The strength and toughness of the composites after the corrosion test have been determined.

2 Experimental Procedures

Alumina (AKP-50, Sumitomo Chem. Co., Ltd, Japan) and various amounts of silver oxide (Ag_2O, Johnson Matthey Co., UK) were ball milled together in ethyl alcohol for 4 h. The slurry was dried with a rotary evaporator. The powder compacts were prepared by uniaxially pressing at 56 MPa. The silver oxide was decomposed to silver and oxygen during initial heating.[1–3] Sintering was performed at 1600°C for 1 h in air.

Since the partial pressure of liquid silver at elevated temperature is high (10 mmHg at 1600°C, 23 mmHg at 1700°C),[4] a silver-free surface layer was formed.[2] After removing the silver-free layer by grinding, the volume fraction of silver after sintering was recalculated by counting the point fraction on the polished surfaces. The size of silver inclusions was determined by using the linear intercept technique. The polished specimens were thermally etched at 1500°C for 1 h to reveal the grain boundaries of alumina. The size of the matrix grains was also determined by using the linear intercept technique. More than 200 grains or inclusions were counted.

The sintered specimens were machined longitudinally with a 325-grit resin-bonded diamond wheel at a cutting depth of 5 μm/pass. The silver-free layer was removed during the grinding procedure. The final dimensions of the samples were $3 \times 4 \times 36$ mm^3. The ground specimens were soaked in an aqueous nitric acid (1 M) solution at 40°C. After a certain time, the specimens were removed, washed in deionized water and subsequently in acetone for 10 min.

The strength of the samples was determined by the four-point bend technique under ambient conditions. The upper and lower spans were 10 and 30 mm, respectively, and a loading rate of 0·5 mm min^{-1} was used. The fracture toughness was determined by the single-edge notched beam (SENB) technique, the notch being generated by cutting with a diamond saw before the corrosion test. The electrical resistivity of the composites was measured by the standard two-probe technique, using silver paint for contacts. Phase identification was performed by X-ray diffractometry (XRD), and the microstructure was observed by a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDX). Chemical analysis was also conducted by applying a plasma evaporation technique (TC-136, LECO Co., USA).

3 Results and Discussion

The silver content after sintering, the relative density, the matrix grain size, the size of the silver inclusions and the electrical resistivity of the Al_2O_3/Ag composites are shown in Table 1. The fracture surfaces of the composites before sintering are shown in Fig. 1. From Table 1, both the strength and toughness of alumina are enhanced due to the addition of silver inclusions. The toughness enhancement is attributed mainly to the plastic deformation of the metallic inclusions. The strengthening effect is attributed both to the matrix refinement and the toughness enhancement.[1]

The electrical resistivity of the composite containing 2·5 vol% Ag is higher than that of the composite containing 10 vol% Ag (Table 1). This indicates that the connectivity of the silver inclusions increases with the amount of silver inclusions. The weight loss of the Al_2O_3/Ag composites is shown as a function of corrosion time in Fig. 2, while the strength and the toughness of the composites are shown in Figs 3 and 4, respectively. Each point in the figure is the average value of three testing bars; error bars show one standard deviation. The weight loss of the alumina specimens is negligible as is their strength and toughness change.

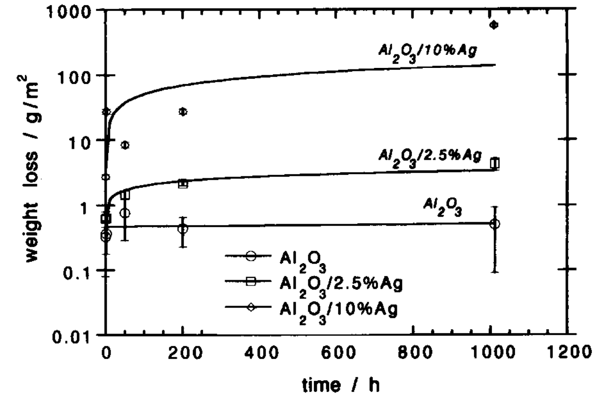

Fig. 2. Weight loss of the composites as a function of corrosion time.

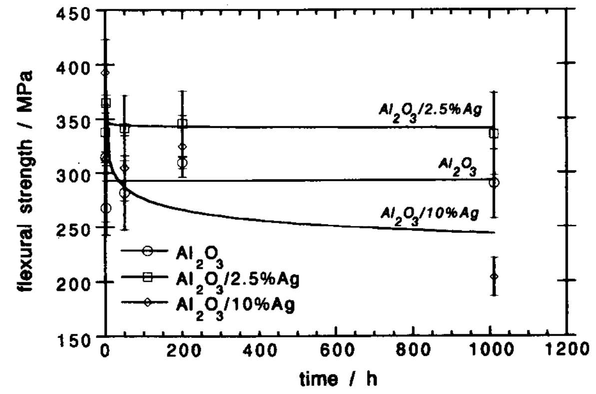

Fig. 3. Flexural strength of the composites as a function of corrosion time.

Table 1. The silver content, relative density, matrix grain size, inclusion size, flexural strength, fracture toughness and electrical resistivity of the Al_2O_3/Ag composites (composites sintered at 1600°C for 1 h)

Silver content after sintering (vol%)	*Relative density (%)*	*Matrix grain size (μm)*	*Inclusion size (μm)*	*Flexural strength (MPa)*	*Fracture toughness (MPa $m^{0·5}$)*	*Electrical resistivity (Ω cm)*
0	97·8	5·2	–	325	4·0	$1·1 \times 10^{14}$
2·5	97·9	4·5	1·2	351	4·6	$8·4 \times 10^{13}$
1·0	96·6	4·1	2·5	394	4·7	$1·8 \times 10^{13}$

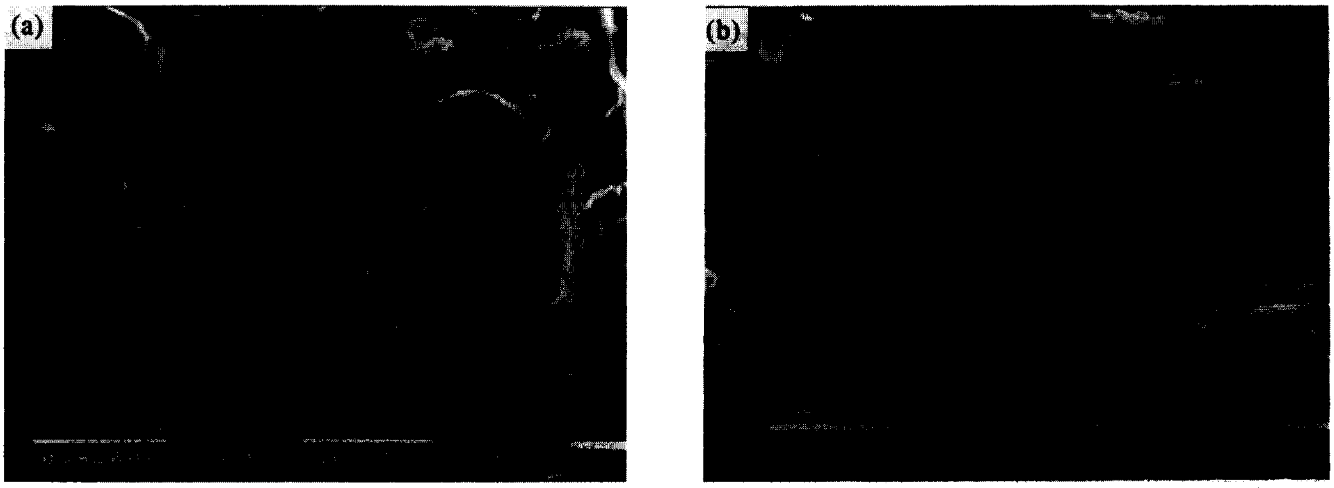

Fig. 1. Fracture surfaces of composites containing (a) 2·5 and (b) 10 vol% silver before corrosion.

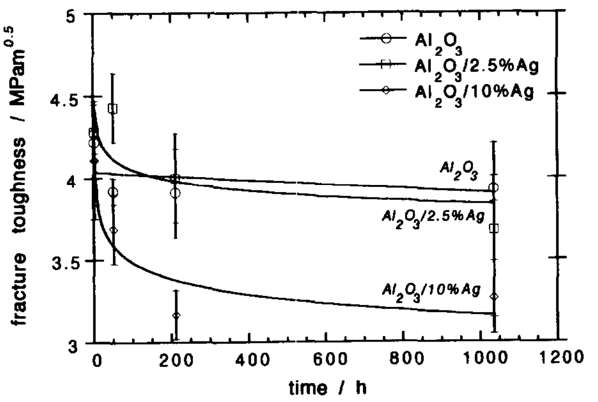

Fig. 4. Fracture toughness of the composites as a function of corrosion time.

3.1 Corrosion behaviour of Al_2O_3/2·5% Ag composite

From Table 1, it can be seen that the strength and toughness of alumina are enhanced by 8% and 15%, respectively, with 2·5 vol% silver addition. The weight loss of the composites increases rapidly during the first 2 h of exposure. This results from the dissolution of the exposed silver inclusions.[5] Subsequent weight loss is negligible. This suggests that the internal silver inclusions are well protected by the alumina matrix. Since the critical flaw size calculated from the strength and toughness (Table 1) for the as-received composite is 100 μm, the silver inclusions in the composites containing 2·5 vol% are much smaller than the critical flaw size. Therefore, the presence of the silver-depleted surface layer does not affect the strength of the composites. However, as the exposed silver inclusions are removed after corrosion, the number of silver inclusions to interact with the crack is decreased. The toughness of the composite is thus reduced as soon as the exposed silver inclusions are dissolved. Since the internal silver inclusions are well protected, the toughness of the composite after corrosion drops by only 15%.

3.2 Corrosion behaviour of Al_2O_3/10% Ag composite

The strength and toughness of alumina is enhanced by 21% and 18%, respectively, with 10 vol% silver addition. The weight loss of the composite continues to increase with increasing corrosion time. It suggests that the silver inclusions are interconnected to each other and therefore corrosion can progress through the structure by leaching out the silver phase. The strength and toughness is dramatically decreased as the composites are corroded for longer than 200 h. The fracture surface of an Al_2O_3/10% Ag composite after corrosion for 1000 h is shown in Fig. 5. Three distinct regions can be

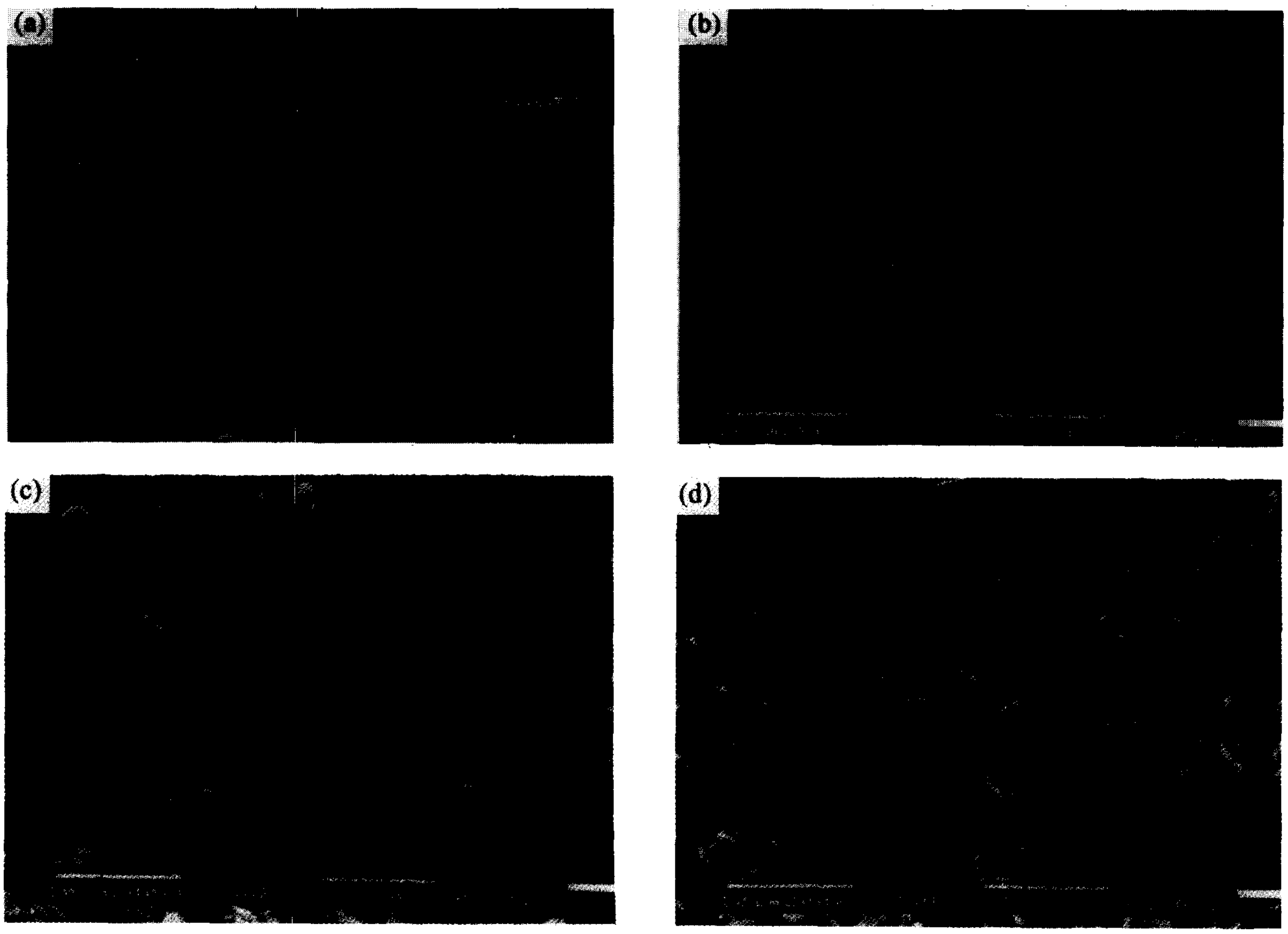

Fig. 5. (a) Fracture surface of the Al_2O_3/10% Ag composite after corrosion for 1000 h. The surface region (S), central region (C) and the intermediate region (I) are shown in (b), (d) and (c), respectively.

found on the fracture surface, Fig. 5(a). The region near the surface is shown in Fig. 5(b). The centre of the composite is shown in Fig. 5(d). The intermediate region between the surface region and central region is shown in Fig. 5(c). Only limited silver inclusions can be observed in the region near the surface. The central region of the corroded specimens is similar to the as-received composites, Fig. 1(b). In the intermediate region, the surface is covered with small particles, the amount of which is too small to be identified using XRD analysis. However, nitrogen is detected by applying the plasma evaporation technique and silver is detected by using the EDX analysis, suggesting that the small particles are silver nitrate.

After the corrosion test, the specimens were removed from the acid solution and the acid near the surface removed during the subsequent washing steps. Nevertheless, acid remained far into the structure. After drying, silver nitrate particles were deposited on the surface of the alumina grains. Since the toughening agents (silver inclusions) are almost removed completely from the crack front during corrosion, the toughness is reduced significantly. Pores are left behind after corrosion, thereby degrading the strength. For example, for the composite containing 10% Ag, the toughness is decreased by 30% and the strength by 50% after corrosion for 1000 h.

4 Conclusions

The corrosion behaviour of Al_2O_3/2·5% Ag and Al_2O_3/10% Ag composites in nitric acid has been investigated. For the Al_2O_3/2·5% Ag composites, the silver inclusions are well separated from each other. As the composites are soaked in nitric acid, only the silver inclusions exposed to the outer surface are dissolved, other silver inclusions within the composites being well protected by the alumina matrix. Therefore, the strength of the Al_2O_3/2·5% Ag composites is not affected by nitric acid. However, the toughness is reduced slightly. When 10 vol% silver is incorporated into alumina, the silver inclusions are interconnected to each other. Therefore, not only the exposed silver inclusions but also the internal silver inclusions are attacked by the acid. The weight loss of the composites containing 10 vol% silver is thus increased with increasing corrosion time. After corrosion in nitric acid, the silver inclusions within the crack front are removed and pores are formed instead, so that the strength and toughness are reduced significantly.

Acknowledgement

The valuable comments given by Prof. R. J. Brook, Oxford University, are gratefully acknowledged.

References

1. Tuan, W. H. & Chou, W. B., Toughening alumina with silver inclusions. *Proc. 2nd Conf. of European Ceram. Soc.*, ed. G. Ziegler & H. Hausner. Deutsche Keramische Gesellschaft e.V., Germany, 1991, Vol. 2, p. 1703.
2. Wang, J., Ponton, C. N. & Marquis, P. M., Silver-toughened alumina ceramics. *Br. Ceram. Trans.*, **92** (1993) 67.
3. Chou, W. B. & Tuan, W. H., Toughening and strengthening alumina with silver inclusions. *J. Eur. Ceram. Soc.*, **15** (1995) 291.
4. Wise, E. W. & Coxe, C. D., Silver and silver alloys. In *Metal Handbook*, ed. T. Lyman. Amer. Soc. Metals, OH, 1961, Vol. 1, p. 1181.
5. Leach, R. H., Silver and silver alloys. In *The Corrosion Handbook*, ed. H. H. Chlig. John Wiley & Sons, (1948), p. 314.