Reaction sintering fabrication of (AlN, TiN)–Al$_2$O$_3$ composite[☆]

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Abstract

The (AlN, TiN)–Al$_2$O$_3$ composites were fabricated by reaction sintering powder mixtures containing 10–30 wt.% (Al, Ti)–Al$_2$O$_3$ at 1420–1520°C in nitrogen. It was found that the densification and mechanical properties of the sintered composites depended strongly on the Al, Ti contents of the starting powder and hot pressing parameters. Reaction sintering 20 wt.% (Al, Ti)–Al$_2$O$_3$ powder in nitrogen in 1520°C for 30 min yields (AlN, TiN)–Al$_2$O$_3$ composites with the best mechanical properties, with a hardness HRA of 94.1, bending strength of 687 MPa, and fracture toughness of 6.5 MPa m$^{1/2}$. Microstructure analysis indicated that TiN is present as well dispersed particulates within a matrix of Al$_2$O$_3$. The AlN identified by XRD was not directly observed, but probably resides at the Al$_2$O$_3$ grain boundary. The fracture mode of these composites was observed to be transgranular.
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1. Introduction

Sintered alumina with its unique combination of high hardness, corrosion resistant and wear resistance is a material widely adopted by industry. Unfortunately, the main

shortcoming of alumina is its brittleness, low toughness and sensitivity to thermally induced stress, which makes it prone to catastrophic failure. It has been shown that brittle solids can be toughened by incorporating inclusions into them [1]. Titanium nitride (TiN) has high melting point (2950°C), very good hardness and chemical stability. In that way, the addition of TiN to alumina leads to an improvement in its strength and fracture toughness [2,3]. Aluminium nitride (AlN) has low specific weight, excellent thermal conductivity (319 W m^{-1} K^{-1}) and a thermal expansion coefficient closed to that of alumina [4]. The purpose of this paper is to fabricate the composites in the (AlN, TiN)–Al_2O_3 system combining the useful properties of the three materials using the directed nitridition technique [5].

In this process, inexpensive raw materials, Al, Ti and Al_2O_3, are attrition milled and hot pressed in nitrogen atmosphere. On reaction the compacts transformed into Al_2O_3 composites containing AlN and TiN. In addition, the mechanical properties and the microstructure are analysed.

2. Experimental procedure

The composite compositions studied are given in Table 1. Al_2O_3 (α-Al_2O_3 ≥ 99%, Zhangjiakou Easter Special Ceramic Material Co., Ltd, PR China), and Al (purity ≥ 95%, Tianjin Chemical Reagent Co., Ltd), Ti (purity ≥ 99.9%, Shanghai Chemical Reagent Co., Ltd) were attrition milled together in heptane for 15 h. The grinding medium used was 1Cr8Ni9Ti alloy balls. The mixed slurry was dried in a vacuum. The dried cake was crushed and passed through a 200-mesh sieve. The sintering was performed by hot pressing (High Multi 5000) at 1420 and 1550°C using a graphite die for 30 min. The pressure applied was 30 MPa under flowing nitrogen used as a reactive gas. Its pressure was kept 0.9 MPa. The dimensions of the hot pressed specimens were 42 mm dia. × 5 mm thick.

The final density was determined by Archimedes' principle. The sintered speci-mens were cut with a diamond saw and ground into 3 mm × 4 mm × 36 mm pieces. Three-point-bending strength (span 30 mm) was evaluated with a strain rate of 0.5 mm min^{-1}. The fracture toughness (K_{IC}) was performed by Vickers' indentation with a load of 308.7 N and holding time of 5 s. The phase identification was made by XRD (Rigaku Denk D/max-rA, Japan). Specimens were polished by grinding with diamond slurry to 3.5 μm. The composition distribution was determined with Electron Probe Microanalyser (EPMA; JEOL JXA-8800R, Japan). Samples were

Table 1
Compositions of starting powders

Sample	Al (wt.%)	Ti (wt.%)	Al_2O_3 (wt.%)
Z1	5	5	90
Z2	10	10	80
Z3	15	15	70

thermal etched in air in 1350°C for 30 min to reveal the grain boundary of the Al_2O_3. The thermally etched surface, and fracture surface microstructures were observed by SEM (Hitachi S-2500, Japan).

3. Result and discussion

3.1. Phase composition of composites

In the process nitrogen was used as sintering atmosphere. Both Al and Ti in the starting powder could react with N_2 to form AlN and TiN:

$$2Al + N_2 = 2AlN \tag{1}$$

$$2Ti + N_2 = 2TiN. \tag{2}$$

The thermodynamic calculation of ΔG^0 for reactions 1 and 2 [6] gave value of 282.47°C and -374.77 kJ mol^{-1} respectively at 1600 K. From the Van't Hoff formula the equilibrium pressures of nitrogen for the two reactions at 1600 K are 6.08×10^{-5} and 5.89×10^{-8} Pa, much lower than the pressure used for the hot pressing experiments. The nitrogen partial pressure was kept at 0.9 MPa, which was far higher than the calculated equilibrium value. So the reactions 1 and 2 were thermodynamically possible.

The XRD patterns of powder mixtures containing 20 wt.% (Ti, Al)–Al_2O_3 milled 15 h and after hot processing at 1420°C for 0.5 h are shown in Fig. 1. The mixed
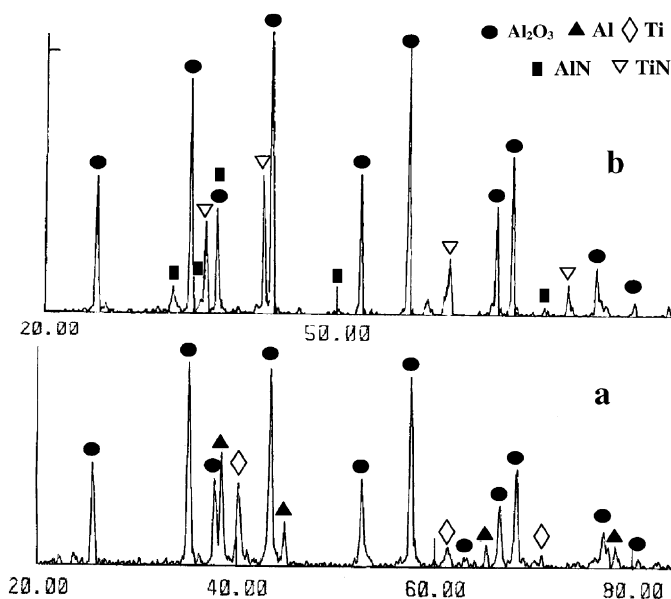

Fig. 1. X-ray diffraction spectrum of 20 wt.% (Ti, Al)–Al_2O_3 powder (a) milled 15 h and (b) sintered at 1420°C, 30 min.

powder consists of Al, Ti and α-Al_2O_3, indicating that no reactions take place during milling. In the sintered sample, peaks related to Al and Ti can no longer be identified, whereas new peaks appear. XRD analysis reveals that the new phase compositions consist of AlN and TiN. So Al and Ti in the starting powder have respectively reacted with N_2 to form AlN and TiN during sintering. In addition, the nitridation of the metal powders seems to be complete with the limits of the XRD detection limits.

3.2. Sintering process of composites

The relative densities of the fired composites are shown as a function of Ti, Al content and sintered temperature in Fig. 2. The sintered temperature can increase the relative density of the specimens with the starting powders containing 10 and 20 wt.% (Al, Ti), however, a higher fired temperature decreases the density of the sample with 30 wt.% (Al, Ti) content. The value of relative density increases with increasing (Al, Ti) contents of the original powder, indicating that the addition of Al and Ti aids densification of the composites. When sintering the starting powder containing 30 wt.% (Ti, Al) at 1450°C, the relative density is >98%. Whereas, to get the same density with the starting powder of 20 wt.% (Ti, Al) it needed to be sintered at 1520°C and the 10 wt.% (Ti, Al) powder should be sintered at about 1550°C. The element distribution of the sintered samples from 30 wt.% (Ti, Al) powders was not uniform from EMPA analysis.

3.3. Mechanical properties

The hardness of the composites is shown as a function of sintering temperature and starting composition in Fig. 3. The hardness of the composites increase with the increasing sintering temperature and decrease with increasing AlN and TiN contents consistent with the higher sintered densities. When hot pressing at 1520°C, the hardness of the sintered composite of 20 wt.% (Al, Ti) starting powder can reach a Rockwell hardness HRA of 94.1. The hardness values of the three composition specimens are all higher than HRA 90.
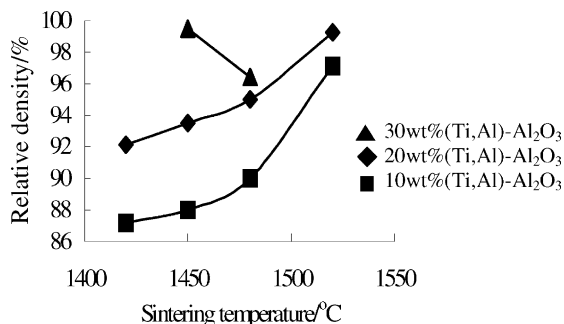

Fig. 2. Relative densities of the Ti–Al–Al_2O_3 powders of different content at different sintering temperatures.
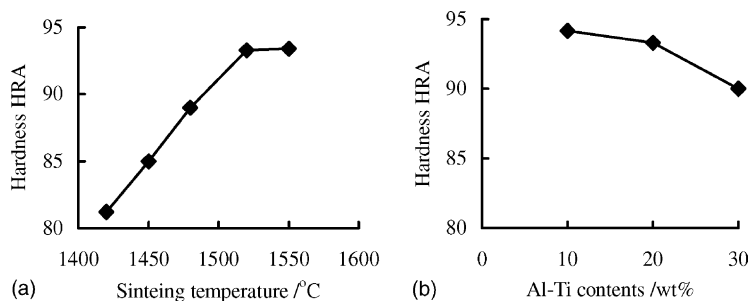
Fig. 3. Variation of the Rockwell hardness HRA (a) of 20 wt.% (AlN, TiN)–Al_2O_3 composites with sintering temperature and (b) with Ti–Al contents.

The bending strength and toughness of the composites, as average values for four to six specimens, is shown as a function of sintering temperature in Fig. 4.

It can be seen that the bending strength and toughness increase with increasing hot pressing temperature. We see that once the density of >99% is achieved (around 1520°C) the properties reach a maximum and then remain on a plateau. The strength and toughness of the sintered sample of 20 wt.% (Al, Ti) starting composition are 687 MPa and 6.5 MPa m$^{1/2}$, respectively. For comparing the mechanical properties of the composites, the alumina powder was hot-pressed at 1650°C for 30 min. The bending strength and fracture toughness of the Al_2O_3 were 361 MPa and 4.9 MPa m$^{1/2}$, which are lower than that of the composite.

3.4. Composite microstructure

Fig. 5 shows an SEM micrograph of an AlN–TiN–Al_2O_3 polished surface for the 20 wt.% (Al, Ti)–Al_2O_3 composition sintered at 1520°C and the corresponding X-ray images for N, O, Al, Ti observed with EPMA. Combining these results with the XRD findings, the bright particles are identified as TiN and dark phase is Al_2O_3. The TiN is a well dispersed particulate phase in a matrix of Al_2O_3, and the grains appear to be elongated. The melting point of aluminium is relatively low, a small
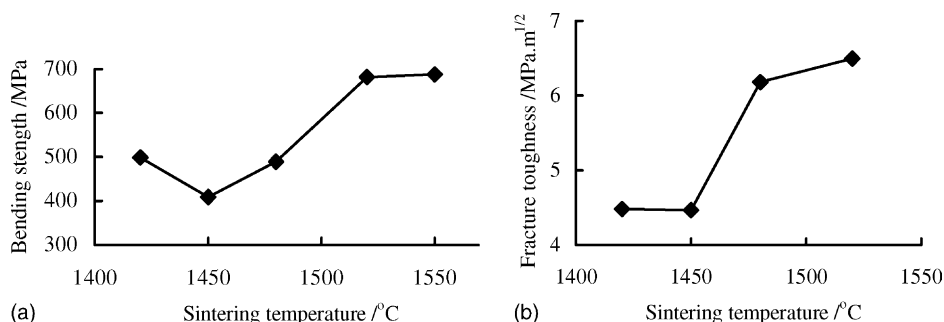

Fig. 4. Variation of (a) bending strength and (b) the fracture toughness (K_{IC}) of 20 wt.% (AlN, TiN)–Al_2O_3 composite with sintering temperature.
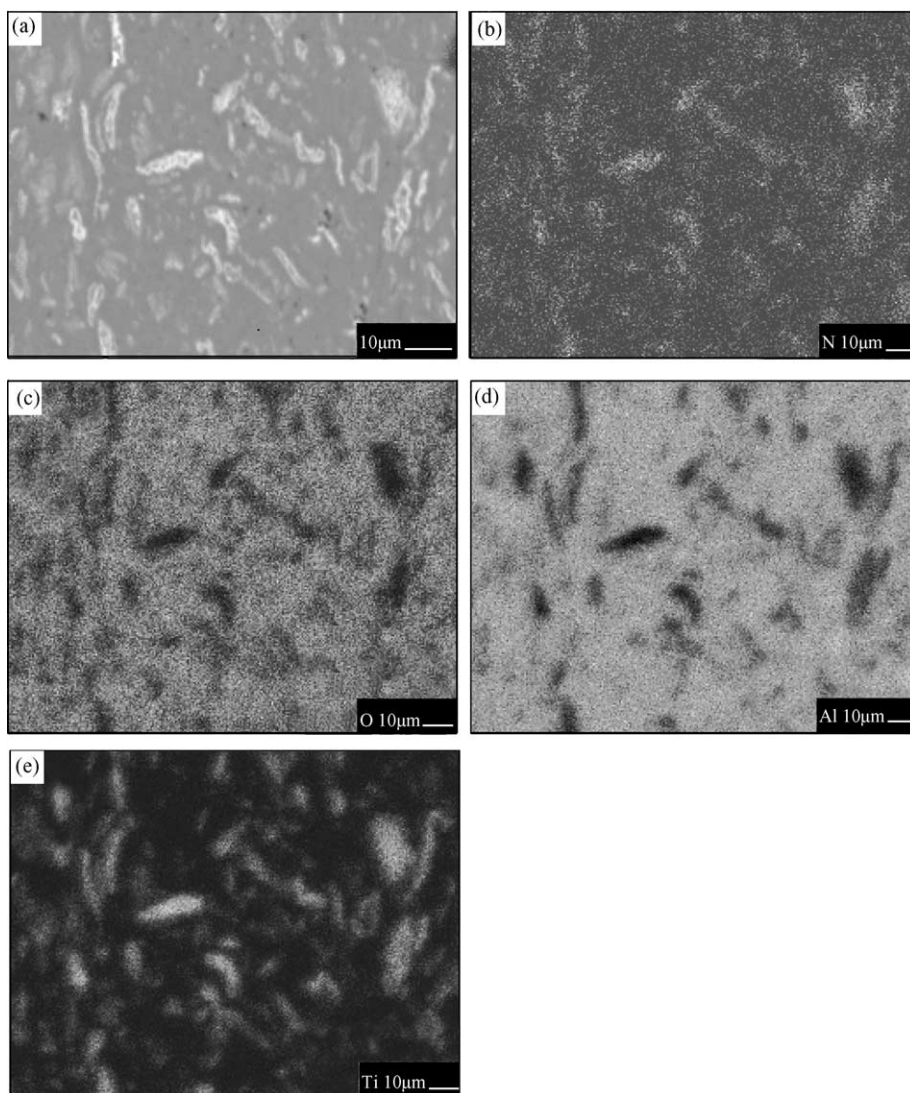
Fig. 5. EPMA observation of AlN–TiN–Al$_2$O$_3$ sample surface micrograph (a) and X-ray images of N (b), O (c), Al (d) and Ti (e), respectively. Bar = 10 μm.

quantity of liquid aluminium may form and transform into AlN (seen in XRD) possibly located at grain boundaries of the alumina and coexisting with titanium nitride.

The morphology of the as-received Al$_2$O$_3$ particles is shown in Fig. 6. The shape is approximately equiaxed and the average size is estimated about 3 μm from SEM photographs. The composites of 20 wt.% (AlN, TiN)–Al$_2$O$_3$ sintered in 1420 and 1520°C were thermally etched at 1350°C for 0.5 h in air to reveal the morphology of the Al$_2$O$_3$ grains. The unpolished surface microstructure in Fig. 7 shows significant elongation of the Al$_2$O$_3$ grains at the high temperature.
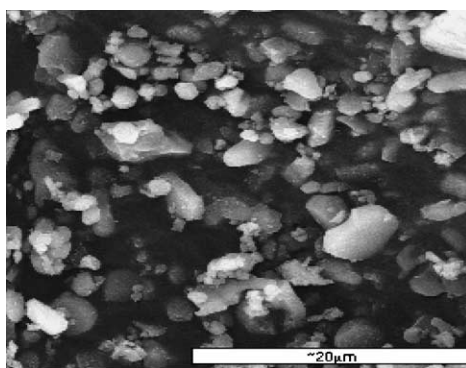
Fig. 6. The morphology of the as-received Al_2O_3 powder.

Typical interactions between the indentation crack and composite microstructure are shown in Fig. 8. When 20 wt.% (Al, Ti) is added to Al_2O_3, the toughness of the composite is increased from 4.47 to 6.5 MPa m$^{1/2}$ when hot pressed at 1520°C, implying that the presence of TiN and AlN enhance the toughness of Al_2O_3. Fig. 8 indicates the cracks can propagate though the TiN grains, indicating that the strength of Al_2O_3 and TiN (AlN) interface is high. The TiN (and possibly AlN) can also inhibit the propagation of cracks, as cracks were not always continuous. The toughness of the composite is therefore improved.

The fracture surfaces of AlN–TiN–Al_2O_3 composites of 20 wt.% (Al, Ti)–Al_2O_3 starting composition sintered at 1420 and 1520°C are shown in Fig. 9. It can be seen that the composite structure is significant porosity (around 8%) when the sintering temperature is 1420°C, and the fracture mode is an intergranular fracture. As the sintering temperatures are elevated to 1520°C, we approach full density (>99%) and the structure is very compacted. Transgranular fracture is its main fracture mode, which is the major reason for the high mechanical properties.
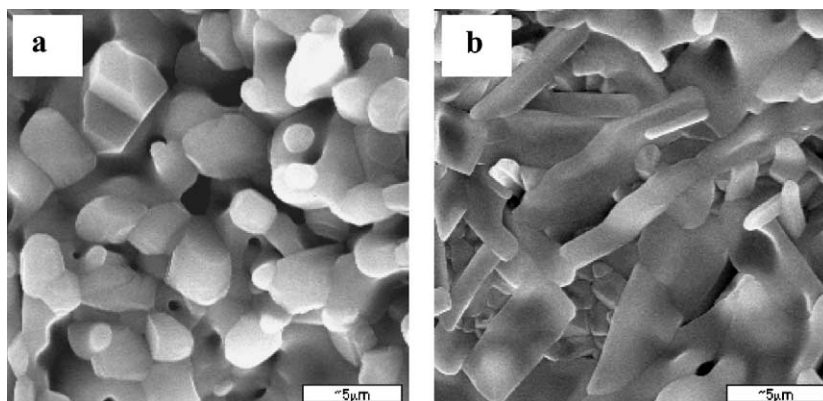

Fig. 7. SEM of surface of thermally etched AlN–TiN–Al_2O_3 composites prepare from hot-pressed (a) 1420°C and (b) 1520°C, respectively.
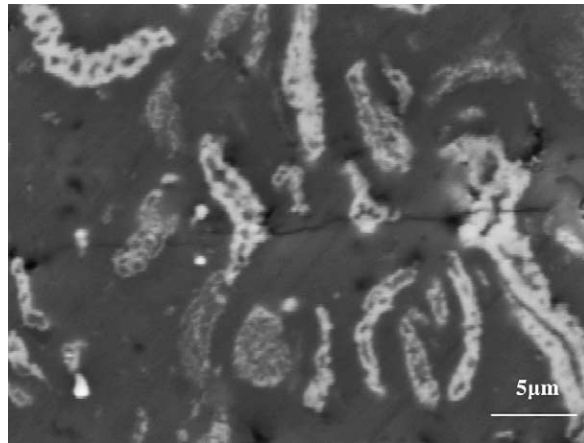
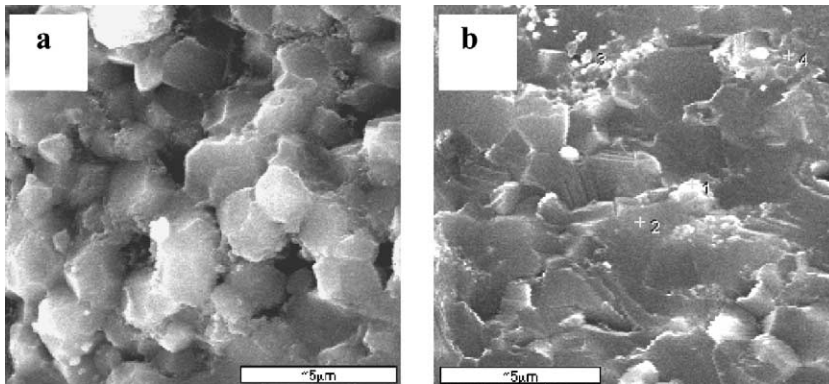Fig. 8. Interactions between crack and TiN, AlN grains, crack is introduced to surface by indentation.

Fig. 9. SEM micrograph of fracture surface of 20 wt.% (AlN, TiN)–Al_2O_3 at different sintering conditions (a) 1420°C, 30 min and (b) 1520°C, 30 min.

4. Conclusions

1. AlN–TiN–Al_2O_3 composites have been produced by ball milling Al, Ti and Al_2O_3 mixtures and direct reaction with N_2 in a hot-press producing composites with relative densities higher than 98%.

2. Mechanical properties of the composites depend on hot processing parameters and starting compositions. For a 20 wt.% (Al, Ti)–Al_2O_3 powder mixture sintered at 1520°C for 0.5 h, the composite Rockwell hardness was HRA 94.1, bending strength was 687 MPa and toughness was 6.5 MPa $m^{1/2}$.

3. The microstructure of the composites was observed, indicating that TiN exists as a well dispersed particulate phase in a matrix of Al_2O_3. AlN was not directly observed but detected by XRD and may exist at the TiN–Al_2O_3 grain boundary interface.

4. Fully dense composites (>99%) show excellent mechanical properties and a transgranular fracture mode.

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