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Manufacture and Properties of Al_2O_3–TiN Particulate Composites

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Abstract

Dense Al_2O_3–TiN composites with 5–25 vol% TiN were manufactured by hot pressing technique. The effect of the content of a dispersion-toughening aid, TiN, on the mechanical properties, electrical resistivity, oxidation resistance and wear resistance were studied and related to the microstructure. The ceramics with a content of 25 vol% TiN were characterized by the highest strength, 567 MPa, and the lowest electrical resistivity, $2{\cdot}5\times10^{-3}$ Ω.cm. The material was suitable for electrical discharge machining. © *1998 Published by Elsevier Science Limited.*

1 Introduction

Alumina ceramics containing SiC or TiC additives are established cutting tool materials.[1] Titanium nitride, TiN_x, is an important technological material with remarkable properties (high melting point: 2950°C for $x=1$, extreme hardness: 18–21 GPa, high thermal conductivity: 21 ± 1 W/m.K, and low room temperature resistivity: $3{\cdot}34\times10^{-7}$ Ω.cm).[2] The application of titanium nitride to thin films and coatings for wear resistance of cutting tools are important and well known. Recently, the properties of TiN particle reinforced alumina or silicon nitride composites were widely studied because the addition of the electroconductive second phase in quantities higher than 20–30 vol% to the matrix material were reported to increase some mechanical properties, and at the same time drastically lower the electrical resistivity of the ceramic composites to below 10^{-5} Ω.cm.[3–7] It is expected that these composites could find applications as wear resistance materials and cutting tools. The good electrical conductivity of the composites also results in their use as heating elements, igniters and heat exchangers. The additional advantage of the composites is that components of complex shape can be produced by using electrical discharge machines.

Therefore this study was devoted to Al_2O_3–TiN particulate composites and compares the microstructural development, mechanical properties, oxidation and wear resistance and electrical conductivity to the TiN content in the composite material. Moreover, electrical discharge machining (EDM) tests were performed and the treated surfaces were characterized. It was expected that the introduction of TiN particles improves not only the electrical conductivity of the monolithic alumina but also the strength, toughness and wear resistance.

2 Experimental

Alcoa A16 SG alumina powder was selected as the matrix raw material. TiN powder in the shape of particles from H. C. Starck GmbH, grade C, was used as the second phase. The properties of the starting raw materials are listed in Table 1.

Each Al_2O_3 matrix powder batch with the addition of TiN from 5–25 vol%, in 5% intervals, was ball-milled using ethyl alcohol as the solvent. The slurries were homogenized for 20 h in the ball mill and then dried. The granulates to be hot-pressed were made by sieving through a 0·2 mm sieve. The Al_2O_3–TiN granulates were hot-pressed in a high-density graphite die coated with hBN at temperatures from 1650 to 1750°C for 45 min under a pressure of 26 MPa in vacuum. The resulting composite discs were cut into bars of size $4{\cdot}0\times3{\cdot}5\times50$ mm^3. As a reference, a monolithic alumina sample was produced by hot pressing at 1550°C for 45 min.

The density of the samples was measured using the water immersion technique. A theoretical value of 3·98 g cm^{-3} for alumina and 5·44 g cm^{-3} for TiN was taken to calculate the density of composites.

Table 1. Characteristics of alumina and titanium nitride powders

Properties	*Al_2O_3, A16 SG*	*TiN, grade C*
Crystalographic structure	α-Al_2O_3	Cubic TiN
Average particle size, μm	0·45	1·00
Specific density, g cm^{-3}	3·98	5·44
Specific surface area (BET), m^2 g^{-1}	8·7	3·7

The theoretical value of each composite density was calculated with the rule of mixtures assuming that no reaction takes place between the matrix material and the second phase.

The microstructure was observed using optical microscopy and SEM on polished and fractured surfaces of the composites. X-ray diffraction was used to characterize the phase composition.

A four-point bending test (outer span—40 mm, inner span—20 mm) with the crack plane parallel to the hot-press direction and a cross-head speed of 0·5 mm min^{-1} was used to measure the room temperature bending strength (σ) (modulus of rupture, MOR). A minimum of five samples was used to determine the value of bending strength.

The fracture toughness (K_{1c}) was measured by both Chevron test (CT) and indentation (IT) methods. The bars used to measure K_{1c} value by Chevron test were notched with diamond coated copper blades of 50 μm in thickness. A four point bend fixture was used for K_{1c} evaluation. For calculation of K_{1c} by indentation test, the cracks induced by a Vickers pyramid under a load of 98 N were measured and the Niihara formula applied.[8]

The Young's modulus (E) was measured on bars by the frequency resonance method.

The Vickers microhardness (H_v) of the composities was calculated from the average results of five indentations performed under a load 98 N on a polished surface of the sample.

The thermal expansion coefficient (α) was measured using a Netsch dilatometer within the temperature range of 20–1000°C with a heating rate of 5°C min^{-1}.

Oxidation resistance was evaluated on polished samples of dimensions 4·0×3·5×10 mm^3, at 650–1250°C in air for 24 h. The weight gain (weight/surface) was continuously recorded by a TG–DTA apparatus and the oxidize surface was characterized by XRD and SEM.

Electrical resistivity (ρ) was measured by the four-probe method at room temperature, with a distance between the contact points of 5 mm. Abrasive wear (WR) testing was performed using a wear test method developed in the University of Mining and Metallurgy, Poland.[9] Wear testing was performed by pressing samples of size 30 mm in diameter and 5 mm thickness against a rotating cast iron disc of diameter 50 mm covered by rubber onto which a suspension of an abrasive medium (SiC powder, 0·5 mm) was added and uniformly distributed. The applied pressure was 44 N. The results are reported as a volume of removed material from the testing disc after 5000 rotation cycles.

The EDM test was done using Charmilles, type D1TR, die-sinking machine (also known as a vertical erosion machine) for cutting holes. This type of machine is capable of cutting or sinking very complicated shapes into a workpiece. The EDM can be applied to ceramics, including single phase and ceramic–ceramic composites, if the electrical resistivity is below 100 Ω.cm.[10]

3 Results and Discussion

3.1 Densification and microstructure

The hot-pressed Al_2O_3–TiN composites were fully dense, with the densification degree (RD) in the range of 99–100% of the theoretical density (Table 2). The presence of an inert TiN phase in the alumina matrix which has limited sinterability decreases the densification rate of the composites. Therefore, the temperature of hot pressing was increased from 1550°C for the alumina matrix to 1750°C for the composite with 25 vol% TiN to reach a good densification of the sample.

A microscopic study of the polished surfaces of the hot-pressed samples showed that the TiN particles of diameter 0·2–2·5 μm were evenly distributed in the alumina matrix in all tested composites

Table 2. Properties of the hot-pressed Al_2O_3–TiN composites

Composite (vol% TiN)	*Density*		*Electrical resistivity* (Ω.*cm*)	*Thermal exp. coef.** ($10^{-6}C^{-1}$)	*Young's modulus (GPa)*	*Toughness inde. test*† ($MPa.m^{1/2}$)	*Toughness Chevron test* ($MPa.m^{1/2}$)	*Micro-hardness (GPa)*	*Wear resistance* (mm^3)
	(g cm^{-3})	*(%)*							
0	3·98	100·0	$>10^{13}$	9·1	376 ± 29	4·6 ± 0·3	4·6 ± 0·2	19·4 ± 0·9	42·6
5	4·02	99·2	$>10^{12}$	9·0	367 ± 10	4·6 ± 0·2	4·7 ± 0·3	18·4 ± 1·2	81·4
10	4·10	99·4	$>10^{12}$	8·9	375 ± 8	4·8 ± 0·4	4·8 ± 0·2	18·4 ± 0·9	63·8
15	4·18	99·5	$>10^{12}$	8·7	386 ± 7	5·2 ± 0·5	5·2 ± 0·4	18·4 ± 0·8	69·6
20	4·25	99·5	3·8	8·6	383 ± 8	5·2 ± 0·3	5·0 ± 0·3	18·3 ± 1·0	51·3
25	4·31	99·2	$2·5\times10^{-3}$	8·5	381 ± 21	4·9 ± 0·6	4·7 ± 0·5	18·4 ± 0·9	69·8

*Expansion coefficient; †indentation.

(Fig. 1). The TiN crystals were located between the alumina grains or, in the case of a small TiN crystals, were incorporated into the alumina grains. The crystals of alumina of sizes up to 4 μm, with an average size approximately 2 μm, were characterized by uniform, multifaceted, isometric forms. In the composite with 25 vol% TiN, titanium nitride grains formed a near-continuous network in the alumina matrix (Fig. 2). The XRD study showed only the presence of α-Al_2O_3 and cubic TiN in the hot-pressed composites. No chemical reaction between the second phase and the matrix was observed in the tested composites.

3.2 Electrical conductivity

The electrical resistivity of the composites decreases with increasing amount of TiN phase and reaches a minimum ($2{\cdot}5\times10^{-3}\,\Omega$.cm) for the composite with 25 vol% TiN (Table 2). In the region of low dispersoid concentrations, the particles are incorporated in the insulating matrix and the resistivity of the composites is relatively high, above $10^{12}\,\Omega$.cm. At a certain dispersoid content (above 20 vol%), a network of the conducting phase within the insulating one is formed (Fig. 2). As a consequence, the resistivity of the composite shows a drastic decrease due to the low value of this conductivity network. The dependence of the electrical resistivity/conductivity in the temperature range of 20–300°C was measured for the composite containing 25 vol% TiN–Al_2O_3 (Fig. 3). The electrical conductivity decreased with the increase of the temperature from a value of 400 to 275 Siemens.cm. This type conductivity, decreasing with the temperature growth is typical for metals and is also observed for the TiN–Al_2O_3 composites containing the fine TiN grains.[3,4]

3.3 Mechanical properties

Mechanical properties of the hot-pressed composites are summarized in Table 2 and Fig. 4.

The Young's modulus values of the composites slightly increase with an increase in TiN content, from 376 GPa for the matrix to 386 GPa for the composite with 15 vol% TiN. This is a logical consequence of using a nitride refractory compound which is stiffer than the alumina matrix. The room temperature bending strength of hot-pressed composites, with a TiN content up to 20 vol%, is nearly the same as the alumina matrix. This value is significantly higher for the composite with 25 vol% TiN. In the latter composite the flexural strength is much higher than that expected from the improvement of fracture toughness, indicating that the critical flow size of the alumina matrix was significantly reduced by the addition of the TiN phase. The critical flow size calculated from the

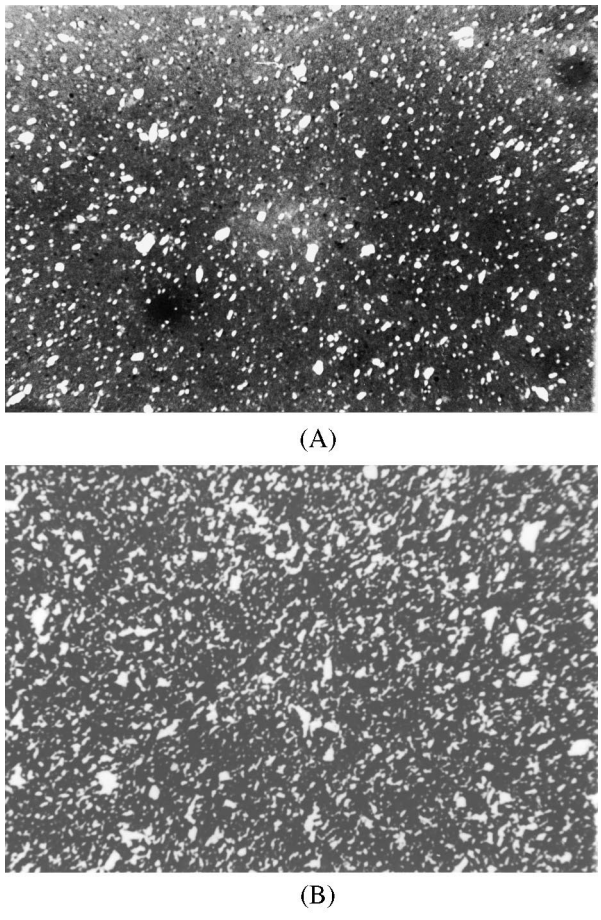

Fig. 1. Optical microscopy of polished surface of the hot-pressed (A) 5 vol% TiN–Al_2O_3 and (B) 25 vol% TiN–Al_2O_3 composites. White areas are TiN particles. Magnification: 500×.

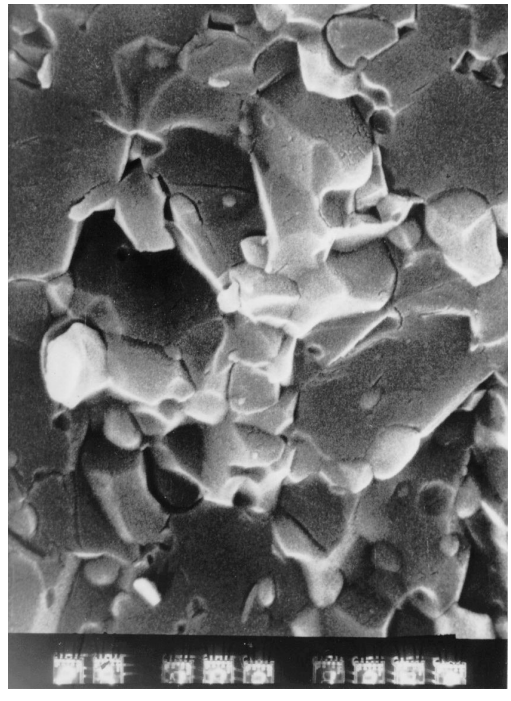

Fig. 2. SEM micrograph of fracture surface of the hot-pressed 25 vol% TiN–Al_2O_3 composite. The TiN grains (white-grey) create nearly continuous network in the alumina matrix (grey). Magnification: 10 000×.

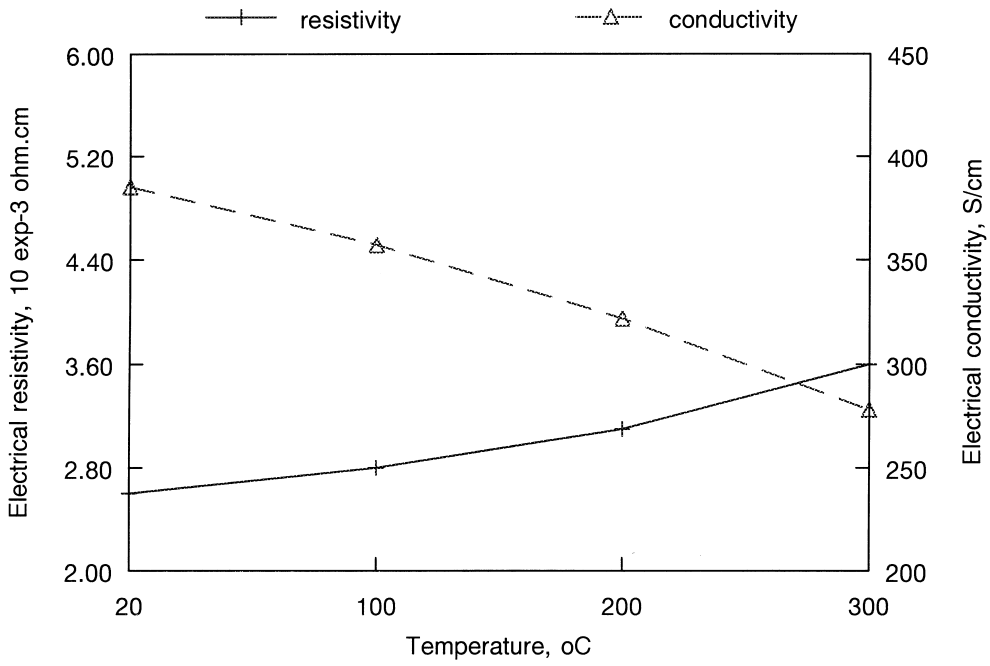

Fig. 3. Electrical resistivity/conductivity of 25 vol% TiN–Al_2O_3 composite as a function of temperature.

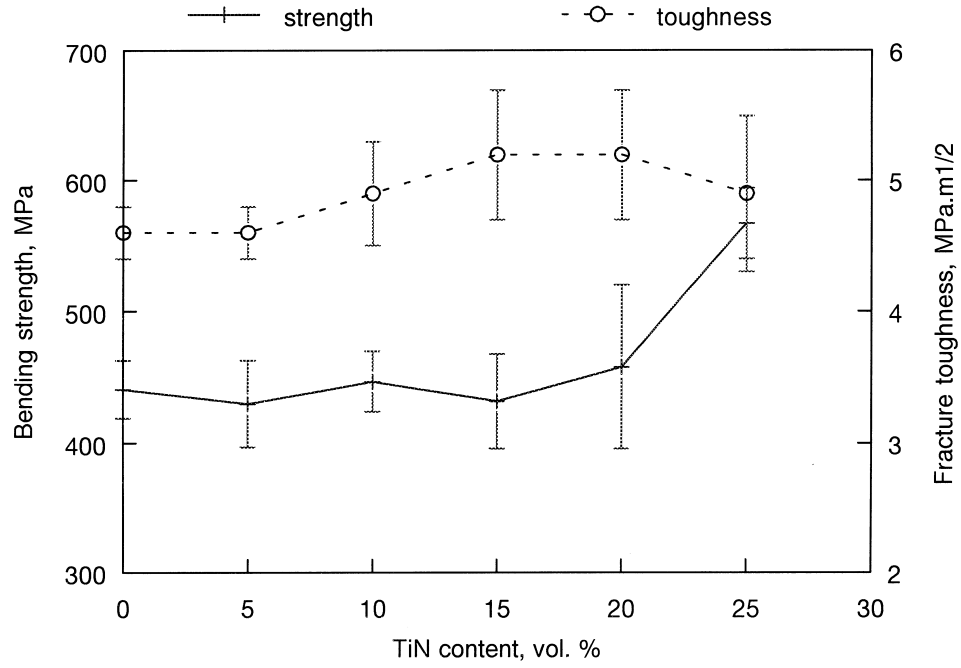

Fig. 4. Room temperature bending strength and fracture toughness (IT) versus quantity of titanium nitride.

Griffith equation for the alumina was 108 μm, and for the composite with 25 vol% TiN 74 μm. This means that it is possible to reduce the critical flow size in the Al_2O_3–TiN composites by increasing the fine TiN phase content. The results of the fracture toughness measured by Chevron notch technique (Table 2) and indentation method (Fig. 4) are in a good agreement. The addition of fine TiN particles has only a small influence on the improvement of the fracture toughness of manufactured composites. The small discrepancy between the measured values can be explained by the differences in the both used techniques. The highest value of K_{1c} was measured for the composites with the content of 15 and 20 vol% TiN, 5·2 MPa.$m^{1/2}$, in comparison to 4·6 MPa.$m^{1/2}$, evaluated for the alumina matrix. The explanation of a prevailing toughening mechanism is difficult, due to the number of mechanisms that can be active at the same time. Crack deflection is clearly evident, as can be seen on micrographs in Fig. 5. In both tested composites, with the content of 10 and 25 vol% TiN, the

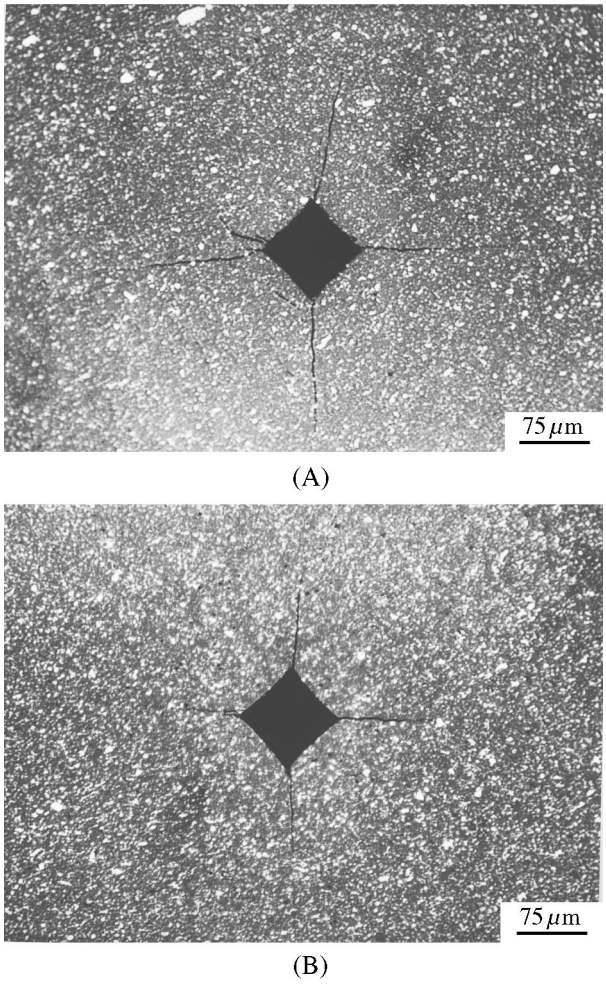

Fig. 5. Crack propagation in the composite (A) with 10 vol% and (B) 25 vol% TiN particulates.

crack was propagated almost straight from the indentation corner. A slight deflection is connected with the intergranular nature of crack propagation. It is clearly shown that the fine TiN grains did not form a strong barrier for the cracks. Crack pinning and crack bridging are the other two possible toughening mechanisms in the particulate Al_2O_3-TiN composites. Other mechanisms such as residual stresses and microcracks can be excluded due to a very similar value of the thermal expansion coefficients of both constituent phases.[1,11]

It was expected that the introduction of the TiN phase to the alumina matrix should have resulted in a slight increase in the hardness of the composites. However, the measured values of H_v were lower than the micro-hardness of the alumina matrix and were stabilized on the level of 18·4 GPa, regardless of TiN content. The only explanation of this phenomenon is the influence of the degree of densification, which was slightly lower than the degree of densification of the alumina matrix (99·2–99·5 and 100%, respectively). The Al_2O_3–TiN composites manufactured elsewhere were characterized by the higher value of hardness than the base line material.[1–4]

3.4 Thermal properties

The thermal expansion coefficient of the composites is slightly lower than that of the base line material, and decreases almost linearly with the second phase content, which was expected, owing to the lower thermal expansion coefficient of TiN ($8{\cdot}1–8{\cdot}8\times10^{-6}C^{-1}$) in comparison to the alumina matrix (Table 2). The experimental values of the thermal expansion coefficient are in good agreement with those calculated with the rule of mixtures according to the equation:

$$\alpha = \alpha_m.V_m + \alpha_p.V_v \qquad (1)$$

where V_m and V_p are the respective volume fractions.

The measured values are slightly higher than those parameters reported in the literature.[1–3] No hysteresis have been observed on the dilatometric curves suggesting the absence of microcracks in the manufactured composites.

3.5 Wear resistance

A strong attention is devoted to the tribological properties of the particulate reinforced ceramic composites. TiN-based composites are considered as good wear resistance materials.[11] Investigation of the effect of TiN content on the wear resistance of Al_2O_3–TiN composites showed a slightly lower resistance to wear for all manufactured composites in comparison to that of the alumina matrix. The best performance was measured for 20 vol% TiN–Al_2O_3 composite, however the measured value was still lower than the wear resistance of the alumina matrix. The lower values of the wear resistance of the developed composites than the matrix material can be to some degree related to the lower hardness of the hot pressed composites.[12] This, however, does not exclude them in the wear resistance applications if other properties are in favour of their use. On the other hand, the wear resistance measurement technique used and coupled material have a strong influence on the measured properties and using a different technique, i.e. pin-on-disc against corundum, the opposite results are obtained. It is known that TiN-based composites have a higher wear resistance against corundum and diamond than against AlN and SiC.[6] The predominant wear mechanism seems to be the tribo-oxidation during which the TiN is oxidized to TiO_2 on the sliding surface.[11] The higher wear resistance of Al_2O_3–TiN composites with a higher TiN content was related to the higher mechanical properties of the composites.

3.6 Oxidation resistance

The oxidation resistance of the composite with 20 vol% TiN was measured within the temperature range of 650 to 1250°C (Fig. 6). The thermal stability of the composites can be directly related to the amount of TiN which is an easy-to-oxidize phase. The weight gain starts at approximately 800°C. However, the oxidation reaction begins at a lower temperature (app. 500°C) with no detectable weight change (Fig. 7). The only crystalline phase detected on the oxidized surface is TiO_2 (rutile), which has poor protective properties.[4] The growth of a continuous rutile layer on the surface of Al_2O_3–TiN composite should be related

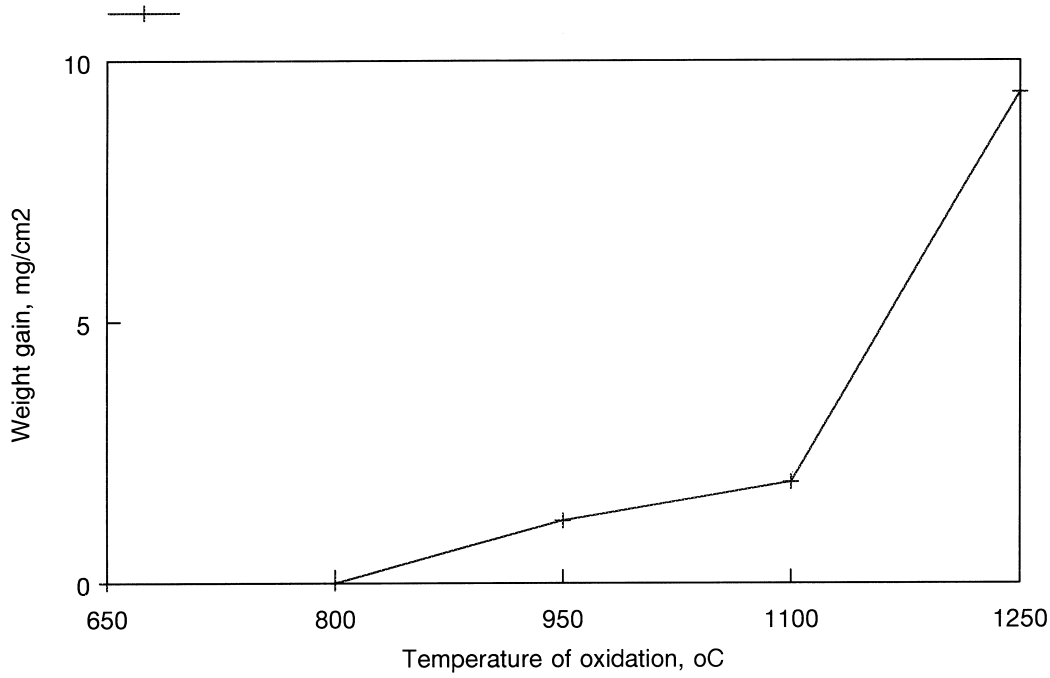

Fig. 6. Weight gain (weight/surface) after 24 h oxidation of the composite with 20 vol% TiN versus temperature of oxidation.

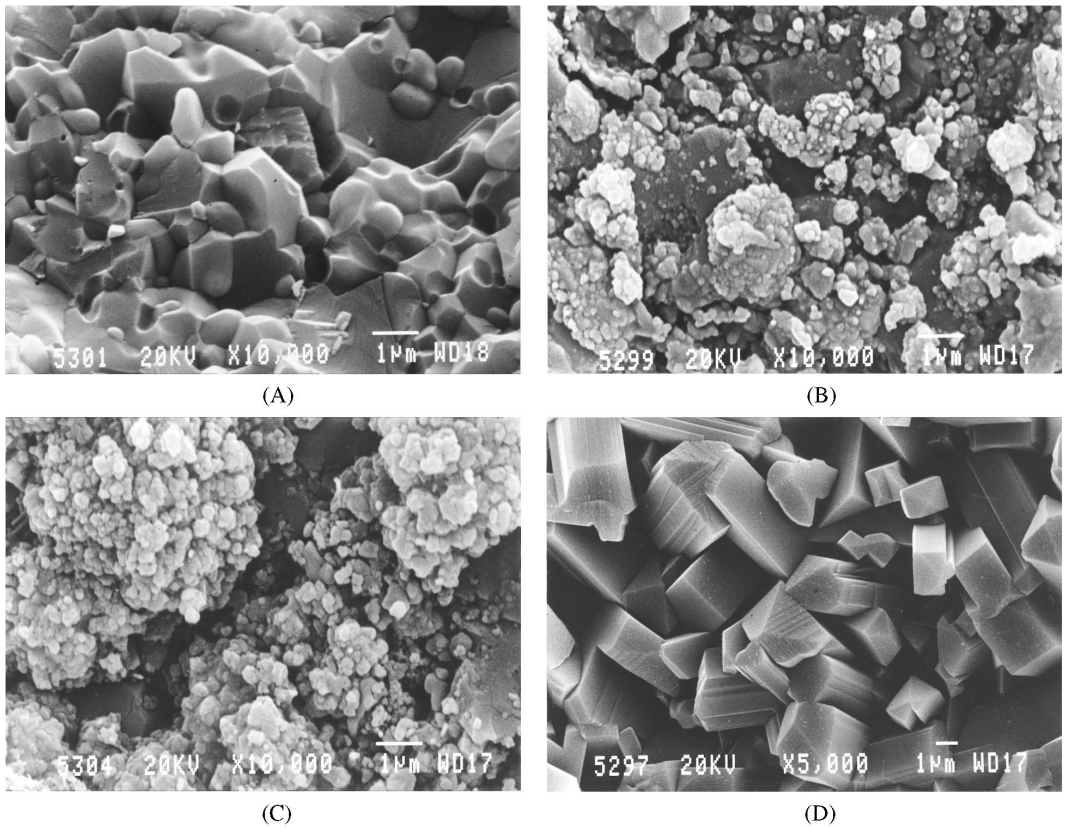

Fig. 7. Evaluation of the surface morphology of the oxidized composite with 20 vol% TiN at (A) 400°C, (B) 650°C, (C) 800°C and (D) 950°C.

to the diffusion of titanium to the surface of the composite and its oxidation runs according to the reaction:

$$2TiN + O_2 = 2TiO_2 + N_2 \quad (2)$$

The reaction $TiN \rightarrow TiO_2$ (rutile) results in a large volume expansion (27·6%) which generates cracks on the alumina–titanium nitride particle interface and as a consequence some spalling occurs which promotes the oxidation of the TiN particles present beneath the surface of the sample. The oxidation of 20 vol% TiN–Al_2O_3 composite increases with the temperature and the massive oxidation occurs at temperatures higher than 1100°C.

3.7 Electrical discharge machining

EDM tests were carried out on the composites with 20 and 25 vol% TiN using a die-sinking machine. In die-sinking machines, the workpiece is the cathode and the shaping tool is the anode. A copper electrode and kerosene dielectric were used in the machining experiments. Holes of 10 mm in diameter and 1·8 mm deep were drilled in each composite. A cutting speed of 0·35 mm min^{-1} was measured for the composite with 25 vol% TiN. The measured cutting rates were significantly lower than the reported 1·5–5 mm min^{-1} for the Si_3N_4 ceramics with the content of 30–50 vol% TiN machined by the wire EDM.[5] The roughness of the surface was approximately 10 μm because discharges create craters with varying diameters and positions (Fig. 8). Melting and evaporation of the electrodes is the most common method for erosion and the one traditionally explained and modelled. Therefore these two processes have an influence on the quality of the machined surface, covered by a layer of melted and resolidated droplets. It is estimated that the amount of material resolidified vary from 20 to 60%.[10] This process is attractive only for machining hard and brittle ceramics like alumina-based and Si_3N_4-based composites because it places no mechanical stress on the workpiece. EDM also gives an extremely fine surface, often in micrometer range.

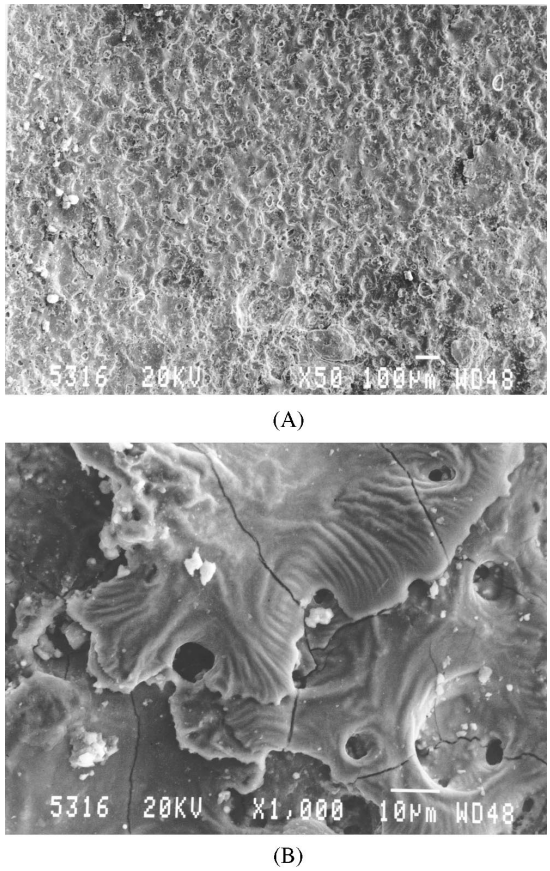

Fig. 8. Morphology of the EDM surface of 25 vol% TiN composite showing: (A) melt-formation droplets, (B) formation of melted layer approximately 10 μm thick on the surface with extensive cracking in.

4 Conclusions

A series of particulate composites in the system of Al_3O_3–TiN was developed. The investigations lead to the following conclusions:

1. Dense Al_2O_3–TiN composites can be produced by hot pressing technique, with no detrimental effects to the mechanical properties of the matrix.
2. A minimum content of 25 vol% TiN is necessary to obtain the conductivity of a composite, which is suitable for EDM.
3. When fine TiN particles are added to the Al_2O_3 matrix in the quantity up to 25 vol% the Young's modulus, room temperature bending strength and fracture toughness slightly increase. In contrast, other properties like hardness, thermal expansion coefficient and wear resistance decrease.
4. The Al_2O_3–TiN composites rapidly oxidize above 800°C, and therefore cannot be recommended for applications at temperatures in excess of this.
5. The particulate alumina–titanium nitride composites are a new class of structural materials with enhanced mechanical properties which can find application as wear resistant materials.

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