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RBAO Composites Containing TiN and TiN/TiC

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Abstract

TiC and TiN were tested as candidate materials for particle reinforcement of reaction bonded aluminium oxide (RBAO). As part of the reaction bonding process Al-containing green bodies have to be heated in air in order to oxidize the Al; therefore the oxidation behaviour of any added particles is of critical importance. Previous studies have shown that neither TiC nor TiN is sufficiently oxidation-resistant to withstand the heating cycle necessary to completely oxidize the Al in the process. Therefore, two alternative approaches were investigated. First, TiC and TiN were retained in incompletely reacted RBAO, resulting in an Al_2O_3–TiC/TiN composite with alloy and possibly intermetallic phases. These metal phases were obtained from Al and Ti/Zr which formed when Al reduced TiO_2 and, to a lesser extent, ZrO_2. Second, the reaction of AlN and TiO_2 to form Al_2O_3 and TiN at temperatures above 1350°C was investigated. The resulting material contained Al_2O_3, ZrO_2, TiN and a nitrogen-containing aluminium titanate. © 1996 Elsevier Science Limited.

TiC und TiN wurden als Kandidatmaterialien zur Partikelverstärkung von reaktionsgebundenem Aluminiumoxid (RBAO) untersucht. Da die Al-haltigen Grünkörper als Teil des Prozesses an Luft einer Wärmebehandlung unterzogen werden, ist die Oxidationsbeständigkeit der zugesetzten Partikel von großer Bedeutung. Voruntersuchungen haben gezeigt, daß weder TiC noch TiN ausreichend oxidationsbeständig sind, um den zur Al-Oxidation erforderlichen Heizzyklus zu überstehen. Aus diesem Grunde wurden zwei alternative Verfahren untersucht. Im ersten Verfahren wurden TiC und TiN in unvollständig reagiertem RBAO erhalten. Dies resultierte in einem Al_2O_3–TiC/TiN Verbundmaterial mit Legierungen und möglicherweise intermetallischen Phasen. Diese Phasen enthielten Al und Ti/Zr; die letzteren entstanden bei der Reduktion von TiO_2 und, in geringerem Grad, ZrO_2, durch Al. Im zweiten Verfahren wurde die Reaktion von AlN und TiO_2 zu Al_2O_3 und TiN bei Temperaturen oberhalb 1350°C untersucht. Das dabei entstandene Material enthielt Al_2O_3, ZrO_2, TiN, sowie ein stickstoffhaltiges Aluminiumtitanat.

1 Introduction

The toughening of ceramic materials by incorporating submicrometre-sized particles is of considerable interest because of the dramatic improvements in the mechanical properties of ceramics by adding as little as 5 vol% nanometre-sized particles.[1] For Al_2O_3/SiC, Niihara[1] reported room-temperature increases in toughness from 3·5 to 4·8 MPa $m^{1/2}$. Other workers have found less dramatic, but still significant, improvements of mechanical properties such as bending strength and wear resistance.[2] TiC and TiN offer additional interesting properties because of their hardness and elastic modulus. The low electrical resistivity of TiC and TiN can also make composites containing these materials suitable for electrical discharge machining. Alumina/TiC composites show improved wear resistance and find application for cutting tools, while alumina/TiN composites are promising materials for cutting tools and bearings.

The reaction bonding of aluminium oxide (RBAO) was developed recently at TUHH as a method of fabricating high-strength, fine-grained, low-shrinkage alumina, mullite, or composites of these materials.[3,4] In this process, Al/Al_2O_3 mixtures are attrition-milled in non-aqueous milling media to avoid hydrolysis of the Al. The green bodies are heat-treated in air to oxidize the metal phase to nanometre-sized oxide particles which sinter and bond the original alumina particles. The oxidation of Al is accompanied by a 28% volume increase which partially compensates for the sintering shrinkage. In most cases, ZrO_2 is introduced by the wear of TZP milling balls and helps to control grain growth and improve the mechanical properties. The resulting materials have a fine grain size of approximately 1 μm. The necessity of firing RBAO green bodies in air in order to oxidize the Al makes the oxidation behaviour of any added non-oxide particles a crucial factor. TiN is reported to show superior oxidation resistance to TiC.[5,6] However, TiN powder has been reported to be completely oxidized at a temperature of 700°C after heating in air at a rate of 5°C min^{-1}.[7] At this temperature, the oxidation of Al in the reaction bonding process is not completed.[3,8] Although the temperature at which complete Al oxidation is achieved will vary with parameters such as milling intensity, compaction pressure and powder composition, a value below 800°C has never been reported. Only in the presence of ZrO_2 does oxidation of Al occur at somewhat lower temperatures than in ZrO_2-free samples.[8]

The purpose of this work was to explore two alternative methods of fabricating TiN and TiN/TiC-containing RBAO composites. In the first method, the fact that Al is capable of reducing the oxides of various other metals was used to fabricate metal/ceramic composites by firing partly reacted RBAO bodies containing Al and metal oxides, such as TiO_2 or ZrO_2, in an inert atmosphere. In our case, Al was reacted with TiO_2, and, to a lesser extent, ZrO_2, to form different intermetallic Al/Ti/(Zr) phases. By firing partly reacted RBAO bodies in an inert atmosphere, it was also possible to retain non-oxide particles in the composite which would otherwise not survive the complete oxidation step.

In the second method, a reaction sintering process was investigated as an alternative approach to achieve TiN-containing RBAO. In this method, instead of directly adding TiN to the precursor powder, TiN was obtained by an exchange reaction during the heating process: AlN and TiO_2 were reacted to form TiN and Al_2O_3 at temperatures above 1350°C.[9,10] The oxidation resistance of AlN up to a temperature of 800°C[11] makes this an interesting route for the reaction bonding process.

2 Experimental

The starting materials and the compositions of the precursor powders used in this work are listed in Table 1. The powder batches were attrition-milled for 6 h at 680 rev min^{-1} in an alumina vessel using 3 mm TZP balls and ethanol as milling medium. A small volume of air was passed into the vessel during milling to ensure complete passivation of the Al phase and allow safe handling of the milled powders. The powders were dried for 2 days in a porcelain bowl at room temperature in a fume-hood and sieved through a 125 μm sieve. Bars were uniaxially pressed at 50 MPa, followed by isopressing at 300 or 200 MPa, with the exception of K5AlN/TiN samples, which were only uniaxially pressed. Phase analysis was carried out using a Siemens X-ray diffractometer and Cu K_α radiation. Differential thermogravimetric analyses and thermogravimetric analyses (DTA/TG) were carried out in air up to 1000°C at a heating rate of 1°C min^{-1}.

The K5TiC samples were heated in air to 480°C; at this temperature the TiC was completely oxidized as indicated by previous DTA/TG data while most of the Al remained unoxidized, followed by sintering in argon at 1600°C for 2 h; this treatment was designated cycle A. The sample of the same batch for scanning electron microscopy (SEM) was sintered at 1550°C for 90 min. In order to fabricate TiN-containing composites, the K5TiN1 and K5TiN2 samples were heated in air to 520°C; at 520°C approximately half the original TiN was oxidized according to DTA/TG, followed by sintering in argon at 1600°C for 2 h; this treatment was designated cycle B. To fabricate a TiC-containing composite, the IMC3 samples contained TiO_2 in the precursor powder as an oxygen donor for Al. The presence of TiO_2 eliminated the need for an oxidation step in air and allowed the TiC, pre-added to the composition, to remain unoxidized. These samples were sintered in argon at 1550°C without a prior oxidation step and were designated treatment cycle C. The amount of TiO_2 in the IMG3 composition was calculated to be completely reduced by Al, thus avoiding the formation of aluminium titanate from the remaining TiO_2. The heating/cooling rates for the IMC3 series were 1°C min^{-1} to 1000°C, then 3°C min^{-1} to 1550°C and 10°C min^{-1} to room

Table 1. Powder compositions used in preparation of the samples

Material characteristics, type and source	*Compositions (vol%) and designations*				
	K5TiC	*K5TiN1*	*K5TiN2*	*IMC3*	*K5AlN/TiN*
Al, <50 μm	45	45	45	48	45
Al_2O_3, 0·4 μm, A16, Alcoa	40	40	40	19	25
ZrO_2, 0·57 μm, HSY 3·0, Daiichi Kigenso	5	5	5	5	5
TiC, 1–1·5 μm, H.C. Starck	10	0	0	7·5	0
TiN no. 1, 2 μm, New Japan Metal Corporation	0	10	0	0	0
TiN no. 2, 45 $m^2 g^{-1}$, Tioxide	0	0	10	0	10
AlN, grain size unknown	0	0	0	0	15
TiO_2, 1 μm, rutile, Aldrich	0	0	0	20·5	0

temperature. The K5AlN/TiN samples were heated in air to 720°C, then sintered in Ar at 1550°C for 1·5 h, designated treatment cycle D.

Powder X-ray diffraction (XRD) was used to monitor the phase content after the various heating cycle procedures.

Bars for mechanical property testing were diamond machined for 3 × 3 mm cross-section. The tension side was polished to a 1 μm finish. Flexural strength was measured in four-point bending using an outer span of 20 mm and an inner span of 7 mm with a crosshead speed of 0.2 mm min^{-1}. Fracture toughness was calculated using the Vickers indentation crack method with loads of 100 N.

3 Results and Discussion

3.1 Oxidation of TiN and TiC particles during RBAO process

DTA/TG data of the K5TiC and K5TiN samples showed no further weight gain after 800°C (see Figs 1 and 2). The DTA/TG data at 800°C correlate well with reported data measured at 820°C on ZrO_2-containing RBAO.[3]

In order to investigate the oxidation behaviour of the TiC and TiN phases, DTA/TG was performed on pure TiC and TiN powders. The DTA data of TiC exhibited a single maximum of the reaction rate at 400°C (see Fig. 3). The TG recorded no further weight gain after 480°C. The DTA data of the TiN powder had two maxima in the reaction rate, one at 470°C and a second more pronounced one at 590°C, with no further weight gain after 680°C (Fig. 4).

The results of the DTA/TG measurements indicate that the oxidation of TiC and TiN is completed by 480°C and 680°C, respectively. These values are considerably lower than the 800°C found necessary to completely oxidize the Al in the reaction bonding process. The oxidation behaviour of TiN in a fabricated composite was also monitored by XRD. After heating a K5TiN2 sample in air to 550°C, TiN could no longer be detected; the material now exhibited strong rutile peaks instead (see Fig. 5) in addition to Al_2O_3 and tetragonal ZrO_2 phases.

As TiN could be clearly identified in the precursor composite batch powder, this result indicates that a substantial fraction of the initial TiN was already oxidized to TiO_2 at 500°C. Aluminium was still detectable in the 550°C-sample, although the intensity of the peaks had diminished considerably. After heating in air to 820°C, the intensity of the rutile peaks had increased further and no remaining Al could be detected. The K5TiC sample showed the same phase composition after heating to 820°C. These results indicate that neither TiC nor TiN is

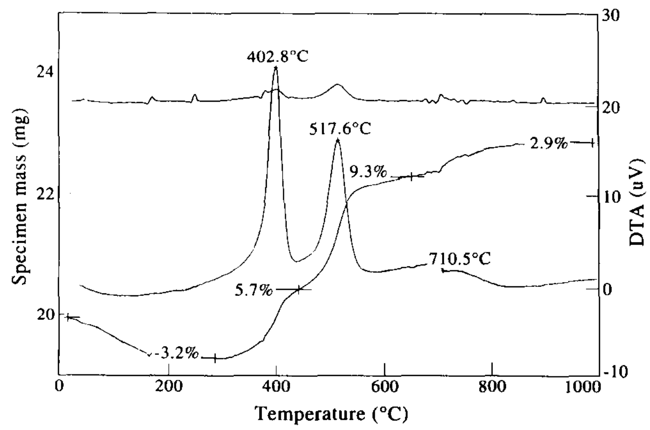


Fig. 1. DTA/TG of K5TiC.

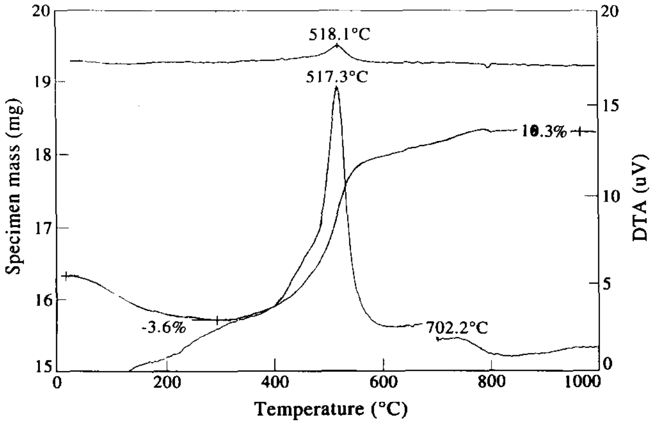


Fig. 2. DTA/TG of K5TiN.

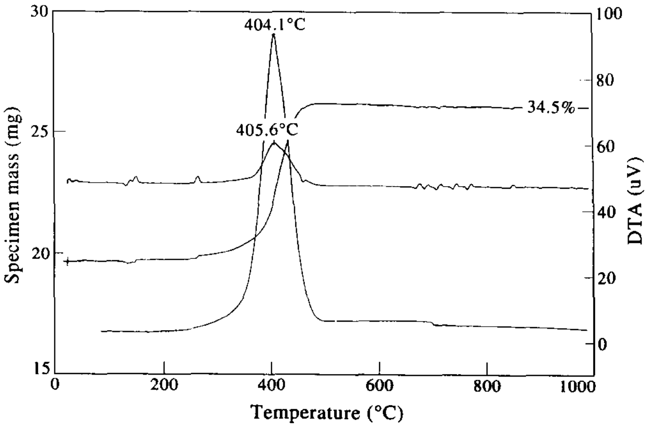


Fig. 3. DTA/TG of TiC.

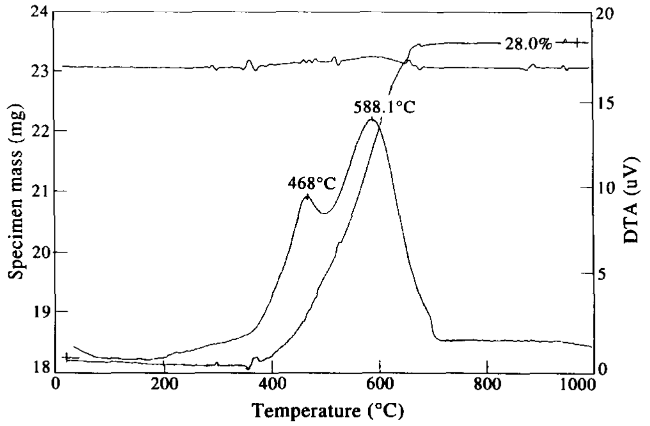


Fig. 4. DTA/TG of TiN.

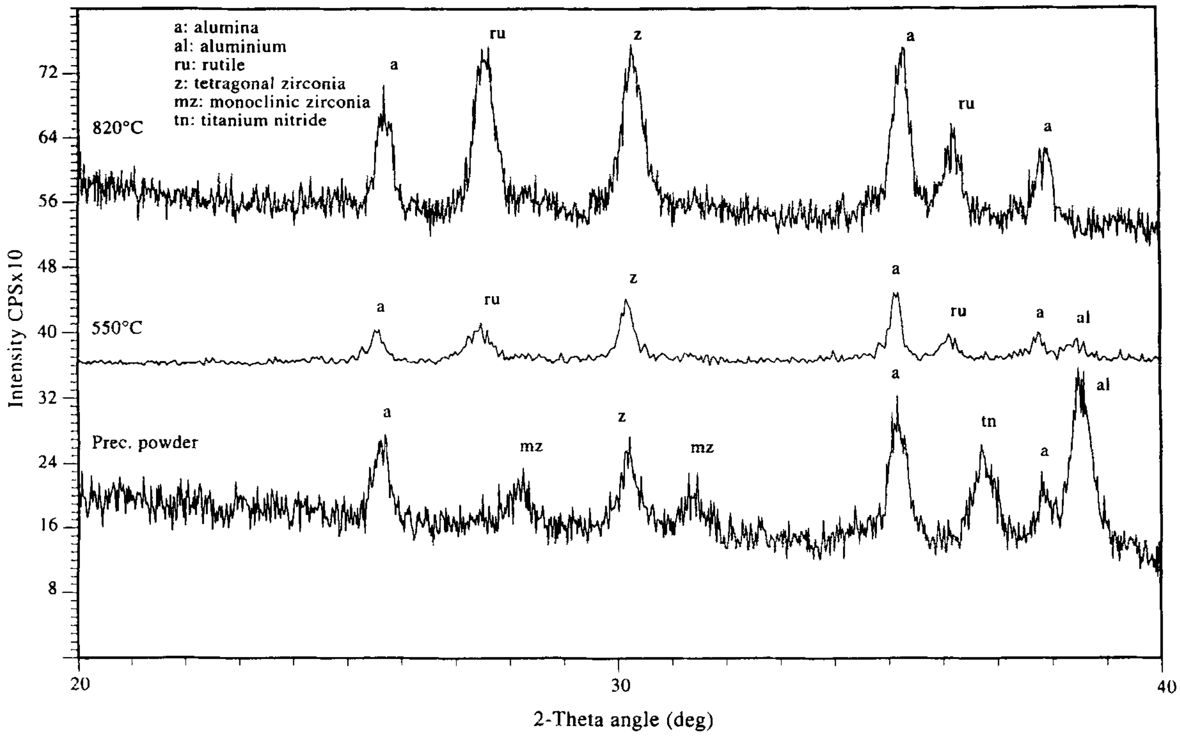


Fig. 5. XRD of K5TiN2 after heating to different temperatures.

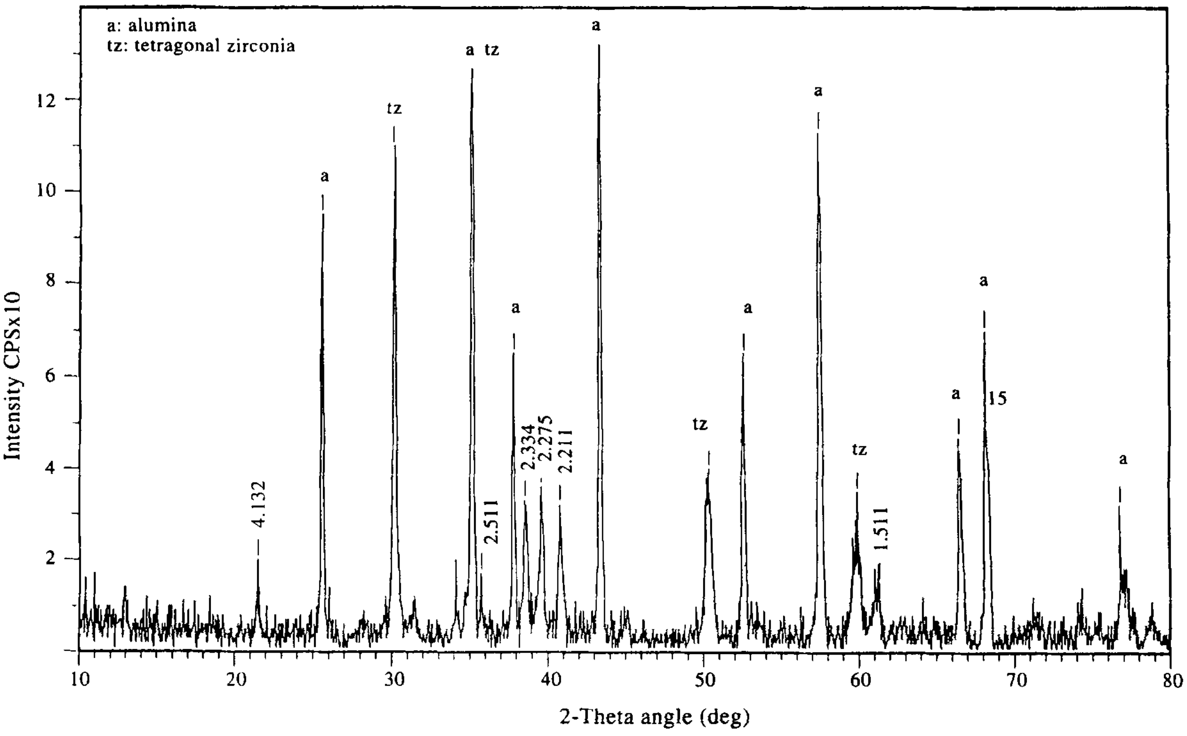


Fig. 6. XRD of K5TiC heated in air to 480°C, then sintered in argon at 1600°C for 2 h.

sufficiently oxidation-resistant to survive the air heating cycle which is necessary to completely oxidize the Al in the reaction bonding process.

3.2 RBAO composite containing intermetallic phases from incomplete precursor reactions

To investigate the consolidation properties of incompletely reacted Ti-containing RBAO, the firing of samples with incompletely oxidized Al was continued in argon, to 1650°C. XRD of a cross-section of a K5TiC sample sintered according to cycle A revealed that, in addition to Al_2O_3 and ZrO_2, several peaks could not be matched to any phase in the JCPDS file (Fig. 6). No peaks of TiO_2, TiC or aluminum titanate were identified in the spectrum. The absence of TiO_2 is reinforced by the fact that the ZrO_2 peaks are not shifted towards higher 2θ values as is commonly observed when ZrO_2 takes

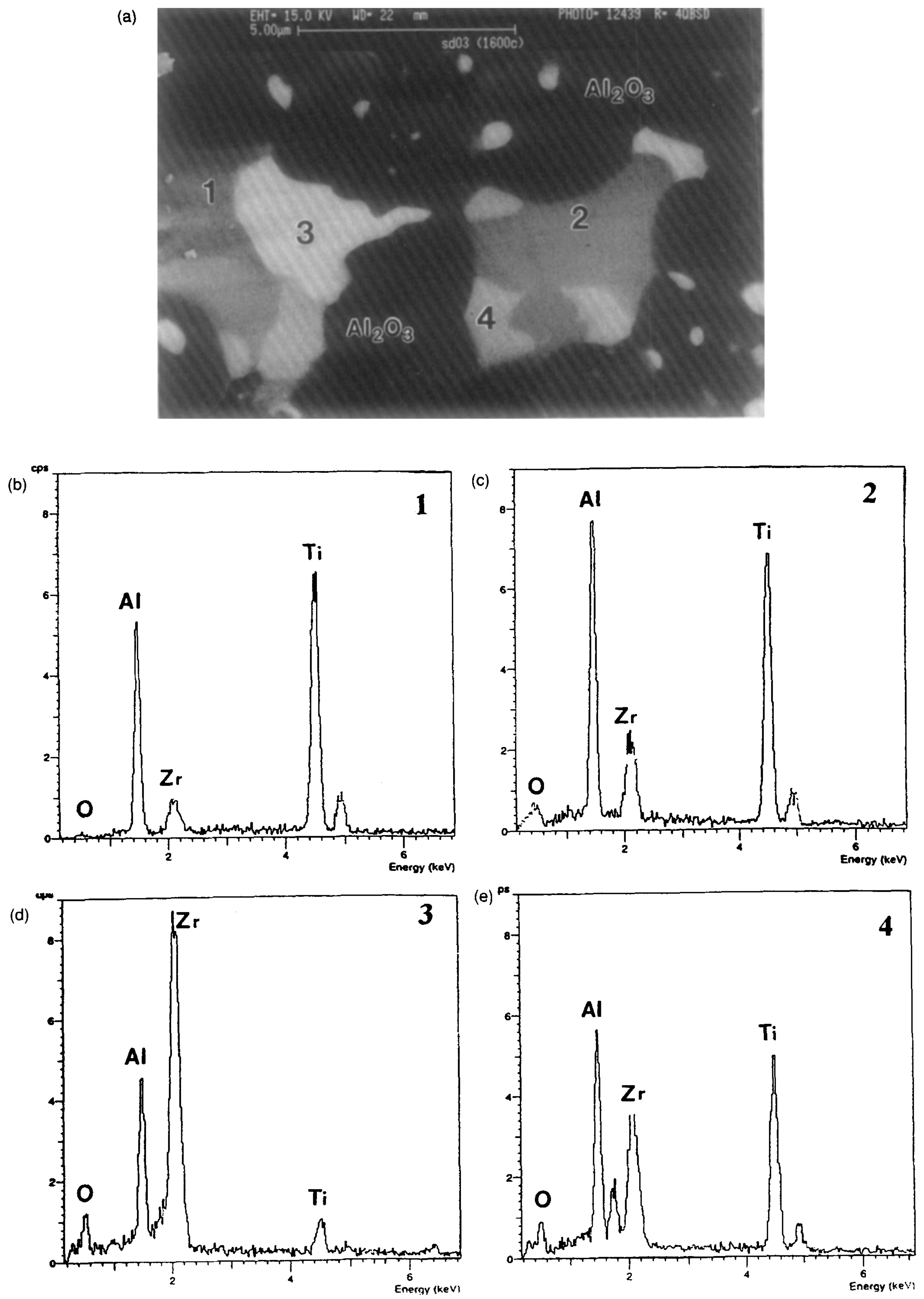


Fig. 7. SEM/EDX of K5TiC heated in air to 480°C, then sintered in argon at 1600°C for 2 h.

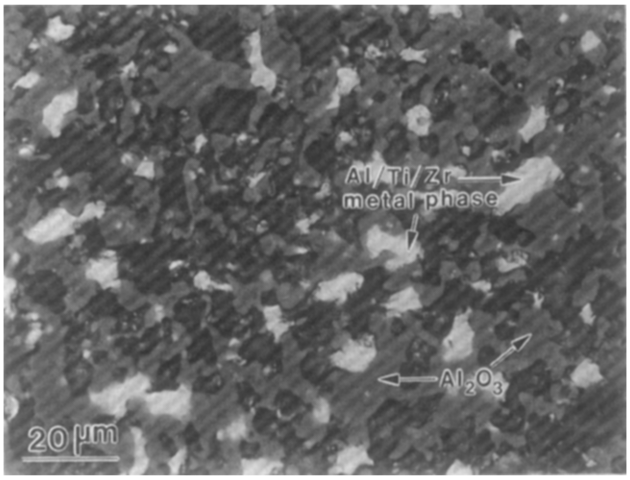


Fig. 8. Optical micrograph of K5TiC heated in air to 480°C, then sintered in argon at 1600°C for 2 h.

up TiO_2 in solid solution,[12] and may also indicate that no TiO_2 was present at high temperatures.

An SEM backscattered electron image and EDX analyses of the material are shown in Figs 7(a)–(e). The EDX analyses, in Figs 7(b)–(e), confirm the presence of different Al/Ti alloy phases. Figure 7(b) shows an Al/Ti phase with small amounts of Zr; estimations of the peak heights indicate that this phase contains Al and Ti approximately in a 1:1 ratio indicating that it may be at the intermetallic composition. A second intermetallic phase which also contains Al and Ti in a 1:1 ratio, but has a higher Zr content is shown in Fig. 7(c). It is possible that there is a third intermetallic phase, Fig. 7(e), but the relatively high oxygen peak measured here makes it possible that this phase is actually zirconia; the presence of Al and Ti peaks in the EDX spectrum could be ascribed to electron-beam spread.

The presence of ternary intermetallic phases explains why no matches for the XRD peaks were found in the JCPDS file, where only binary metallic phases of Al, Ti and Zr are listed. An optical micrograph of the same material sintered according to cycle A is shown in Fig. 8. Sample K5TiC had a bending strength of 240 MPa of a density of 80%.

3.3 RBAO composite containing TiN and TiC from incompletely reacted precursors

K5TiN1 and K5TiN2 samples sintered according to cycle B were 95% dense. XRD of cross-sections indicated the presence of TiN in the sintered material. In the case of K5TiN1, XRD revealed no phases other than alumina, zirconia and TiN (see Fig. 9). In the case of K5TiN1, XRD indicated alumina, zirconia and TiN (see Fig. 9). In the case of K5Tinl, XRD indicated alumia, zirconia, TiN and further peaks that could not be identified. Both materials show micrometre-sized TiN particles in polished optical microscope sections (see Figs 10(a) and (b)). The K5TiN1 sample had a bend strength of 350 MPa, a toughness of 2.4 MPa $m^{1/2}$ and a hardness of 20.4 GPa. The K5TiN2 sample had a bending strength of 280 MPa, a toughness of 2.4 MPa $m^{1/2}$ and a hardness of 14·6 GPa. The hardness of K5TiN1 is higher than that of TiN-free RBAO (20 vol% ZrO_2), which is 17·8 GPa, albeit this hardness difference might be attributed to the higher ZrO_2 content: 5 vol% vs. 20 vol% for the RBAO materials.

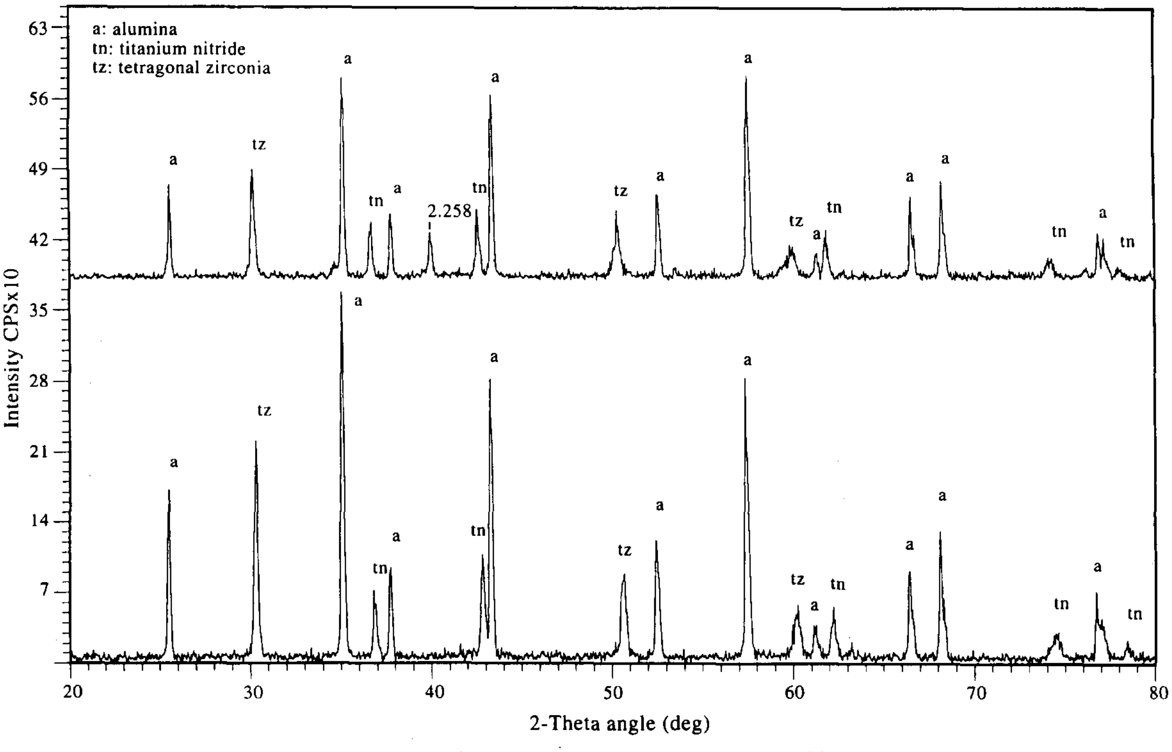
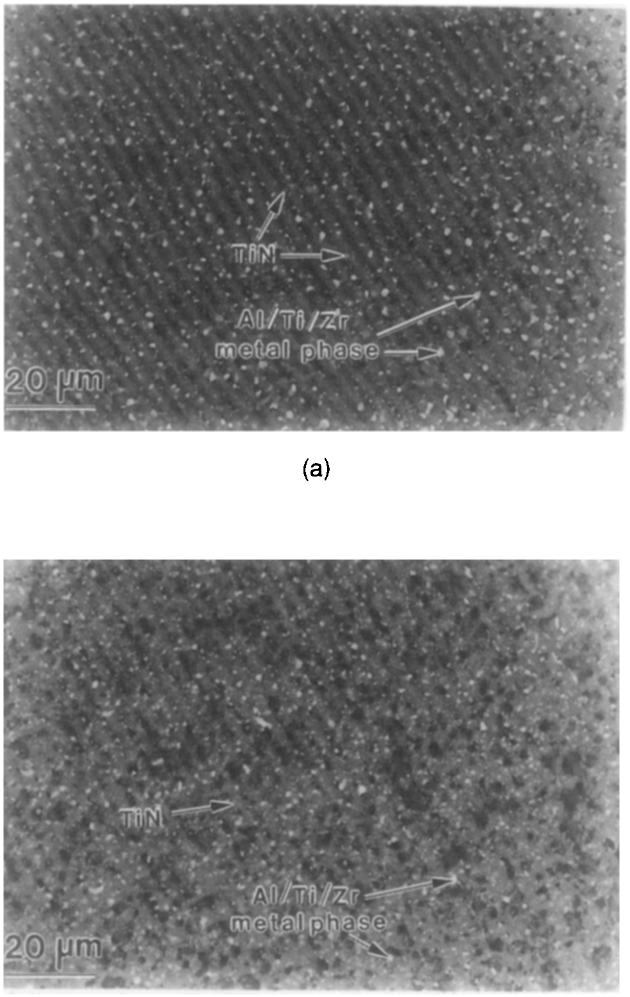


Fig. 9. XRD of K5TiN1 (bottom) and K5TiN2 (top) heated in air to 520°C, then sintered in argon.



(a)

(b)

Fig. 10. Optical micrographs of (a) K5TiN1 and (b) K5TiN2; both samples were sintered in air to 520°C, then sintered in argon at 1600°C for 2 h. Dark matrix material is alumina.

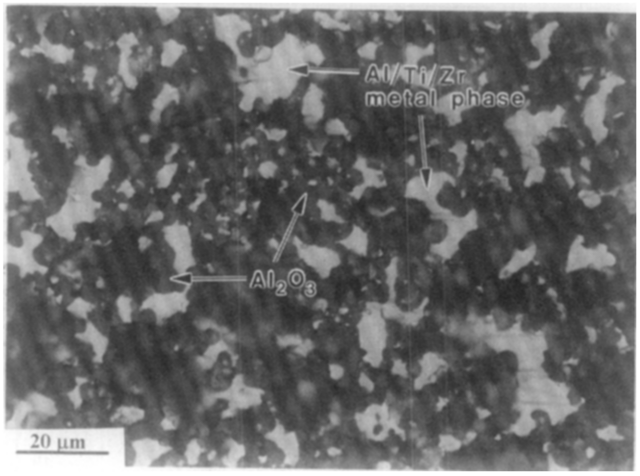


Fig. 12. Optical micrograph of IMC3.

IMC3 samples were 80% dense after sintering and had a bending strength of 170 MPa. The XRD plot of this material is shown in Fig. 11, and the TiC phase can be clearly identified. An optical micrograph of this material is shown in Fig. 12. The metallic phases appear as clusters up to 20 μm in size. The actual grain size could be smaller than the cluster size as the actual grain boundaries were not observed.

3.4 TiN-containing RBAO via reaction of AlN and TiO_2

XRD of a K5AlN/TiN sample indicated no AlN remaining after heating 820°C. The maximum oxidation temperature was reduced to 720°C. XRD of the sample after heating in air to 720°C showed strong rutile peaks, but no remaining TiN, Al or AlN

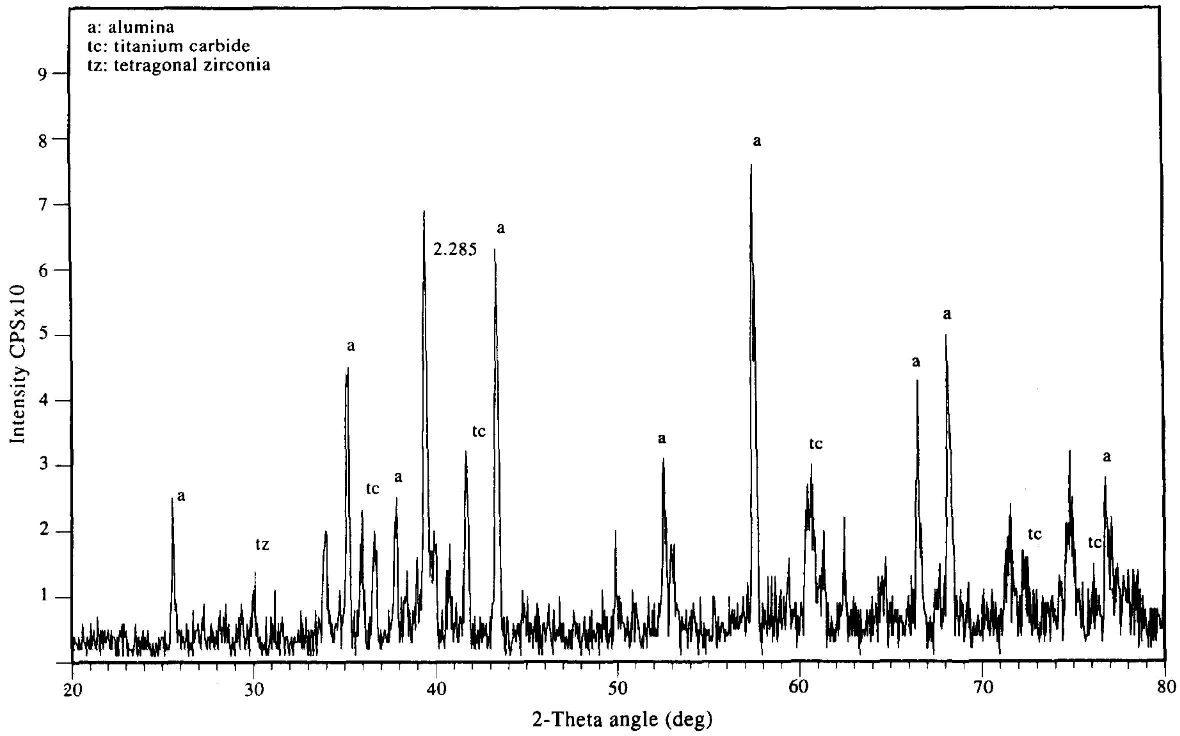


Fig. 11. XRD data for IMC3.

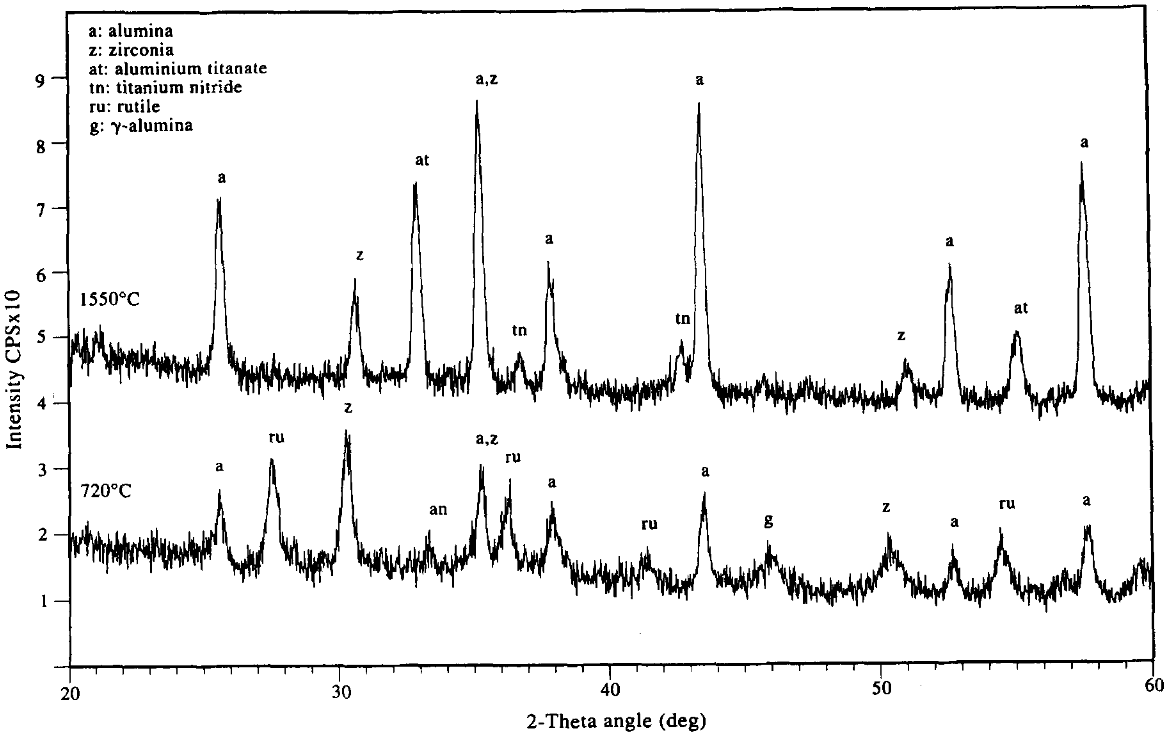


Fig. 13. XRD of K5AlN/TiN after heating in air to 720°C and sintering in argon at 1550°C.

could still be detected. After sintering at 1550°C in argon, XRD revealed alumina, zirconia, a nitrogen-containing aluminium–titanium oxide of pseudobrookite structure[13] (JCPDS No. 42-1279) and TiN (Fig. 13). The material was black overall but showed gold-coloured TiN grains on polished sections in the optical microscope (Fig. 14). Even though these samples were only uniaxially pressed as no isopress was available at the time that the samples were made, they still achieved a 96% fired density, a flexural strength of 280 MPa and a toughness of 3·3 MPa m$^{1/2}$. The average grain size was approximately 2 μm. Transmission electron microscopy (TEM) examination also indicated that no remaining Al was present in the sample that had only been oxidized up to 720°C and that TiN particles were approximately 1 μm in size (see Fig. 15). EDX analysis in the TEM and SEM showed that, in these samples, zirconia generally contained Ti. The alumina phase of K5AlN/TiN examined by EDX in the TEM appears to be Ti-free, but it must be remembered that the solid solubility limit of 0·27 wt%[14] would be below the limit of EDX detectability. The fact that EDX analysis of the alumina phase in the SEM usually shows some Ti can be attributed to electron-beam spread.

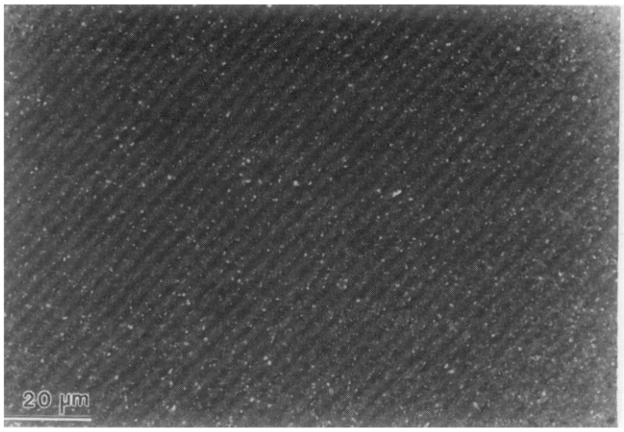


Fig. 14. Optical micrograph of K5AlN/TiN.

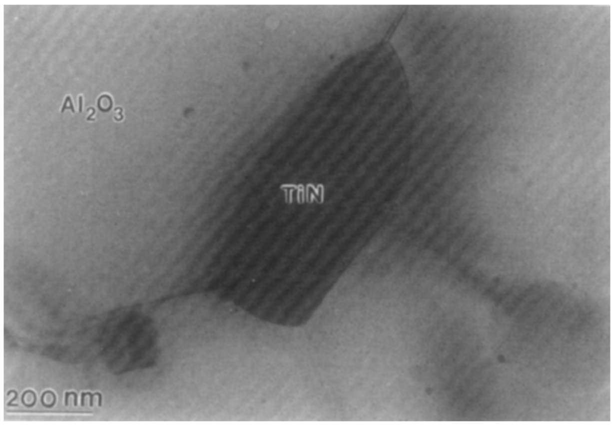


Fig. 15. TEM micrograph of a TiN particle in K5AlN/TiN.

The presence of pseudobrookite (PB) could indicate that the reaction of AlN and TiO$_2$ to form Al$_2$O$_3$ and TiN had not gone to completion, as PB has been previously reported as an intermediate step in the reaction.[10] Another possibility for the presence of PB was that, although in the initial precursor powder the molar ratio of TiN to AlN was 1·5:2 (a ratio that has been reported to result in a low PB content[9]), the TiN:AlN ratio was changed because part of the AlN oxidized during heating in air. When the molar ratio was changed to result in a more TiO_2-rich composition as previously observed, the amount of PB also increased.[9]

In order to fabricate TiN-containing RBAO via the reaction described here, the originally added TiN was permitted to completely oxidize to TiO_2. As TiO_2 later reacts to form TiN again, it should be possible to add TiO_2 to the green compact in the first place. However, the reaction TiO_2 to TiN is accompanied by 39% volume shrinkage. Therefore, the initial addition of TiN has the advantage of compensating for this shrinkage by introducing an equal volume increase from the oxidation of TiN to TiO_2 first.

4 Summary and Conclusions

The present work has shown that TiC and TiN are not sufficiently oxidation-resistant to survive the heating cycle that is generally used to achieve complete oxidation of Al in the RBAO process. However, if the oxidation step is arrested before completion and the samples are subsequently sintered in an inert atmosphere, TiN- and TiC-containing ceramic/metal composites can be readily obtained. The metallic phase in these composites consists of various Al/Ti/Zr alloy phases, possibly intermetallic, that are formed when the remaining unoxidized Al reduces TiO_2 and ZrO_2.

A ceramic/metal/TiN-containing composite was obtained which achieved a hardness of 20·4 GPa and a flexural strength of 350 MPa. (Table 2 lists the physical properties of samples prepared in this study.) This strength is lower than that of conventional RBAO, where strengths of more than 600 MPa are commonly achieved. Through careful process control it should be possible to obtain a variety of cermet/TiN compositions by starting from one precursor powder composition and adjusting the temperature at which the reaction sintering atmosphere is changed from air to inert gas. Such control would change the ratio of the Al to TiO_2 phases in the pre-sintered sample and lead to different volume contents and compositions of alloy/intermetallic phases in the consolidated materials.

A method for fabricating TiN-containing RBAO has been proposed. While retention of TiN through addition to the precursor powder was not successful due to TiN completely oxidizing before Al oxidation was completed, the reaction of AlN and TiO_2 to form Al_2O_3 and TiN at temperatures >1350°C could be successfully employed for the RBAO process used here because AlN is more oxidation-resistant than TiN. The grain size of the TiN phase obtained was approximately 1 μm; however smaller grain sizes should be possible by adjusting processing parameters.

Table 2. Physical properties of the RBAO–TiN and TiN/TiC-containing composites

Sample	*Fired density (%)*	*Hardness (GPa)*	*Bend strength (MPa)*	K_{IC} *(MPa m$^{1/2}$)*
K5TiN1	95	20	350	2·4
K5TIN2	95	14·6	280	2·4
IMC3	80		170	
K5AlN/Tin	96		280	3·3

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References

1. Niihara, K., New design concept of structural ceramics. *J. Ceram. Soc. Jpn, Int. Edn*, **99**(10) (1991) 945–52.
2. Walker, C. N., Borsa, C. E., Todd, R. I., Davidge, R. W. & Brook, R. J., Fabrication, characterisation and properties of alumina matrix nanocomposites. In *Novel Synthesis and Processing Ceramics, Br. Ceram. Proc. 53*, ed. F. R. Sale. The Institute of Materials, London, 1994.
3. Wu, S., Holz, D. & Claussen, N., Mechanisms and kinetics of reaction-bonded aluminum oxide ceramics. *J. Am. Ceram. Soc.*, **76**(4) (1993) 970–80.
4. Holz, D., Wu, S., Scheppokat, S. & Claussen, N., Effect of processing parameters on phase and microstructure evolution in RBAO Ceramics. *J. Am. Ceram. Soc.*, **77**(10) (1994) 2509–17.
5. Kochergina, A. A. & Fedoseev, D. V., Oxidation of untradispersed powders of titanium carbide and titanium nitride. *Inorg. Mater.*, **26**(3) (1990) 549–50. Translated from *Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy*, **26**(3) (1990) 648–9.
6. McKee, D. W., The oxidation of dispersed refractory metal compounds and their behaviour as carbon oxidation catalysts. *Carbon*, **24**(3) (1986) 331–6.
7. Bellosi, A., Tampieri A. & Liu Y.-Z., Oxidation behaviour of electroconductive Si_3N_4–TiN composites. *Mater. Sci. Eng.*, **A127** (1990) 115–22.
8. Holz, D., Processing and characterisation of reaction-bonded Al_2O_3–ZrO_2 ceramics. PhD Thesis, TUHH, Hamburg, 1994, (in German).
9. Mukerji, J. & Biswas, S. K., Synthesis, properties and oxidation of alumina–titanium nitride composites, *J. Am. Ceram. Soc.*, **73**(1) (1990) 142–5.
10. Mocellin, A. & Bayer, G., Chemical and microstructural investigation of high-temperature interactions between AlN and TiO_2. *J. Mater. Sci.*, **20** (1985) 3697–704.
11. Bellosi, A., Landi, E. & Tampieri, A., Oxidation behaviour of aluminium nitride. *J. Mater. Res.*, **8**(3) (1993) 565–72.
12. Bannister, M. J. & Barnes, J. M., The solubility of TiO_2 in ZrO_2. In *Proc. of the Twelfth Australian Ceramics Conference*, 1986, pp. 241–5. The Australian Ceramic Soc.
13. Perera, D. S. & Bowden, M. E., Nitrogen-containing aluminium titanate. *J. Mater. Sci.*, **26**(6) (1991) 1585–7.
14. Hwang, C.-S., Nakagawa, Z. & Hamano, K., Microstructure and mechanical strength of TiO_2-doped Al_2O_3-ceramics fired in vacuum atmosphere. *J. Ceram Soc. Jpn., Int. Edn*, **101**(5) (1993) 1025–30.