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SiC-reinforcement of an Al_2O_3–γAlON composite

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Abstract

Three phase Al_2O_3–A1ON–SiC composites can be obtained by hot-pressing Al_2O_3–AlN–SiC mixtures under 40 MPa at temperatures around 1700°C. Silicon carbide can be added in the form of powders or platelets. In the case of powder, densification and aluminum oxynitride formation occur at higher temperatures than in the case of platelets, because of a steric and chemical hindrance by SiC on both Al_2O_3 densification and the Al_2O_3–AlN reaction. Composites containing powders present the highest values for rupture moduli of up to 800 MPa and toughnesses close to those of alumina (4 MPa$\sqrt{m}$). For platelets, a composite containing 20 vol.% SiC with a size of $d_{50}=8$ μm produces a reinforcement effect ($K_{1C}=6$–7 MPa$\sqrt{m}$).

Keywords: AlON; Al_2O_3; Composites; Hot pressing; Mechanical properties; Platelets; SiC

1. Introduction

Al_2O_3–γAlON (alumina–γ–aluminium oxynitride) two-phase composites offer better high temperature mechanical properties and better friction resistance against steel than alumina.[1]

Al_2O_3–γAlON–SiC three-phase composites have been developed to enhance strength and toughness.[2] The choice of silicon carbide addition was due to its relatively lower thermal expansion coefficient allowing toughening effects by such mechanisms as microcracking. Furthermore, the good thermal conductivity is an interesting property regarding resistance to damage resulting from thermal quench. Although SiC brings about a sintering inhibiting effect on the matrix which makes it necessary to use hot pressing for bringing the composite to complete densification, the benefits remain considerable. Platelets have been studied mainly for composite reinforcement to enhance toughness in preference to whiskers that represent a health risk for users.[3–4] Our objective in the present work has been to compare platelet reinforcement and powder reinforcement, and to optimise the resulting properties.

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2. Methods

2.1. Fabrication process

A scheme of the composite fabrication process is given (Fig. 1). The milling medium was alcohol to avoid AlN hydrolysis. γAlON is obtained by the sintering reaction between alumina and AlN:

$$\frac{4-x}{3}Al_2O_3 + xAlN \rightarrow Al^{\frac{8+x}{3}}O_{4-x}N_x$$

where x can vary from 0.61 to 0.31.

We prepared three different kinds of composite, one with a 25 m^2/g αSiC powder, one with a 15 m^2/g βSiC powder, and the last with 16 μm mean size SiC platelets milled to obtain batches with different platelet size and aspect ratio (Table 1).

Each composition was hot-pressed (uniaxial pressure) in graphite dies under nitrogen. The heating rate was 30°C/min, under a pressure of 10 MPa, and the cooling rate 50°C/min, without pressure. The soaking conditions were: temperature in the range 1670–1800°C, time 30 min, pressure 40 MPa.

Initial compositions were calculated in order to attain composites with about 64 vol.% Al_2O_3–16 vol.% AlON–20 vol.% SiC. Because the γ-phase is a solid

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solution whose composition varies with the sintering temperature, it is necessary to measure for each sample the γAlON content by X-ray diffraction.

2.2. X-ray diffraction

X-ray diffraction was performed on an apparatus fitted with linear detector and Cobalt anticathode. Diffraction diagrams were used to determine the γAlON phase content in the samples on the basis of a curve established from diffraction diagrams of standard pellets made with alumina and AlON powders mixtures. AlON powder was obtained from a 75 mol% Al_2O_3–25 mol% AlN mixture, heated in a graphite furnace for 6 h at 1725°C under static nitrogen atmosphere. The powder did not contain any detectable alumina or AlN according to the X-ray diagrams.

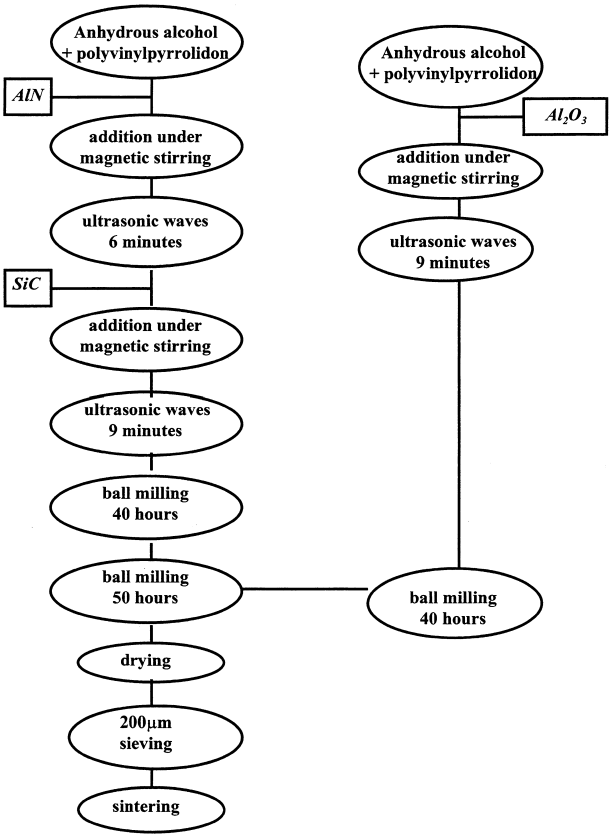


Fig. 1. Powder metallurgy process ($T = 1700$–1750°C, 30 min soaking time, 40 MPa, nitrogen atmosphere) to make Al_2O_3–AlON–SiC composites.

The diffraction curve (Fig. 2) was computed using the (400) γAlON peak and the (113) Al_2O_3 peak, both chosen for the reason of their θ-proximity and because they are quite isolated in the X-ray diagrams when one considers the SiC presence in the Al_2O_3–AlON–SiC composites. Unfortunately, the (400) γAlON peak is very close to the (202) α-alumina peak, which has a low intensity. We chose to plot the known compositions of our pellets against the calculated ratio of integrated intensity peaks:

$$\frac{I^{\gamma AlON}_{(400)} + I^{\alpha Al_2O_3}_{(202)}}{I^{\gamma AlON}_{(400)} + I^{\alpha Al_2O_3}_{(202)} + I^{\alpha Al_2O_3}_{(113)}} \quad (1)$$

The maximal estimated error was calculated to be 2 vol.%.

The γAlON stoichiometric composition itself was determined from the procedure of Willems,[5] whereby the lattice parameter is calculated from the relative positions of the (400) γAlON peak and the (113) α-alumina one. From the lattice parameter measured on the γAlON powder, the stoichiometric composition is then calculated: we found 2.718 Al_2O_3–AlN, while a 3 Al_2O_3–AlN result had been expected on the basis of the reactants. The difference arises from a solid–gas reaction at high temperature where nitrogen reacts with the alumina and the existing γAlON to give a different final composition.

After the volumic mass was determined by Archimedes' method for each sample, the densification rate was calculated, taking into account its composition known by X-ray diffraction analyses.

2.3. Mechanical properties

In order to determine sample toughnesses (see below), Young's moduli were calculated from each sample composition, or measured by ultrasonic propagation on a few samples for verification purposes. (Note: the

Table 1
Characteristics of commercial powders and platelets

Powder or platelets	Supplier	Specific area (m^2/g)	Crystalline form
Al_2O_3 CR6 Powder	Baïkowski, France	6	α + (γ)
SiC α UF25 Powder	Lonza, Germany	25	α mainly 6H
SiC β B10 Powder	Starck, Germany	15	β > 97.5%
		Mean grain size (μm)	
SiC platelets	Third Millenium Tech. Inc., USA	16	α 4H, 6H
AlN B powder	Starck, Germany	3.2	Hexagonal

values are not simply related to the microstructures but it was generally observed, as expected, that Young's modulus increased for smaller SiC grain size.)

The rupture moduli measurements were performed on $17 \times 4 \times 3$ mm^3 samples polished and chamfered to 2 μm at least. Loading speed was 0.1 mm/min for all tests on an INSTRON apparatus with a 500 kN force cell.

Toughness measurements were performed by means of the Indentation Strength in Bending method (ISB) where the defect is created with a 5 kg Vickers indentation and the test itself performed in three point bending. The toughness formula used is:

$$K_{Ic} = \alpha \times 10^{-6}.\left(\frac{E}{Hv}\right)^{1/8}.\left(\sigma.P^{1/3}\right)^{3/4}$$

in which α is a geometrical constant in the range $\alpha = 0.59 \pm 0.12$. In the present work, $\alpha = 0.7$ was chosen to relate these results to other measurements performed by means of the single edge notch beam (SENB) method.

P is the indentation force in N; E is the Young modulus and Hv is the Vickers hardness, both expressed in consistent units; σ is the bending strength measured after indentation in Pa.

This method offers the twofold advantage of good reproducibleness and very easy applicability. In respect to the former,

$$\frac{\Delta K_{Ic}}{K_{Ic}} \leqslant 10\%$$

Vickers hardness measurements were performed under a 10 N load applied for 30 s.

3. Results

3.1. Influence of SiC morphology

3.1.1. Sintering results

Three types of composites were hot pressed at different temperatures using β (15 m^2/g) powder or α (25 m^2/g) SiC powder, or platelets with 8 μm mean size. The shrinkage was initially followed and then composite densification rate and final γAlON content were compared. Fig. 3 represents the shrinkage rate versus temperature during heating (heating rate: 30°C/min). In terms of sintering characteristics, a maximal shrinkage speed temperature can be observed, increasing as a function of a higher SiC specific surface. This phenomenon corresponds to an increasing sintering inhibiting influence of the SiC when the granulometry is smaller.

This can also be observed in terms of absolute densification, with highier values being achieved at a lower temperature with platelets (Fig. 4). AlON percentage is relatively higher at a similar sintering temperature for samples with platelets than for those with 25 m^2/g SiC powder (Fig. 5). In the Fig. 6 it can be shown that, for all samples, the same reactivity evolution related to obtained densification is observed, so the spinel oxynitride formation is beneficial to the composite densification as described before.[6]

3.1.2. Mechanical properties of composites reinforced with powders or platelets

In this section, the mechanical properties of the composites are compared. The influence of grain morphology is huge as one can see from Fig. 7. Platelet composites present an average bending strength value of about 400

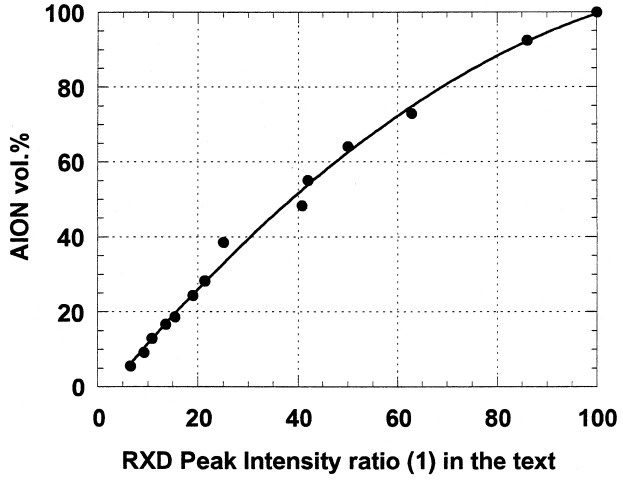


Fig. 2. AlON volume percentage scaling in a Al_2O_3–AlON mixture.

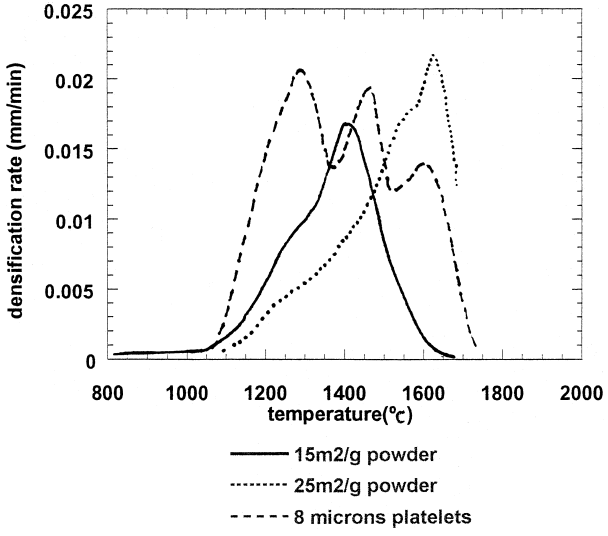


Fig. 3. Shrinkage rate during hot-pressing under 10 MPa of three different composites.

MPa while powder composites present an average value of 700 MPa. This can be linked to the matrix grain growth with platelets, as seen in Fig. 8: microstructure is directly dependent on the sintering inhibiting effect of SiC. If this phase is in the form of powder, SiC fine grains are more efficient to avoid the matrix grain growth.

Low rupture values could be also attributed in the case of platelets to the platelets themselves or some flaws that appear during cooling in such composites and so can constitute the critical defect.

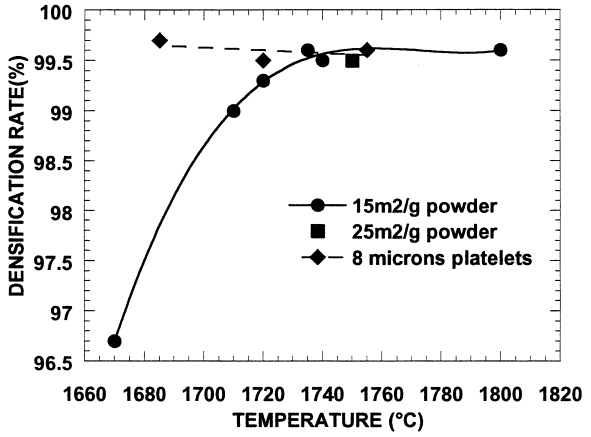


Fig. 4. Densification evolution versus hot-pressing temperature for Al_2O_3–AlON–20 vol.% SiC samples containing SiC powders or platelets.

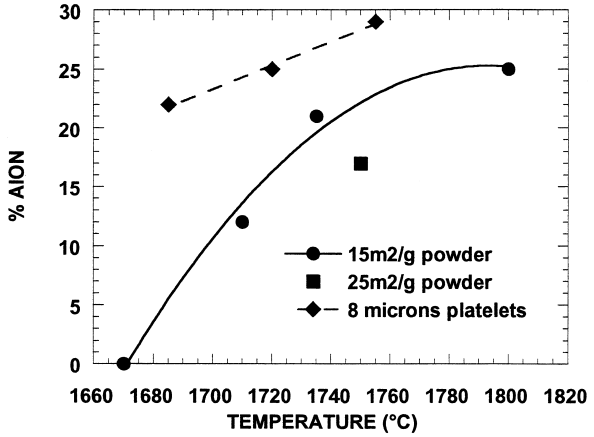


Fig. 5. AlON content versus hot-pressing temperature for Al_2O_3–AlON–20 vol.% SiC samples containing SiC powders or platelets.

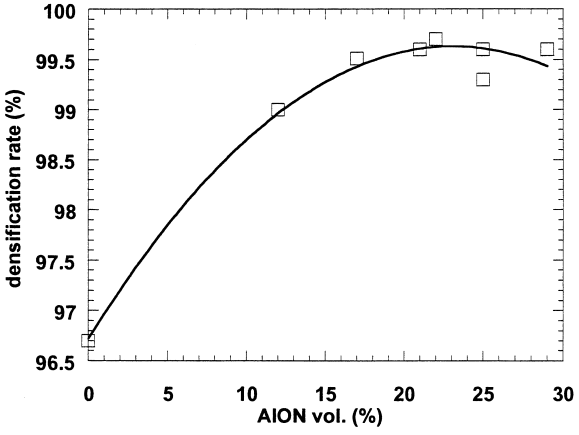


Fig. 6. Densification evolutions versus AlON contents for Al_2O_3–AlON–20 vol.% SiC samples containing SiC powders or platelets.

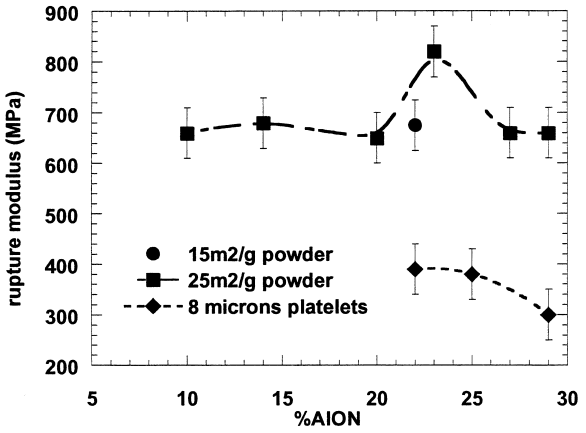
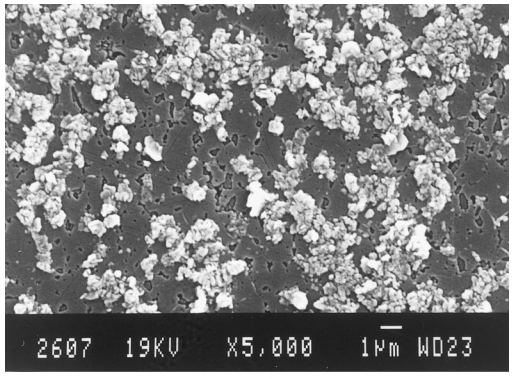
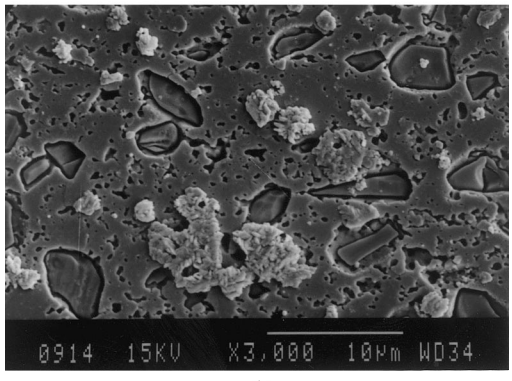


Fig. 7. Strength versus AlON contents for Al_2O_3–AlON–20 vol.% SiC samples containing SiC powders or platelets.



(a)



(b)

Fig. 8. Al_2O_3–AlON–SiC composites microstructures (thermal followed by chemical attack): alumina appears in grey and AlON phase in light grey; SiC grains or platelets are hollowed and appear in dark grey; (a) with SiC powder (25 m^2/g); (b) with SiC platelet (8 μm).

The toughness values are much higher for platelet composites (Fig. 9) where, for 20 vol.% SiC composition, toughness can increase to 6 or 7 MPa$\sqrt{m}$, close to the value obtained with whiskers in literature.[7] In this case, the reinforcement can be due to several mechanisms: crack deflection, branching around platelets, bridging, etc.

As expected, the general evolution of hardness is related to the microstructure (alumina grains and platelet size) and seems to decline with an increasing AlON content (Fig. 10). In the case of composites containing the fine SiC powder, very small grains at grain boundaries are favourable to the hardness.[2]

3.2. Influence of platelet size.

The influence of platelet size was studied, using four different batches with the following mean sizes: 3, 8, 15, and 24 μm (Table 2), and three sintering temperatures (1690–1720–1750°C), during 30 min, under 40 MPa.

The AlON content, densification rate, rupture moduli and toughnesses are indicated in Figs. 11–14. The envelope curves correspond to values obtained for the lowest and highest sintering temperature.

The aluminum oxynitride contents are the lowest for the 8 μm size platelets (Fig. 11). For finer platelets (3 μm), the lower spinel content can be due to the presence of more SiC particles, that inhibit diffusion, and hence the Al_2O_3–AlN reaction to form the oxynitride phase.

Table 2
Platelets size distribution in the batches

Batch	d_{10}[a] (μm)	d_{50}[b] (μm)	d_{90}[c] (μm)	Aspect ratio
$d_{50}=3$ μm	1	3	6	≈3
$d_{50}=8$ μm	2	8	12	≈5
$d_{50}=15$ μm	6	15	25	≈10
$d_{50}=24$ μm	10	24	25	≈10

[a] $d_{10}=x$ μm means there is 10 vol.% grains whose size is equal or lower than x μm.

[b] $d_{50}=y$ μm means there is 50 vol.% grains whose size is equal or lower than y μm.

[c] $d_{90}=z$ μm means there is 90 vol.% grains whose size is equal or lower than z μm.

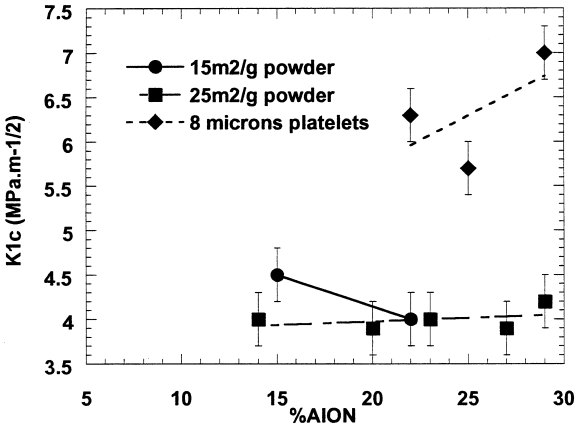


Fig. 9. Toughnesses versus AlON contents for Al_2O_3–AlON–20 vol.% SiC samples containing SiC powders or platelets.

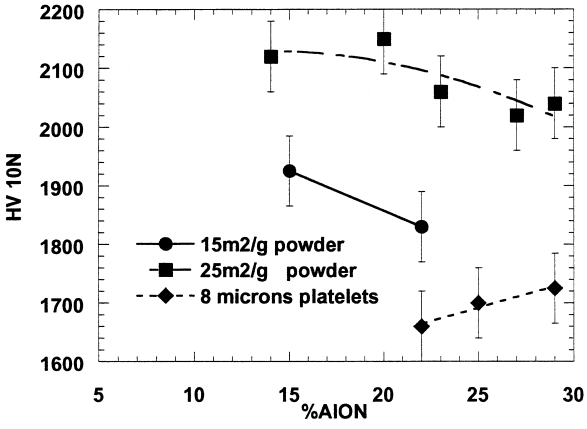


Fig. 10. Hardnesses versus AlON contents for Al_2O_3–AlON–20 vol.% SiC samples containing SiC powders or platelets.

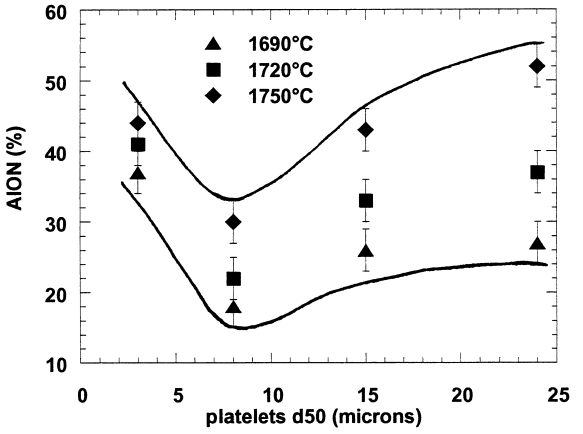


Fig. 11. AlON content in Al_2O_3–AlON–20 vol.% SiC composites versus SiC platelets size.

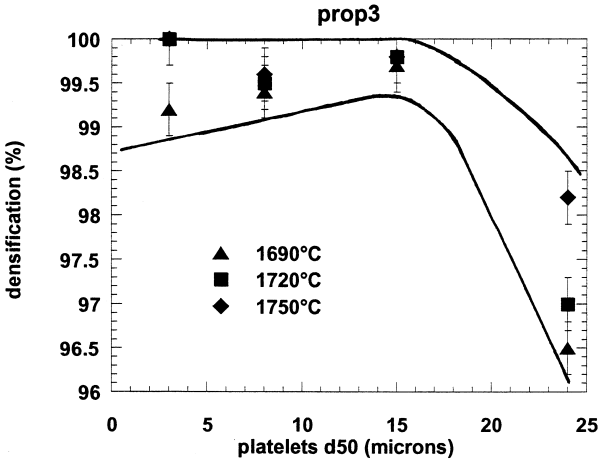


Fig. 12. Densification of Al_2O_3–AlON–20 vol.% SiC composites versus SiC platelets size.

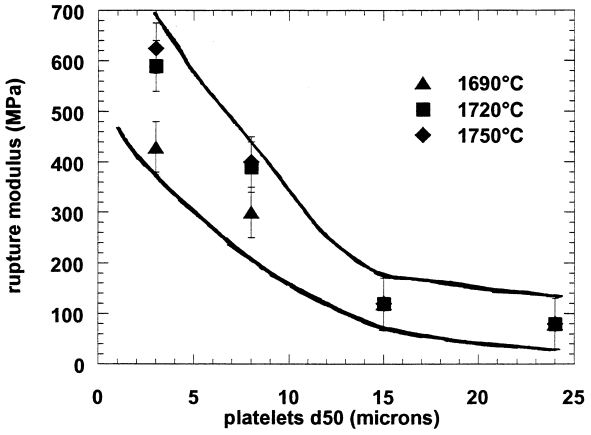


Fig. 13. Rupture moduli of Al_2O_3–AlON–20 vol.% SiC composites versus SiC platelets size.

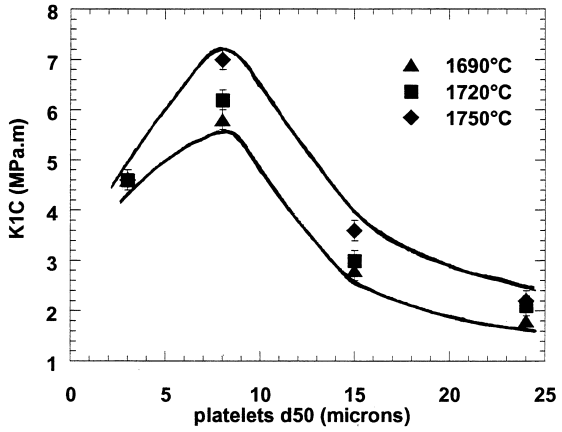


Fig. 14. Toughnesses of Al_2O_3–AlON–20 vol.% SiC composites versus SiC platelets size.

For the upper platelet size, (> 15 μm), one can consider that spontaneous microcracking (even macrocracking) can occur that leads to a stress decrease in the composite. This stress decrease could be favourable to the γ-phase stability and so could explain the high AlON content obtained in these cases (the reaction Al_2O_3–AlN producing AlON leads to a volume increase).

In this system, for 20 vol.% SiC a densification breakdown for large platelets (> 15 μm) has been observed (Fig. 12). This can be explained by the spontaneous development of the microcracks mentioned before, mainly for composites containing the largest platelets (24 μm).

Rupture moduli can be related to composite microstructure: for the lowest platelet size, the alumina grain size is fine (about 2–3 μm) and so the highest values are obtained. Composites containing the largest platelets (15 and 24 μm) present the lowest values in relation with the spontaneous microcracking and/or the high platelet size (Fig. 13).

The toughness is the highest for a 8 μm platelet size. For lower platelet size, the lower value can be related to a lower aspect ratio that cannot permit reinforcement mechanisms as crack deflection or crack branching to occur. There is also a relation between the γAlON phase content and the toughness. As seen before,[1] this phase is not favourable to the composite toughness (Fig. 14).

4. Conclusion

The aim of this work has been to show the possibility of reinforcing–alumina-aluminum oxynitride with silicon carbide powders or platelets, and to compare the properties of such composites.

For composites containing platelets, fracture strenghes are near 400 MPa and toughness values up to 7 Mpa$\sqrt{m}$ for a mean platelet size of 8μm. For lower size, the grinding process leads to some powders production and low aspect ratio. For large platelets macrocracks appear. These two facts explain the toughness decrease.

The three phase Al_2O_3–AlON–SiC composites are good candidates for thermomechanical application as cutting tools.[6]

Acknowledgements

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