Journal of the European Ceramic Society 5 (1989) 23–27

Sintering and Characterization of Al_2O_3–TiB_2 Composites

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(Received 9 June 1988; accepted 24 June 1988)

Abstract

Al_2O_3–TiB_2 composites containing 0–50 wt% TiB_2 were prepared by sintering at 1600–1750°C for 15–120 min in a vacuum. Relative density increased with TiB_2 addition from 97% (no TiB_2) to about 99% (10–40 wt% TiB_2) on sintering at 1750°C for 60 min. TiB_2 behaved as a sintering aid to promote densification by inhibiting rapid grain growth of Al_2O_3. Bending strength and microhardness increased with increasing relative density. In particular, microhardness was so improved as to exceed that of Al_2O_3 and reach 30·1 GPa. Resistivity decreased with increasing TiB_2 content and dropped down to 3×10^{-2} Ω m with 30 wt% TiB_2.

Al_2O_3–TiB_2-Komposite mit TiB_2-Gehalten von 0–50 Gew.% wurden bei 1600 bis 1750°C für 15–120 Minuten in Vakuum gesintert. Die relative Dichte stieg mit zunehmendem TiB_2-Gehalt von 97% (0 Gew.% TiB_2) auf 99% (10–40 Gew.% TiB_2) bei 1750°C und 60 Minuten Haltezeit an. TiB_2 wirkt als Sinterhilfsmittel, daß die Verdichtung durch Unterdrückung des schnellen Kornwachstums von Al_2O_3 fördert. Die Biegefestigkeit und die Mikrohärte stiegen mit ansteigender relativer Dichte an. Speziell die Mikrohärte konnte auf 30·1 GPa verbessert werden, was den Wert für reines Al_2O_3 übertrifft. Der Ohm'sche Widerstand nimmt mit ansteigendem TiB_2-Gehalt auf 3×10^{-2} Ω m für 30 Gew.% TiB_2 ab.

Des composites Al_2O_3–TiB_2 contenant de 0 à 50% en poids de TiB_2 ont été préparés par frittage entre 1600 et 1750°C pendant 15 à 120 min sous vide. La densité relative augmente par addition de TiB_2 de 97% (sans TiB_2) à environ 99% (avec 10 à 40% en poids de TiB_2) lors d'un frittage d'une heure à 1750°C. TiB_2 se comporte en additif de frittage qui améliore la densification en inhibitant la croissance rapide des grains d'alumine. La résistance à la flexion et la microdureté augmentent avec la densité relative. En particulier, la microdureté est tellement améliorée qu'elle dépasse celle de l'alumine pour atteindre 30·1 GPa. La résistivité diminue lorsque l'on augmente la teneur en TiB_2 et chute à 3×10^{-2} Ω m pour 30% en poids de TiB_2.

1 Introduction

Aluminium oxide (Al_2O_3) ceramics are strong and hard but brittle. In order to obtain much higher strength, hardness and fracture toughness, composites have been prepared by dispersing a second phase in an Al_2O_3 matrix.[1–8] The composites with titanium carbide (TiC) are some of the most renowned wear-resistant materials, which have applications as cutting tools.[8,9]

Titanium diboride (TiB_2) is an interesting material, because it is very similar to TiC in many properties, and some of them are better than TiC, as shown in Table 1;[10] for example, hardness, thermal conductivity, electric conductivity and resistance to oxidation. Therefore, composites with TiB_2 instead of TiC would also have applications as cutting tools and wear-resistant materials. However, neither sintering behaviour nor properties of this system have yet been reported.

In the present study, the sintering behaviour of the Al_2O_3–TiB_2 system and the role of TiB_2 in densification were investigated. Mechanical and electrical properties of the composites obtained were

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Journal of the European Ceramic Society 0955-2219/89/$3.50

Table 1. Comparison of several properties of TiB_2 with TiC

	TiB_2	*TiC*
Specific gravity ($g cm^{-3}$)	4·38	4·93
Microhardness (GPa)	33·7 (HV 0·03)	31·7 (HV 0·05)[b]
Resistance to oxidation[a] ($mg cm^{-2}$)	+10	+26·5
Thermal conductivity ($W m^{-1} K^{-1}$)	122 (2027°C)	40 (2400°C)
Resistivity ($10^{-8} \Omega m$)	9	61[b]

[a] Weight change at 1200°C for 120 min in O_2 atmosphere.
[b] Value for $TiC_{0 \cdot 96}$.

evaluated. Since it is difficult to machine super-hard materials by conventional mechanical methods such as grinding, because of their own high hardness, it is necessary to use an alternative method. The electrical property was measured in order to evaluate whether the composites could be machined by electrical discharge machining.

2 Experimental

Starting powders used in the experiments were Al_2O_3 (mean particle size 0·2 μm and 99·9% purity from Fujimi Kenmazai Kogyo Ltd, Inazawa, Japan) and TiB_2, with 1·4 wt% oxygen content and 20 μm average particle diameter from Hermann C. Stark Berlin (Goslar, FRG). TiB_2 powder was wet-ground for 200 h in an alumina ball-mill to 2 μm.

Al_2O_3 and 0–50 wt% TiB_2 were mixed for 5 h in an alumina ball-mill. After drying, the mixtures were pressed into rods of 8 mm diameter × 20 mm length under 30 GPa. These rods were sintered at 1600–1750°C for 15–120 min under 10^{-2}–10^{-3} Pa. The temperature in the furnace was measured with an optical pyrometer and a WRe5-26 thermocouple.

The composites obtained were identified by powder X-ray diffraction (XRD). Their relative density was calculated from the apparent density, which was measured by the Archimedean method, and the theoretical density. The microstructure was examined by scanning electron microscopy (SEM), and bending strength was measured for an as-sintered compact by the three-point bending test. Micro-Vickers hardness was measured at 300 g load for at least ten points on the polished surface. Resistivity was measured at DC 10V.

3 Results and Discussion

3.1 Sintering behaviour

In patterns of any composites, diffraction lines of Al_2O_3 and TiB_2 were observed, indicating that these were the only phases existing in the composites on sintering. Since the lattice parameters of the composites were in good agreement with those of the raw powders, both components were regarded as being unreactive with each other. Accordingly, theoretical density, d, of a composite can be calculated by the following equation:

$$d = 1/\{(1-x)/d_A + x/d_T\}$$

where d_A is specific gravity of Al_2O_3 (3·99 $g cm^{-3}$), d_T is that of TiB_2 (4·38 $g cm^{-3}$) and x is the weight fraction of TiB_2.

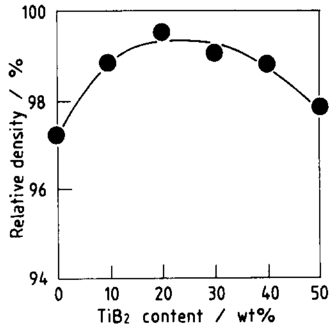

Fig. 1. Relationship between relative density and TiB_2 content of composites prepared at 1750°C for 60 min.

Figure 1 shows the relation between relative density and TiB_2 content of composites prepared at 1750°C for 60 min. Relative density increased with TiB_2 addition from 97% (no TiB_2) to about 99% (10–40 wt% TiB_2). The change in relative density indicates that TiB_2 behaves as a sintering aid and promotes densification. The effect of TiB_2 in inhibiting rapid grain growth of Al_2O_3, as discussed

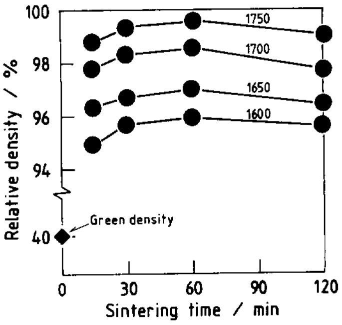

Fig. 2. Densification curves of the composites with 20 wt% TiB_2. Numerals on curves designate sintering temperatures.

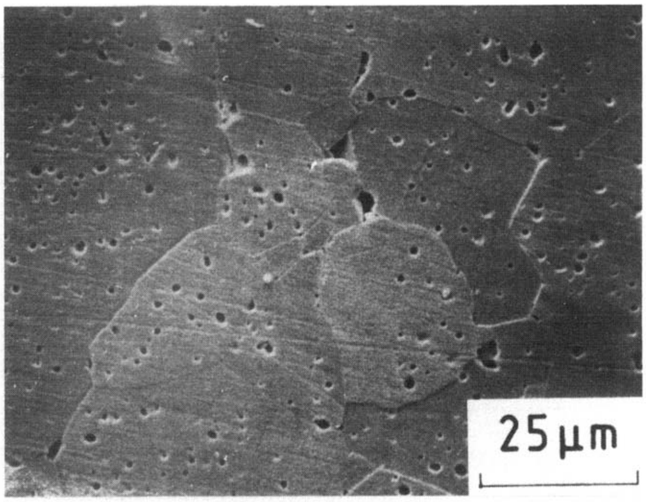

Fig. 3. Polished and etched surface of the pure Al_2O_3 compact. The etching was performed at 200°C for 120 min in H_3PO_4. Note that the dimensions of the pores are enlarged by etching, emphasizing grain boundaries and the number of pores.

in detail later, may contribute to the promotion of densification. Relative density decreased a little with 50 wt% TiB_2. In the case of mixing too much TiB_2, densification was affected by the poor sinterability of TiB_2.

The rate of densification in the composites with 20 wt% TiB_2 was very rapid, as shown in Fig. 2. The relative density, which was about 40% for the green compact, reached 95% at 1600°C after only 15 min; it increased with increasing sintering time up to 60 min but decreased slightly with increasing time up to 120 min. The decrease in relative density on sintering for 120 min is due to the decomposition of Al_2O_3 and/or TiB_2 in the composite, as shown by their weight losses increasing with increasing sintering time. At different temperatures, the composites with maximum relative density were obtained by sintering for 60 min.

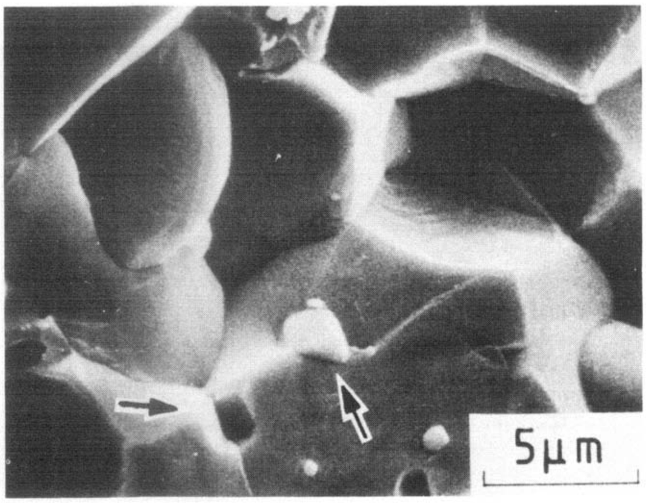

Fig. 4. Fractured surface of the composite with 20 wt% TiB_2. The whitish grains and hollows indicated by arrows correspond to TiB_2 while the greyer areas are Al_2O_3. The hollows are traces of TiB_2 grains, lost when the specimen was fractured.

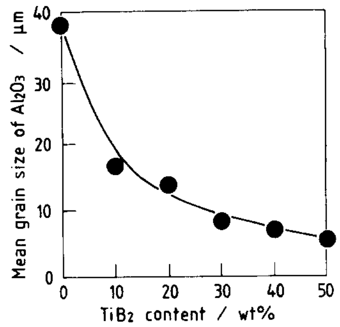

Fig. 5. Effect of TiB_2 content on mean grain size of Al_2O_3 in the composites prepared at 1750°C for 60 min.

Figure 3 shows a scanning electron micrograph of the polished and etched surface of the pure Al_2O_3 compact which was sintered at 1750°C for 60 min. The most important feature of the microstructure is the existence of many pores inside grains. This indicates that the grain growth of Al_2O_3 was very rapid; that is, the pores were entrapped in grains owing to rapid movement of grain boundaries. Since it is difficult to remove such pores inside grains, it is necessary to slow down the movement of grain boundaries. Pores exist also on grain boundaries. Existence of these pores causes a decrease in density of the composite. The grain growth was so significant that the largest grain was about 60 μm in size.

On the other hand, few pores were observed on grain boundaries in the composite with 20 wt% TiB_2 (Fig. 4). Such pores inside grains as shown in Fig. 3 were not observed on the polished surface of this specimen. The growth of Al_2O_3 grains was not as significant as in the composite without TiB_2. The mean grain size of Al_2O_3 was plotted against TiB_2 content (Fig. 5). It is recognized that TiB_2 effectively inhibited grain growth of Al_2O_3. TiB_2 has slowed down movement of the grain boundaries, so that no pore was entrapped in grains. The whitish grains and the hollows indicated by arrows in Fig. 4 correspond to TiB_2. It can be confirmed that they were localized on the grain boundaries of Al_2O_3.

3.2 Characterization

Figure 6 shows the increase in bending strength with increasing relative density, caused by the decrease in porosity as occurs in most materials. The largest value of bending strength observed in the present study was 310 MPa, comparable to that of Al_2O_3 ceramics having a similar grain size.[11] Thus, it is recognized that TiB_2 addition confers little improvement on bending strength.

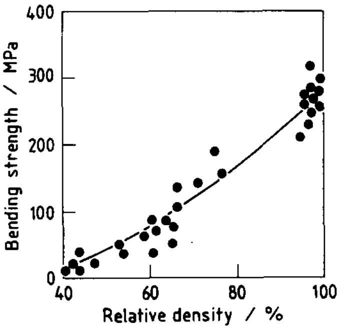

Fig. 6. Change in bending strength with relative density.

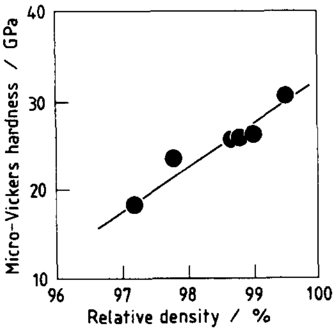

Fig. 7. Change in microhardness (HV 0·3) with relative density.

Figure 7 shows the linear increase of micro-Vickers hardness with increasing relative density, also due to the decrease in porosity. The largest value of hardness exceeded that of Al_2O_3 (19·1 GPa)[12] and reached 30·1 GPa, indicating that TiB_2 addition improves hardness. Moreover, its improvement was very significant with even a slight addition, as the largest value of hardness was observed with 20 wt% TiB_2, and was closer to the value of 33·7 GPa for pure TiB_2 rather than that of Al_2O_3.

Figure 8 shows the relationship between resistivity and relative density. A logarithmic plot of resistivity against relative density gave a straight line, due to the increase in effective sectional area for conduction with decreasing pore size. The resistivity also decreased with increasing TiB_2 content (Fig. 9) from $6 \times 10^7\,\Omega m$ (20 wt% TiB_2) to $3 \times 10^{-2}\,\Omega m$ (30 wt% TiB_2). Whereas TiB_2 grains dispersed discretely in the composites with up to 20 wt% TiB_2, they became connecting with 30 wt% TiB_2. The connection between electrically-conductive TiB_2 grains caused a significant decrease in resistivity.

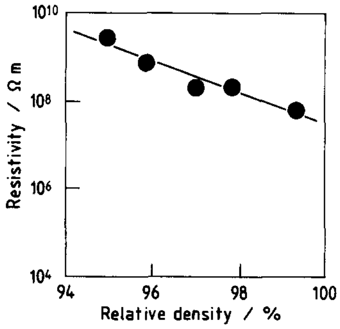

Fig. 8. Change in resistivity with relative density of the composites with 20 wt% TiB_2.

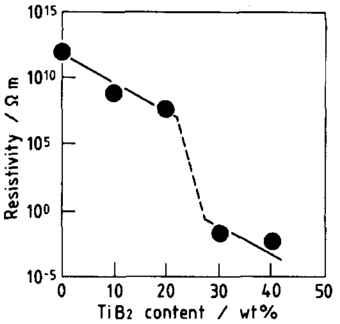

Fig. 9. Effect of TiB_2 content on resistivity of the composites prepared at 1750°C for 60 min.

The resistivities of the composites with up to 20 wt% TiB_2 appear too high to be machined by electrical discharge machining. However, it is expected that this method will be applicable to composites with more than 30 wt% TiB_2, though machining speed may be rather low.

4 Conclusion

The sintering behaviour in the Al_2O_3–TiB_2 system was studied at 1600–1750°C in a vacuum. Promoted densification was observed in the composites with 10–40 wt% TiB_2. The role of TiB_2 was to inhibit rapid grain growth of Al_2O_3, so that TiB_2 behaved as a sintering aid. The maximum values of bending strength and microhardness were 310 MPa and 30·1 GPa, respectively. Resistivity of the composite with more than 30 wt% TiB_2 decreased to less than $3 \times 10^{-2}\,\Omega m$, indicating a possibility that the composites could be machined by electrical discharge machining.

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