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Processing of SiC Whisker-reinforced Zirconia by Extrusion at Elevated Temperature

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Abstract

The extrusion of a zirconia matrix reinforced with 13 vol.% SiC whiskers has been studied at 1550 and 1600°C. This method uses the superplasticity properties of the matrix and allowed fully densified composites to be obtained inside which the whisker orientation approximated the extrusion direction. Microstructures are characterized in terms of whisker alignment and zirconia grain shapes. The room-temperature mechanical properties of extruded material are remarkably improved compared to those of the same composition obtained by hot-pressing. The reinforcement effect, related to the nearly uniaxial whisker alignment, is essentially due to whisker pull-out phenomena even if pull-out lengths did not exceed a few whisker radii.

Das Extrudieren einer mit 13 Vol.% SiC-Whiskern verstärkten ZrO_2-Matrix wurde im Bereich zwischen 1550 und 1600°C untersucht. Die angewandte Methode erlaubt, dank der superplastischen Eigenschaften der Matrix, die Herstellung vollständig verdichteter Verbundwerkstoffe, in denen die Whisker um die Extrusionsrichtung orientiert sind. Die Gefüge werden hinsichtlich der Ausrichtung der Whisker und der Form der ZrO_2-Körner beschrieben. Die mechanischen Eigenschaften des extrudierten Materials bei Raumtemperatur sind denen von heißgepreßtem Material deutlich überlegen. Der Verstärkungseffekt aufgrund der nahezu uniaxial ausgerichteten Whisker beruht im wesentlichen auf Pull-Out-Phänomenen. Dies gilt auch wenn die herausgezogenen Whiskerlängen in der Größenordnung weniger Whiskerradien liegen.

Le processus d'extrusion d'un composite à matrice zircone renforcée par 13% en volume de whiskers de SiC a été étudié à 1550 et 1600°C. Cette technique utilise les propriétés de superplasticité de la matrice et on a permis d'obtenir des composites denses dans lesquels l'orientation des whiskers est proche de la direction d'extrusion. Les microstructures ont été caractérisées par rapport à l'alignement des whiskers et à la forme des grains de zircone. Les propriétés mécaniques, étudiées à température ambiante, ont été comparées à celles du même composite obtenu par pressage uniaxial à chaud; elles apparaissent notablement renforcées. L'effet de renforcement relié à l'alignement presque unidirectionnel des whiskers dans le matériau extrudé est principalement dû à des mécanismes d'arrachement, même si les longueurs extraites n'excèdent pas quelques fois le rayon des whiskers.

1 Introduction

High-strength SiC whiskers are commonly used to reinforce ceramic matrices such as alumina or mullite. Both fracture strength and fracture toughness of the composite are improved relative to those of the matrix, owing to toughening mechanisms like crack deflection and whisker bridging processes.[1–3] In contrast to fibre reinforcement, whisker reinforcement allows the use of conventional ceramic

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processing methods. However, pressureless sintering of whisker-reinforced ceramics leads to bad densified composites with low mechanical properties, because densification is inhibited by the morphology of the whiskers and the low value of diffusion coefficients of silicon and carbon. Consequently, to achieve fully densified reinforced composite, it is necessary to use hot-pressing techniques, whose disadvantage is to limit the shape of the final products, or hot isostatic pressing that needs to solve the container problem.

In this paper an alternative route for the achievement of dense shaped composites is analysed. It consists in using the superplasticity properties of a fine-grained matrix. Indeed, recent works have shown that it is possible to shape fine-grained single-phase ceramics by plastic deformation at elevated temperature.[4–7] It is then of interest to investigate the possibilities for reinforced ceramics with the fine-grained matrix to be formed using the superplasticity properties of their matrix. To this end, the high-temperature extrusion of a whisker-reinforced zirconia matrix has been tested and analysed. The resultant microstructures were characterized by scanning and transmission electron microscopy. Mechanical properties of extruded parts have been compared to those of hot-pressed material from the same powder batch. The hot extrusion technique is a convenient one for the achieving of pieces with precise sizes without subsequent diamond tool machining.

2 Experimental Procedure

The initial mixture was supplied by Céramiques Techniques Desmarquest (Evreux, France).[8] The composite consisted of a 3 mol% yttria partially stabilized tetragonal zirconia matrix reinforced with 13 vol.% silicon carbide whiskers. A zirconia matrix has been chosen in this work because at the present time it is the ceramic that exhibits the most promising superplasticity properties. The green products obtained by slip casting in plaster moulds, to achieve the best homogeneity, were ground and cold pressed in the graphite die used for extrusion. The characteristics of the dies have been already described.[7] In the present work the extrusion diameter ratio ($D = dp/df$) was 2 (dp: piston diameter and df: final diameter 15 mm), one test only being run with a ratio of 3; the die cone angle was 26·6° in both cases. Sliding frictions during extrusion were reduced by covering the die surfaces with graphite paper sheets.

Extrusion experiments took place under vacuum between 1500 and 1600°C. The extrusion stress applied by the piston was maintained to a constant value during the experiments and the piston displacement was recorded as a function of time. For comparison a disk (Ø = 50 mm) of dense material was prepared by uniaxial hot-pressing (1550°C, 45 MPa, 15 min). The microstructure of the extruded composites was examined: (i) in a scanning electron microscope (SEM) on polished surfaces to image the chemical composition and observe the whisker distribution and (ii) by transmission electron microscopy (TEM) on thin foils cut off in planes perpendicular or parallel to the extrusion direction and carbon coated after thinning by ion bombardment.

The resultant mechanical properties were evaluted at room temperature by determining the bend strength and the fracture toughness. The bend strength was measured by three-point bending tests (20 mm span, 2·8 mm × 3·2 mm × 24 mm bars) while the notched beam technique was used for the fracture toughness determination. For all these tests the applied force was parallel to the hot-pressing direction in the hot-pressed bars or perpendicular to the extruded direction for extruded bars. Bars for toughness measurements were notched to 1 mm using a 0·15 mm thick diamond blade. Eight bars were tested for each processing condition.

3 Results and Discussion

Figure 1 shows the piston displacement rate as a function of time for an applied stress of 42 MPa and temperatures of 1550 and 1600°C respectively. The extruded lengths were fourfold and ninefold the piston displacement for the extrusion ratios 2 and 3 respectively. This means that for $D = 2$, the composite suffered an equivalent strain of 3 during its passage in the extrusion cone, corresponding to a strain rate faster than 10^{-3}/s for the test at 1600°C. The apparent decrease in piston displacement rate is partly due to a grain growth phenomenon of the zirconia phase during its stay at high temperature.

From the extruded rods, specimens for density

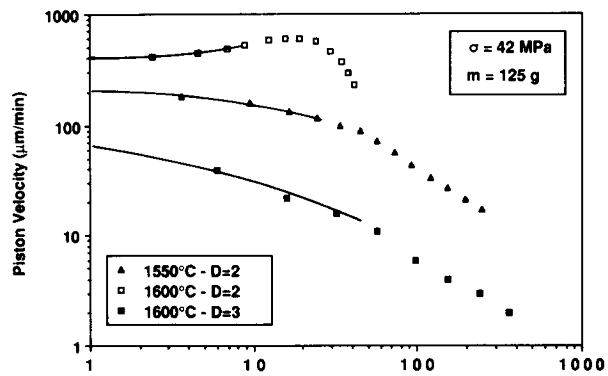

Fig. 1. Piston velocity versus time for different extrusion ratios ($D = 2$ and 3) and test temperatures (1550 and 1600°C).

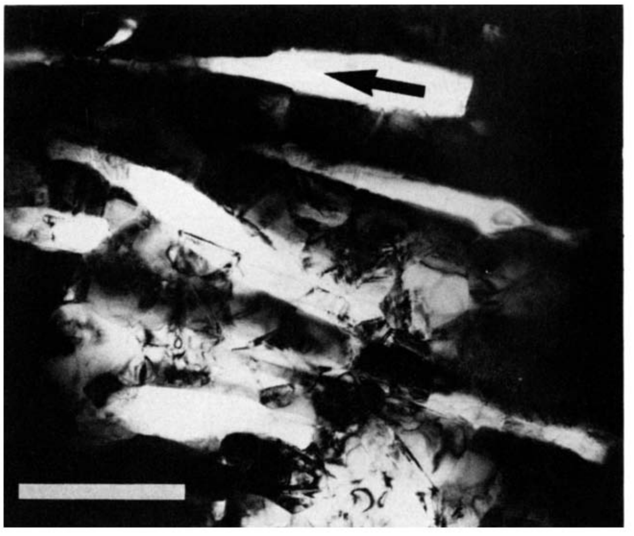

Fig. 2. TEM observation in a foil parallel to the extrusion direction (arrow). Extrusion temperature: 1600°C; scale bar = 2 μm.

measurements were taken in places before, in and after the extrusion cone. It appeared that the density before the entrance in the cone ($\rho = 5{\cdot}72$ g/cm^3) was about the theoretical one. This means that composite densification and extrusion constituted two very distinct steps of the processing. Densification takes place during the heating step which is run under a stress of 10 MPa, this low stress being able to densify but not to extrude. This is in agreement with uniaxial hot-pressing tests performed at a constant heating rate of 750°C/h which indicated that densification was achieved at 1450°C. Density of the extruded parts was also near the theoretical one and no significant difference could be observed between the beginning and the end of extruded rods.

The difference of initial piston velocities at 1550 and 1600°C leads to an apparent extrusion activation energy of about 550 kJ/mol which is a classical value for high-temperature creep of Y-TZP materials. According to the slab analysis of extrusion proposed by Keller *et al.*,[7] it is possible to estimate the piston velocity of such a constant load extrusion process from the uniaxial creep behaviour of the studied material. For a creep test performed at 1350°C under 20 MPa on a hot-pressed sample, the initial strain rate was about 4×10^{-5}/s and the apparent stress exponent, measured by the stress jump technique between 16 and 24 MPa, was about 3. From these data, the slab analysis predicts a piston velocity of about 0·8 mm/min at 1550°C for an extrusion ratio of 2; this estimated velocity is not in such good agreement with the measured one (0·3 mm/min) as in the case of Y-TZP materials[7] but it is the right order of magnitude. Inducing some perturbations in the matter flow, the SiC whiskers can be at the origin of the lack of applicability of the slab analysis.

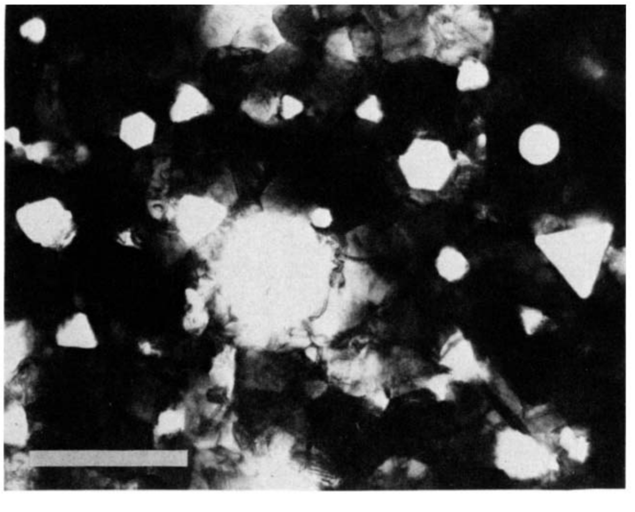

Fig. 3. Same sample as in Fig. 2. TEM observation in a foil perpendicular to the extrusion direction; scale bar = 2 μm.

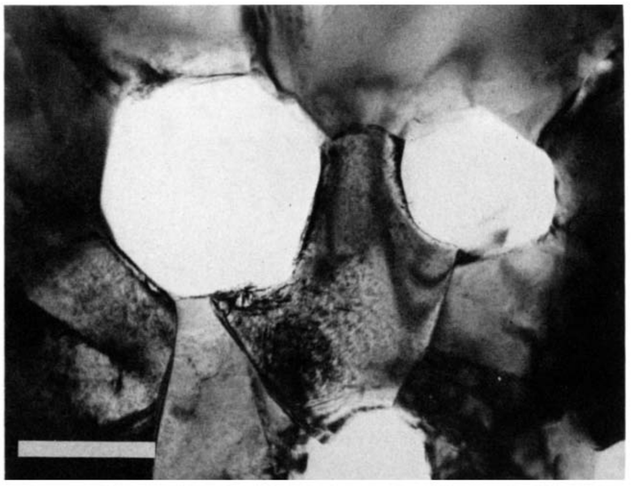

Fig. 4. Accommodation of local strains by a zirconia grain (TEM micrograph). Scale bar = 0·5 μm.

Figures 2 and 3 represent electron transmission micrographs in planes respectively parallel and perpendicular to the extrusion direction for a composite obtained at 1600°C with $D = 2$. One can see that greater than 80% of the whiskers are parallel to the extrusion direction. Owing to the extrusion temperatures, which were low in order to promote a noticeable plastic deformation of the SiC phase, the submicronic zirconia grains adopted the shape of the surrounding whiskers, as Fig. 4 shows. Although in some places small glassy pockets were observed, conventional TEM did not allow the detection of an intergranular vitreous film, a phase that is generally present in zirconia polycrystals.[9,10] This means that its thickness was less than a few nanometers.

SEM investigations confirmed the TEM results: in Fig. 5 observations showing the alignment process of whiskers in the extrusion cone are gathered. That alignment results from shear stresses, generated by the matter flow in the cone, and is well marked on the outer part of the rods, when the shear stresses have their maximum value. Only a few whiskers were broken during the extrusion process. This is

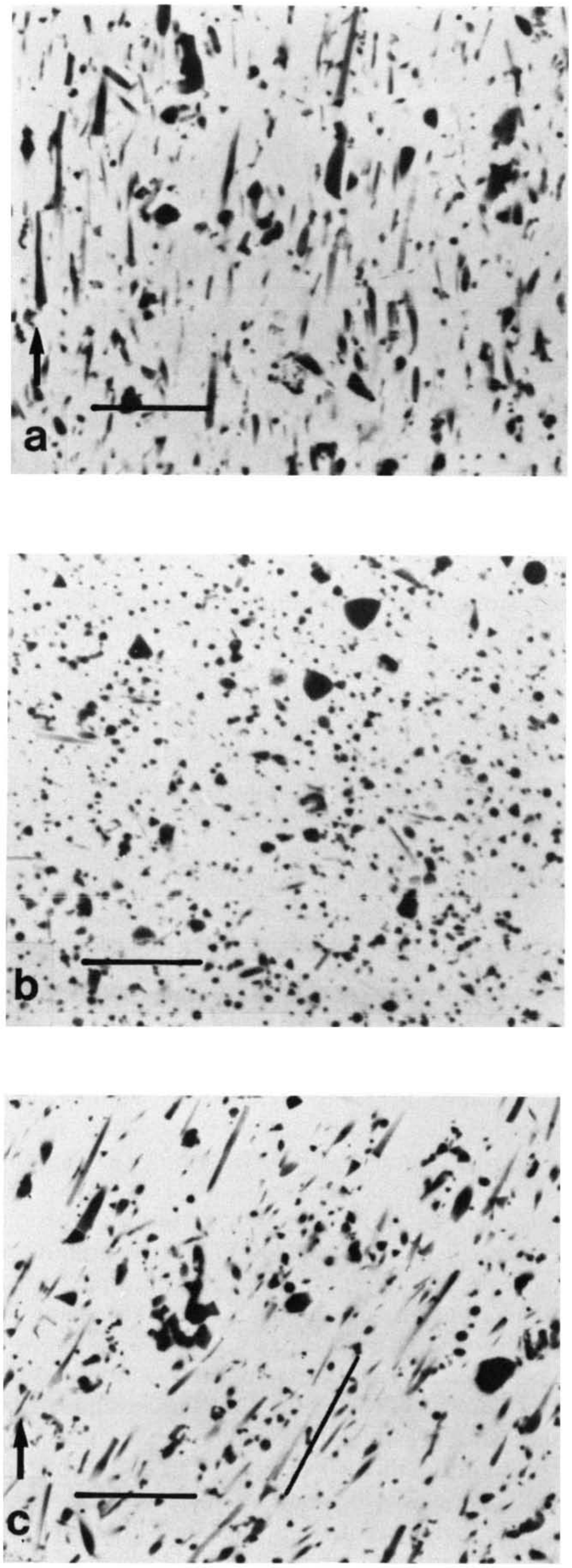

Fig. 5. SEM observations (backscattered electrons) of microstructure on (a) longitudinal and (b) transverse sections at half length of a rod extruded at 1600°C during 40 min (extrusion ratio $D = 2$); the arrow indicates the extrusion direction; (c) an observation of a longitudinal section near the external surface (parallel to the oblique line) in the extrusion cone. Scale bar = 10 μm.

Table 1. Strength and fracture toughness of hot-pressed and extruded TZP/SiC whisker composites

Processing method	*Strength* (*MPa*)	*Toughness* ($MPa\sqrt{m}$)
Hot-pressing	1 180 ± 100	11·8 ± 0·8
Extrusion	1 350 ± 60	15·0 ± 1·3

probably a consequence of the relatively low aspect ratio of the whiskers, about 10. Moreover grain size measurements in a hot-pressed disk (1550°C during 15 min under 45 MPa) and in a sample extruded at the same temperature during 4 h ($D = 2$) showed grain sizes of about 0·55 μm and 0·85 μm respectively. This grain growth can explain a large part of the observed decrease in piston velocity: with a grain size exponent of 3 in the creep rate relationship, such a grain growth induces a factor of 4 in the piston velocity.

The fracture toughness values and flexural strengths of extruded rods and hot-pressed bars are given in Table 1. These values, which compare well with those obtained by Claussen *et al.*[11] in SiC whisker-reinforced TZP, are insensitive to the processing temperature and show an increase in bend strength and fracture toughness of the extruded composite relative to the hot-pressed one. This illustrates the strengthening effect of a uniaxial distribution of whiskers relative to a pseudo-isotropic one. Nevertheless, the difference in the grain sizes of the two kinds of materials can also contribute to a slight increase in the fracture properties in favour of the extruded material, the tetragonal–monoclinic transformation being easier for larger grains, related either to a pure grain size effect or to the Y_2O_3 content.[12] By assuming that fracture originated from elliptical defects, values in Table 1 lead to an approximate defect size of 20 to 30 μm independent of the processing technique. These defects are likely to result from heterogeneities in the starting powder which were not destroyed by plastic deformation during extrusion.

Fracture surfaces of extruded and hot-pressed specimens are presented in Figs 6 and 7 respectively. Due to the relatively small grain size of the zirconia phase, matrix fracture was intergranular and fracture surfaces appeared to be rugged at the microscopic scale, likely to be related to crack deflection mechanisms. Microcrack observations were unusual. According to their orientation relative to the surface fracture, the whisker behaviour during sample rupture was different.

When the whisker axis was close the resultant tensile stress axis, whisker pull-out occurred for each kind of material (Figs 6 and 7). Nevertheless, in those cases, due to premature fracture of whiskers, pull-out lengths were generally limited to a few whisker

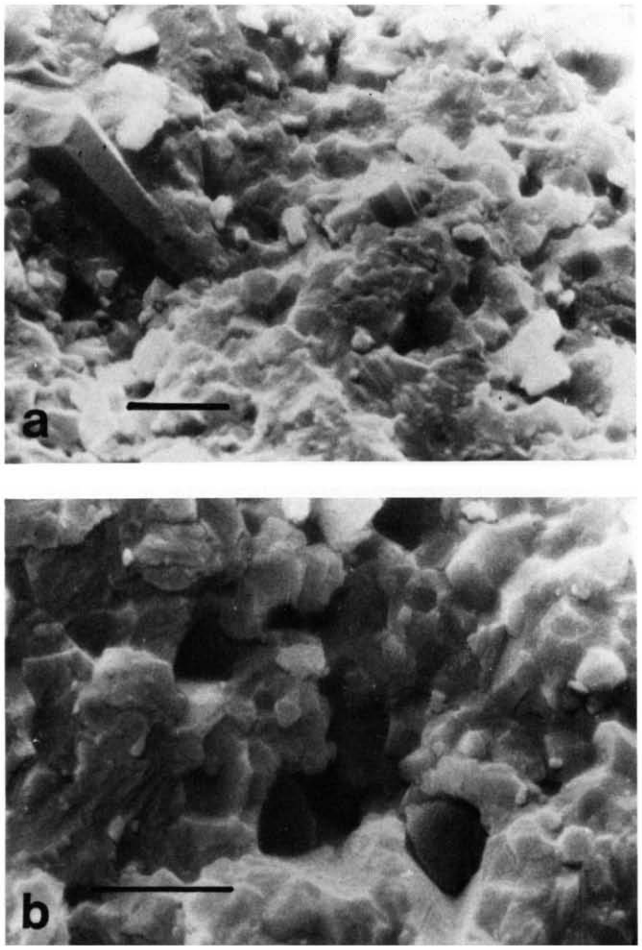

Fig. 6. Rupture surfaces at room temperature of a rod extruded at 1550°C. Scale bar = 2 μm.

Fig. 7. Rupture surfaces at room temperature of samples hot-pressed at 1550°C: (a) crack deflection, (b) interface decohesion for whiskers in the crack plane. Scale bar = 4 μm.

radii. This is probably due to the high compressive radial stress ($\sigma \approx -1{\cdot}5\,\mathrm{GPa}$[13]) resulting from the differential thermal expansion of the two constituents ($\alpha_{SiC} = 4{\cdot}7 \times 10^{-6}/^{\circ}C$, $\alpha_{TZP} = 10 \times 10^{-6}/^{\circ}C$) and inducing a low critical length (a few micrometres).[13] Crack deflection was observed for whiskers at a low angle of the fracture surface (Fig. 7(a)), especially in hot-pressed composites where the randomly oriented whiskers favoured this mechanism, but some debonding also took place for such a whisker orientation.

In agreement with these results the increase in mechanical properties of the extruded material with respect to the hot-pressed one can only be related mainly to the whisker orientation and consequently to the efficiency of the various toughening mechanisms. This means that in the present case the pull out mechanism was more energy consuming than the crack deflection mechanism, even if pull out lengths were small. Moreover, in hot-pressed specimens, interface decohesions without any apparent crack deflection were also frequently observed (Fig. 7(b)), a feature never present in the extruded rods. These decohesions, which correspond to whiskers that were already in the crack plane, did not contribute significantly to an improvement of fracture properties and can partly explain the difference in the mechanical properties between the two materials.

Such a processing could be generalized to other ceramics reinforced with whiskers. The prime condition is that the superplasticity properties of the matrix are maintained during the entire duration of the extrusion. This means that (i) grain size must be as fine as possible at the test onset and (ii) a too excessive grain growth must be avoided. The second requirement can be fulfilled by adding particles of a second phase which impede the grain boundary migration and consequently hinder grain growth. For example, inherent grain growth which is destructive towards superplasticity properties in alumina can be partly hindered by zirconia particles which efficaciously pin the grain boundaries.[14,15] Different shapes of the extruded rods could then be obtained by adjusting the cross-sectional area of the exit aperture.

4 Conclusion

Extrusion at 1550 and 1600°C of a zirconia matrix reinforced with 13 vol.% SiC whiskers has produced fully densified composites inside which the whisker orientation approximated the extrusion direction. The room-temperature mechanical properties are remarkably improved compared to those of the same composition obtained by hot-pressing. The reinforcement effect, related to the uniaxial whisker alignment, was essentially due to the whisker pull-out even if pull-out lengths were small.

Contrary to the work of Claussen & Petzow,[3] where the processing of unidirectionally whisker-reinforced mullite had required two steps, the hot-pressing of ceramic whisker rods after extrusion at room temperature, the present technique has allowed an analogous result to be obtained in one operation only. The shape of the extrusion cone can be adjusted to obtain various sections of the rods without further diamond tool machining.

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