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Hot Isostatic Pressing of SiC-Platelets/Y-TZP Composites*

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Abstract

Composites consisting of Y-TZP matrix with SiC-platelet secondary phase were first densified by a two-step procedure consisting in pressureless sintering, followed by HIPing. Although platelets do not significantly affect matrix packing and microstructure, they modify the transformation of tetragonal into monoclinic zirconia during rupture, mainly according to a load transfer mechanism. In spite of a lower reinforcement by transformation toughening, the composites show higher toughness due to load transfer and crack deflection mechanisms, which are found to be active from room temperature up to 300°C. For higher temperatures, matrix degradation is observed due to cracking or chemical reaction of platelets with oxygen at the matrix–platelet interface.

Verbundwerkstoffe bestehend aus einer Y-TZP-Matrix und SiC-Lamellen als zweite Phase wurden in einem zweistufigen Prozeß, bestehend aus drucklosem Sintern und nachfolgendem HIPen, verdichtet. Obgleich die Lamellen die Dichte der Matrix und das Gefüge nicht wesentlich beeinflussen, verändern sie die Transformation des tetragonalen in das monokline Zirkoniumoxid während des Bruches, hauptsächlich entsprechend eines Lasttransfermechanismuses. Trotz der geringeren Verstärkung der Zähigkeit aufgrund der Transformation, zeigt der Verbundwerkstoff eine höhere Zähigkeit infolge des Lasttransfers und einer Ablenkung des Risses, die zwischen Raumtemperatur und 300°C wirksam ist. Für höhere Temperaturen ist eine Verschlechterung der Matrixeigenschaften infolge von Rißbildung oder einer chemischen Reaktion der Lamellen mit Sauerstoff an der Matrix/Lamellen-Grenzfläche zu beobachten.

Des composites formés par une dispersion de plaquettes de SiC dans une matrice Y-TZP ont été densifiés, d'abord par frittage conventionnel, ensuite par compression isostatique à chaud. Bien que les plaquettes n'affectent pas sensiblement la compaction de la matrice et sa microstructure, elles modifient cependant l'ampleur de la transformation quadratique—monoclinique de la zircone durant la rupture, essentiellement en raison d'un mécanisme par transfert de charge. En dépit d'une contribution plus faible du renforcement par transformation de phase, les composites présentent jusqu'à 300°C une ténacité plus élevée, attribuée au transfert de charge et à des mécanismes de déviation de fissure. Aux températures plus élevées, on observe une dégradation de la matrice se manifestant par une fissuration ou par une réaction chimique des plaquettes avec l'oxygène au niveau de l'interface matrice–plaquette.

1 Introduction

The main problem of ceramics, limiting their use as structural materials, is their brittleness. In order to improve the reliability of such materials, new composites with improved toughness have to be developed.

Toughening of ceramics can be achieved by activating reinforcing mechanisms, such as transformation toughening in the case of TZP,[1] or crack deflection and pull-out in the case of secondary-phase reinforced composites.[2]

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Y-TZP ceramics are characterised by very high room-temperature strength and toughness, the latter being associated with transformation of both chemically and elastic stabilised tetragonal zirconia grains into monoclinic zirconia grains, absorbing the mechanical energy needed for crack propagation. However, with increasing temperature, the transformation of tetragonal into monoclinic zirconia becomes progressively less favourable from a thermodynamic point of view, as a consequence, a sharp decrease of mechanical properties in the 300 to 1000°C temperature range.[3]

In this paper, the processing and characterisation of silicon carbide platelet–zirconia composites are emphasised. Indeed, platelets can lead to composites showing higher toughness than the monophase material, from room temperature up to high-temperatures, as already demonstrated in the case of silicon nitride–SiC-platelet composites.[4]

However, in the zirconia–SiC composite system, residual stresses should arise in the matrix during the cooling step of sintering. The expansion coefficient of SiC platelets ($\alpha = 4{\cdot}6 \times 10^{-6}\,\mathrm{K}^{-1}$) being lower than that of the surrounding matrix ($\alpha = 10 \times 10^{-6}\,\mathrm{K}^{-1}$), platelets are submitted to compressive forces, while tensile forces are created within the matrix. Moreover, the possibility exists that these tensile stresses could be dissipated by martensitic transformation of tetragonal into monoclinic zirconia, at least at temperatures below the martensitic transformation temperature.

2 Experimental

A 3-mol% yttria-stabilised zirconia (TZ3Y, TOSOH, Japan) slurry and an α-SiC platelet (SF and M grades from C-Axis Technology, Canada, aspect ratio 8 and 10, mean size 11 and 23 μm, respectively) slurry were separately prepared, both in methanol, by mechanical stirring followed by 4 h vibration milling with zirconia cylinders in the case of the matrix slurry, or magnetic stirring in the case of the platelet slurry. The two slurries were poured together and homogenised for 2 h in a Turbula mixer using PTFE cylinders. Finally, the solvent was evaporated under magnetic stirring to avoid platelet segregation.

Disks of 40 mm diameter and 10 mm thickness were shaped by uniaxial pressing under 5 MPa, followed by isostatic pressing under 150 MPa. Green densities of the compacts were calculated by measuring pellet weight and dimensions.

Sintering of the composite compacts was carried out at 1550°C for 4 h under argon atmosphere, and was followed by a post-HIP treatment at 1400°C under 200 MPa, also in argon. The densities and open porosities of sintered and post-HIPed samples were measured by water immersion.

The microstructures were examined using SEM after thermal etching. The mean zirconia grain size was calculated as 1·776 times the mean linear intercept.[5]

The tetragonal content (T_c), was evaluated using the relation derived by Porter & Heuer,[6] corrected using R factor calculated by Smith & Newkirk,[7] according to the following equation:

$$T_c = 1 - \left\{ \frac{2{\cdot}234 I_m(11\bar{1})}{I_t(111) + 2{\cdot}234 I_m(11\bar{1})} \right\}$$

where $I_m(11\bar{1})$ and $I_t(111)$ are the X-ray diffraction intensities of the $(11\bar{1})$ and (111) rays of monoclinic and tetragonal zirconia, respectively.

The thermal expansion of post-HIPed samples was followed by linear dilatometry under 0·1 MPa air or argon atmosphere.

The mechanical properties were assessed on post-HIPed samples: Vickers hardness was measured under a load of 5 kg, elastic moduli were calculated from natural vibration mode measurement (Grindosonic), bend strength (σ_f) was measured on five specimens at room temperature and three at high temperatures, using a three point bending test, with a span of 15 mm and a crosshead speed of $0{\cdot}1\,\mathrm{mm\,min^{-1}}$, critical stress intensity factors (K_{IC}) were measured using the SENB technique, with a notch width of 190 microns.

3 Results and Discussion

3.1 Shaping and densification of composites

In Fig. 1 the green density measured for platelet compact composites is compared with that of their corresponding matrix green density, both expressed as a percentage of either the corresponding composite or matrix theoretical density. The latter green density is calculated from the former by considering that platelets show the theoretical density ($3200\,\mathrm{kg\,m^{-3}}$). Although the composite green dens-

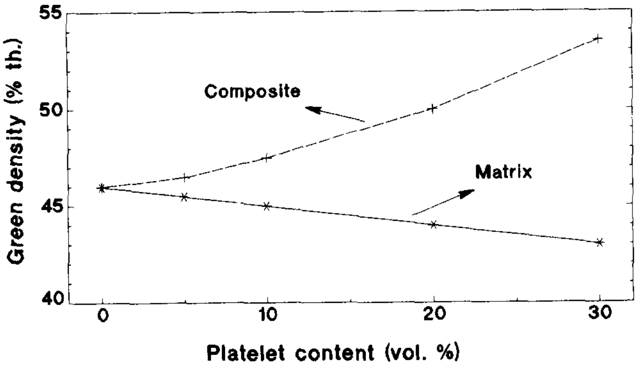


Fig. 1. Green density as function of platelet content for SF platelet composites and their matrix.

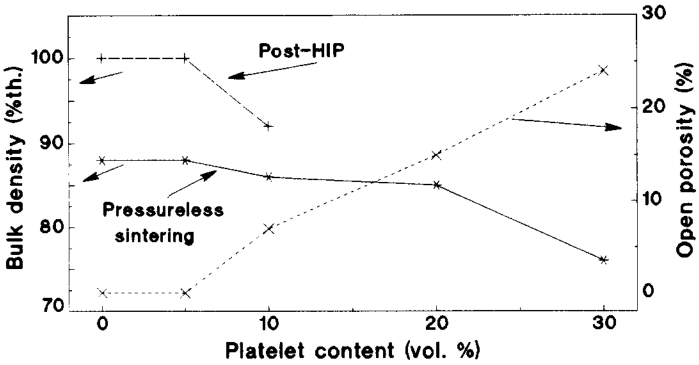


Fig. 2. Densification as function of platelet content before and after post-HIP.

ity increases with platelet content, the presence of the platelets reduces the packing efficiency of the matrix, as can be seen in Fig. 1.

Figure 2 shows bulk density and open porosity after pressureless sintering, as well as post-HIP bulk density. It can be seen that the final density after pressureless sintering is slightly reduced by the presence of platelets, probably due to the less efficient packing of their matrix. However, for platelet contents of 10 vol.% and higher, most of the porosity remains open, impeding full densification after post-HIPing. Fully densified composites can only be obtained with 5 vol.% platelet content.

3.2 Microstructural characteristics of composites

The typical microstructure of 5 vol.% SF platelet composites is represented in Fig. 3. Figure 3(a) shows a SEM observation of the composite after pressureless sintering, where well dispersed platelets can be observed together with remaining pores. After the post-HIP step, a fully densified material is obtained (Fig. 3(b)), with a fine matrix microstructure (Fig. 3(c)), consisting of zirconia grains having a mean size of about 0·7 micron, comparable with the size of the grains constituting the monolithic zirconia material.

3.3 Room-temperature mechanical properties of post-HIPed composites

The room-temperature mechanical properties of the post-HIPed zirconia monolithic material, and of 5 vol.% SF (fine) and M (coarse) platelet composites are summarised in Table 1.

The hardness of the composite is slightly higher than that of the monophase material, because of the higher hardness of the SiC platelets. The increase of the Young's modulus of the composite follows a mixing law.[8]

For the interpretation of toughness and flexural strength results, the presence of residual mechanical stresses in the matrix of the composite and at the platelet–matrix interface have to be taken into account. Although residual tensile matrix stresses are supposed to be present in the case of the composite, no significant difference in tetragonal zirconia content was measured between the monolithic material (100%) and the post-HIPed composite (98%). As grain size appears to be similar in both cases, the close tetragonal zirconia content in both the monolithic material and the composite might be attributed to the presence of residual compressive HIP stresses,[9] which are partly balancing the tensile matrix stresses.

However, when measuring the monoclinic zirconia content on rupture faces obtained after three-point flexural strength tests, for test bars broken at about the same critical rupture stress (800 MPa), tetragonal to monoclinic transformation is significantly higher in the case of the monolithic material compared with the composite. Indeed, for instance, 57% monoclinic content was measured on the rupture faces of the monolithic material, and only 34% was found in the case of a 5% SF platelet composite. These observations suggest a load transfer mechanism.

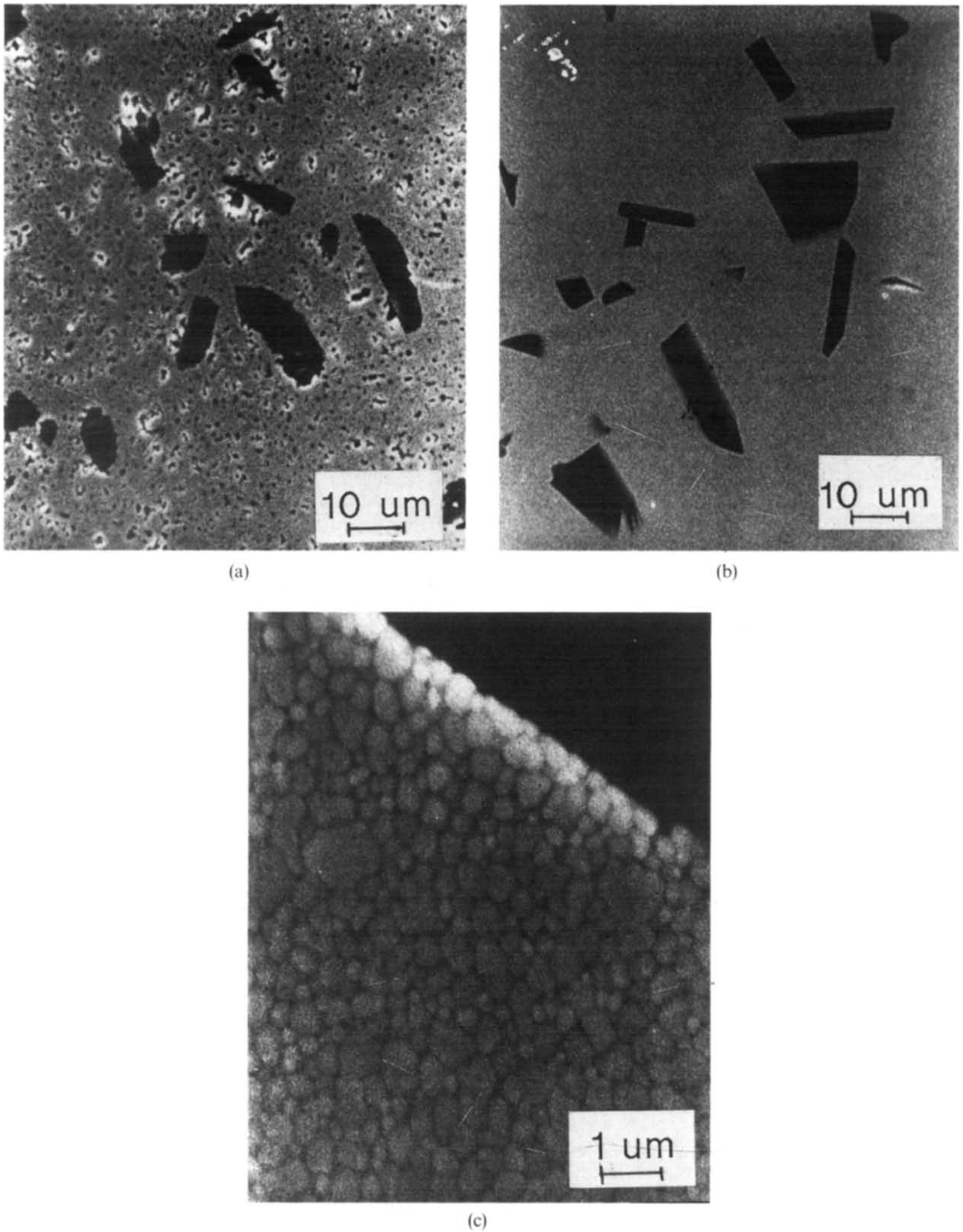
Indeed, the platelet Young's modulus being considerably higher than that of the zirconia matrix (in hexagonal (6H) α-SiC, $E \langle 0001 \rangle$ is 510 GPa, and $E \langle 2\bar{1}\bar{1}0 \rangle$ is 410 GPa, while for the zirconia matrix, the Young's modulus is only 220 GPa), a load transfer mechanism becomes possible. Therefore, stress at the crack tip would be transferred through high modulus platelets, which yields to a decrease of stress intensity at the crack tip. As a consequence, the size of the transformation zone will be reduced.

Lower tetragonal to monoclinic transformation efficiency, and residual stresses which should lower the composite toughness, have to be balanced by reinforcing mechanisms due to the presence of platelets in order to explain the toughness increase.

As already mentioned, a first operative reinforcing mechanism should be load transfer. Other reinforcing mechanisms are basically related to

Table 1. Room-temperature mechanical properties of composites, compared with monolithic material

	E (GPa)	σ_f (MPa)	K_{IC} ($MPa\sqrt{m}$)	H_v (GPa)
Matrix	220	959 ± 82	9·0 ± 0·6	12
Composite (5 vol.% SF platelets)	231	730 ± 58	10·8 ± 0·6	13
Composite (5 vol.% M platelets)	230	510 ± 10	10·0 ± 0·2	—



(a) (b)

(c)

Fig. 3. SEM observation of composite microstructures with 5 vol.% SF platelets: (a) After pressureless sintering; (b) after HIPing; (c) zirconia matrix close to a platelet inclusion.

crack deflection and branching. Indeed, Figs 4 and 5 show evidence of crack deflection and branching during crack propagation after indentation tests. Moreover, for a same indent load, the crack is longer in the case of the matrix, and strongly deviated for the composite.

SEM observation of rupture faces show intergranular crack propagation with respect to platelets (Figs 6 and 7), constituting evidence for crack deflection around platelets. Taking into account the rough aspect of fracture faces, microcracking contribution to toughness, as emphasised by Claussen *et al.*[10] for similar materials, cannot be neglected as a consequence of the large difference in thermal expansion coefficient between the matrix and inclusion.[11]

All these reinforcing mechanisms contribute to a toughness increase. However, it has been noticed

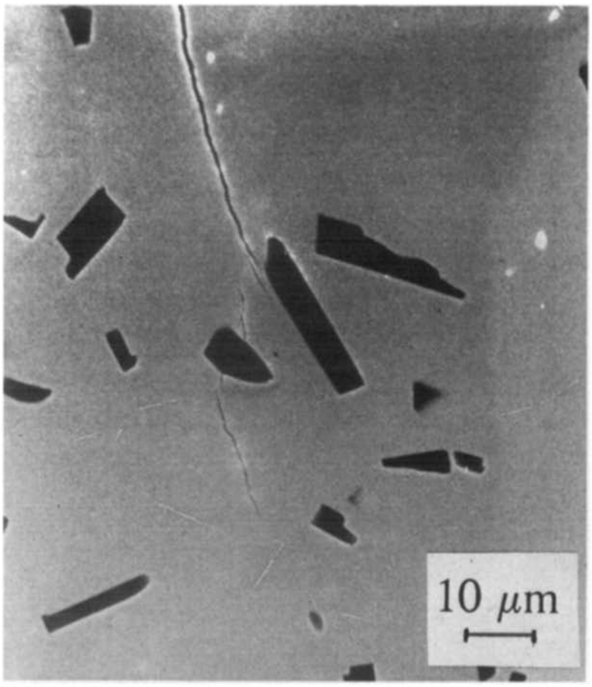


Fig. 4. Optical observation of crack branching during indentation test.

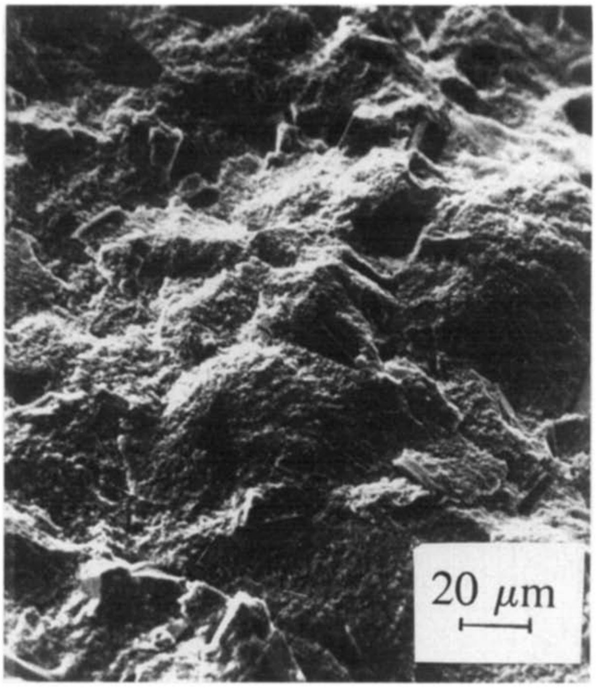


Fig. 6. SEM observation of rough rupture faces of a SF platelet composite after flexural strength test at room temperature.

that load transfer is favoured by a rather strong matrix–inclusion interface, which obviously means that some interaction between platelets and matrix occurred during synthesis, leading to a strong bond between them. Crack deflection around platelets, in order to become operative under these conditions, has then to be explained by the fact that platelets are submitted to compressive stresses, making crack propagation through platelets unfavourable.[12]

The strength reduction of the composite can mainly be attributed to the platelet size, increasing the critical flaw size.[13] Indeed, as shown in Fig. 8, platelets, when oriented parallel to the crack plane, can be observed at the fracture origin. As a consequence, flexural strength is more reduced when bigger M platelets are used.

3.4 High-temperature mechanical properties of post-HIPed composites

Composite toughness is higher than that of the matrix from room temperature up to 300°C, but decreases more rapidly for higher temperatures, where reinforcement, in comparison to the matrix, is no longer observed (Fig. 9).

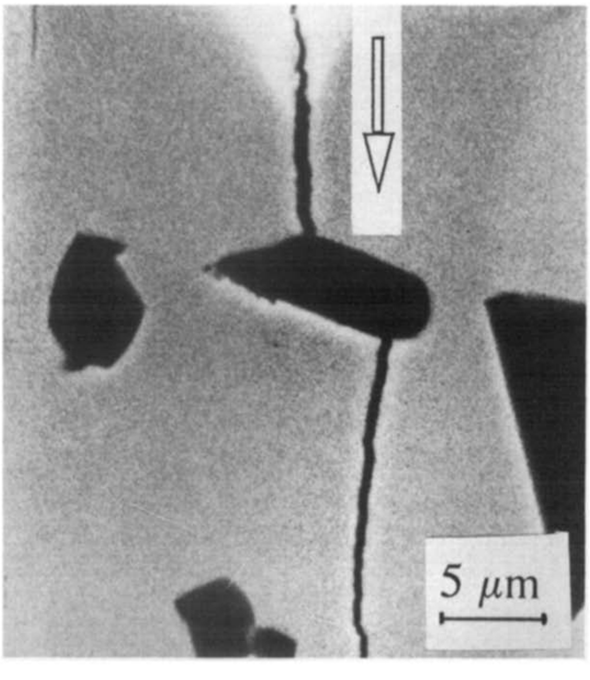


Fig. 5. Optical observation of crack deflection around platelets after indentation.

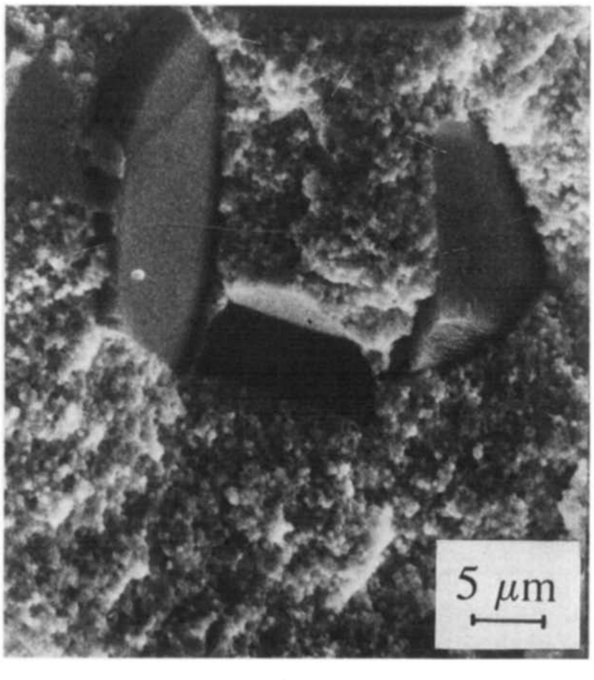


Fig. 7. SEM picture showing intergranular crack propagation with respect to platelets in a SF platelet composite.

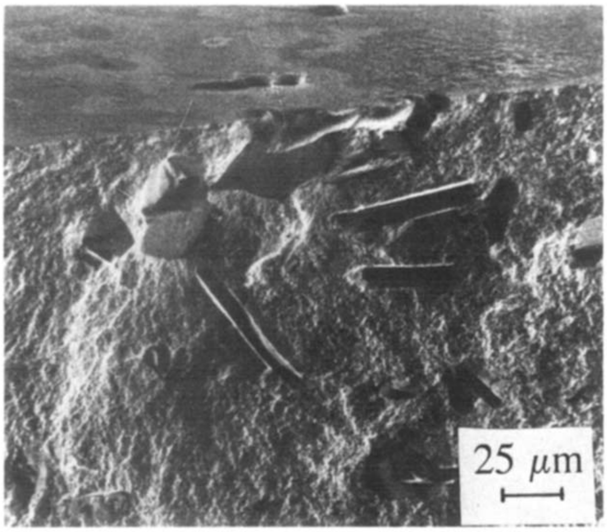


Fig. 8. SEM picture of a M platelet composite rupture faces, showing coarse platelets at the fracture origin.

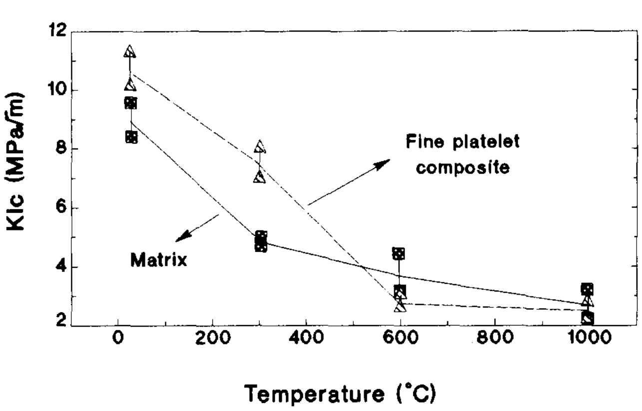


Fig. 9. Temperature dependence of composite toughness compared with that of the monophase material.

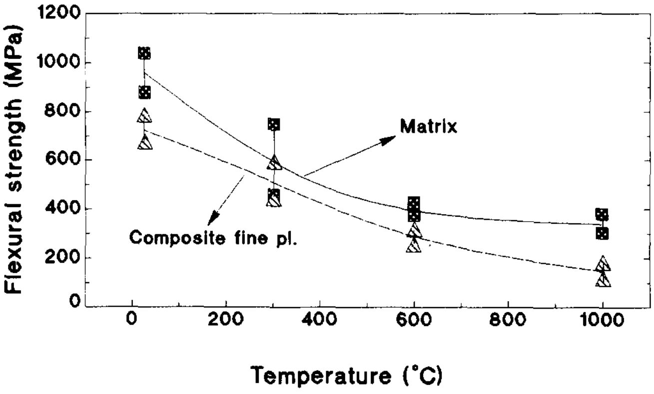


Fig. 10. Temperature dependence of composite flexural strength compared with that of the monophase material.

Flexural strength of both composite and matrix are reduced with increasing temperature (Fig. 10).

From the dilatometry measurements, it can be observed that an expansion of the composite takes place around 300°C (Fig. 11), both in air and under protective argon atmosphere, and therefore it cannot be due to any chemical reaction with atmospheric oxygen. The same kind of expansion was also observed by Akimune *et al.*[9] in the case of a hot-pressed SiC-whisker–Y-TZP composite.

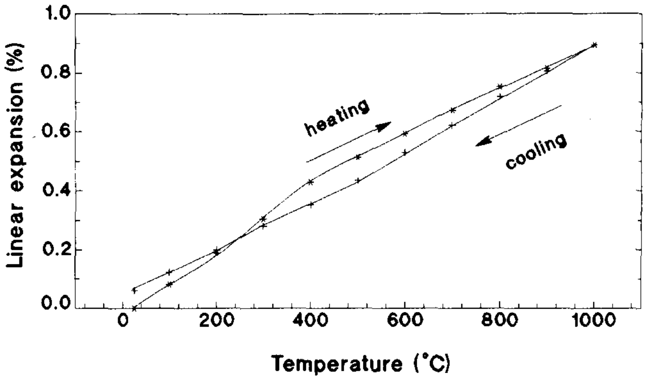


Fig. 11. Thermal expansion of SF platelet composite as a function of temperature.

Annealing of test bars used for flexural rupture measurements showed a tetragonal to monoclinic transformation at 300°C, explaining the volumic expansion observed at that temperature (Fig. 12). Moreover, this phenomenon enables an explanation of why the toughness improvement of the composite is maintained up to 300°C. By annealing of the residual compressive HIP stresses, leaving only expansion mismatch tensile matrix stresses operative, tetragonal to monoclinic transformation occurs, putting the matrix again under compression. The fact that residual tensile matrix stresses are counterbalanced impedes deterioration of the matrix of the composite at that temperature, resulting in a composite with higher toughness, compared with the monolithic material, due to contribution of similar reinforcing mechanisms as at room temperature (load transfer, crack deviation, microcracking).

However, at slightly higher temperature, 600°C for instance, monoclinic zirconia again transforms into tetragonal zirconia, leaving only tensile stresses in the composite matrix, which are still not relaxed at such a low temperature.[11] This probably explains why large cracks were observed at the tensile face of test bars after rupture at 600°C (Fig. 13). This matrix cracking can be suspected of being responsible for the lack of any reinforcement at that temperature.

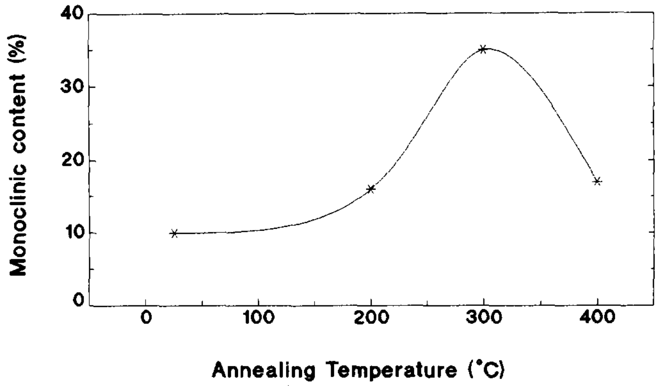


Fig. 12. Monoclinic zirconia content in SF platelet composite flexural strength test bars as a function of annealing temperature (air).

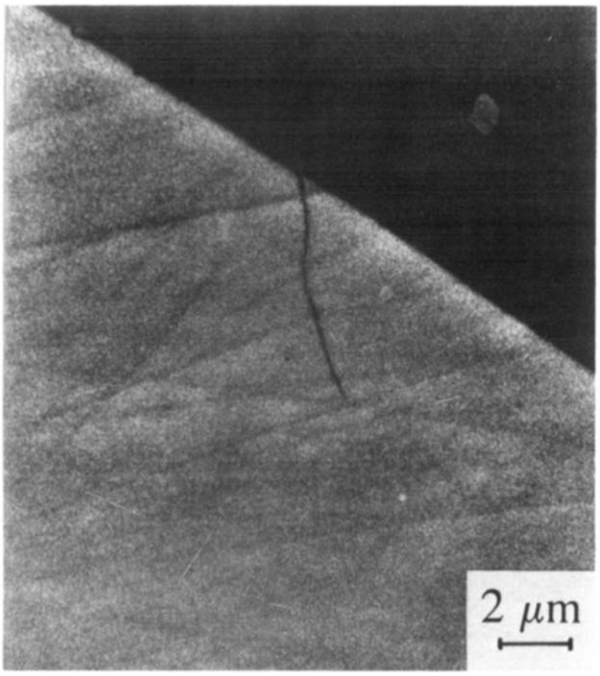


Fig. 13. SEM observation of cracks generated at the flexural side of a test bar broken at 600°C.

At high temperature (1000°C), some chemical interaction between the zirconia matrix and the SiC platelets might take place in the presence of air,[10] Indeed, optical observation of the microstructure after 1 h ageing at 1000°C under air, shows swelling or bloating due to chemical reaction of platelets with air oxygen and consequent carbon monoxide formation[14] at the platelet matrix interface. Formation of a glassy phase and/or bloating might explain the lower mechanical properties of the composite at that temperature.

4 Conclusions

Full densification of SiC-platelet–zirconia composites with 5 vol.% platelet content was achieved by sintering under argon atmosphere, followed by post-HIP.

Microstructures of composites are characterised by a fine matrix grain size (0·7 micron) and a well dispersed SiC-platelet phase.

Room-temperature toughness of the composites is slightly improved through various mechanisms: crack deflection, crack branching, eventually microcracking and also through load transfer, but the contribution to toughening by the tetragonal to monoclinic transformation of zirconia is reduced.

Lower flexural strength, compared with the matrix, is mainly attributed to the platelet size, increasing the critical flaw size.

At high temperatures, toughness of the composite is about 50% higher than that of the matrix, as long as tetragonal to monoclinic martensitic transformation is able to counteract residual tensile stresses. Starting from 600°C, when martensitic transformation becomes less efficient, matrix cracking occurs, whereas at 1000°C in air, chemical interaction between platelets and zirconia matrix takes place, and explains the decrease of composite toughness.

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