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SiC Platelet Orientation in a Liquid-Phase-Sintered Silicon Carbide Composite Formed by Thermoplastic Forming Techniques

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Abstract

Thermoplastic forming techniques were used to study the alignment of the platelets (d_{50} = *14* μm*, aspect ratio 8–10) and the effect on densification of a liquid-phase-sintered silicon carbide composite. Several ceramic parts (test bars, tubes, discs, rings and balls) were manufactured by injection moulding, hot moulding (low-pressure injection moulding) and thermoplastic extrusion methods. Special binders for injection moulding/extrusion and hot moulding were developed. The feedstocks were characterized by torque rheometry in a sigma-blades kneader and by shear-stress-controlled rotation viscosimetry, respectively. The orientation of the platelets in the matrix material was studied by microscopy. An alignment of the platelets corresponding to the flow of the mixtures was observed. In some shapes there was a perfect alignment of the platelets preventing the formation of a platelet framework and resulting in high sintering densities of* > *97% of theoretical with 20% platelet content. This essentially demonstrates the opportunity of making dense, platelet-reinforced composites by pressureless sintering. © 1996 Elsevier Science Limited.*

1 Introduction

Some studies of SiC-whisker reinforced ceramics have shown substantial improvements in fracture toughness and resistance to slow crack growth by the introduction of whiskers into the ceramic matrix.[1] Recently, however, there has been an increasing awareness of the health hazards associated with the manufacture of whisker-containing materials. A possible solution to this problem is replacement of the whiskers by ultrafine, single-crystal, disc-shaped particles, such as α-SiC platelets. For crack bridging and crack deflection, platelets show the same potential as whiskers.

Several papers in the literature discuss silicon carbide platelet-reinforced ceramic composites. Most of them deal with SiC platelet/alumina composites,[2] particularly the influence of forming methods on the platelet orientation.[3] The influence of SiC platelet reinforcement on the toughness and high-temperature creep of silicon nitride has also been described.[4]

Liquid-phase-sintered silicon carbide (LPSSiC) is a relatively new material. The development of a liquid phase sintering process for the densification of ultrafine silicon carbide[5] has offered the opportunity to make dense SiC-platelet-reinforced silicon carbide composites.

In the present work, the influence of forming techniques on the SiC platelet orientation in a liquid-phase-sintered silicon carbide matrix was investigated. Besides forming by dry pressing, the following thermoplastic forming techniques were used: injection moulding, thermoplastic extrusion and hot moulding. For technological and economical reasons it is very important to achieve a pressureless sintering process. By addition of platelets to a pressureless sinterable matrix one should expect a decrease in the sinterability of the composite. Steric hindrance of shrinkage processes during sintering will lead to incomplete densification of composites with higher platelet content, but alignment of platelets during forming can reduce this effect. Thus the intention of our work was to investigate the interaction of shaping and sintering in platelet-containing composites from a technological point of view.

2 Experimental Procedure

2.1 Raw materials

As raw materials α-SiC powder (UF 15, H. C. Starck) and silicon carbide platelets (grade SF, C-Axes Technology) were used. Yttria (grade

Table 1. Properties of powders used

	SiC	Al_2O_3	Y_2O_3
Specific surface area BET ($m^2 g^{-1}$)	15	8–10	10–16
Particle size (μm)			
d_{90}	<0·9	<2·5	<2·5
d_{50}	<0·5	<0·5	<0·8
d_{10}	<0·2	<0·3	<0·4
Purity	>97·0	>99·9	>99·9

Table 2. Properties of SiC platelets

Crystal structure	α-SiC (4H/6H polytype)
Chemical composition (%)	
O	0·18
C_{free}	0·01
Al	0·62
Fe	0·02
Particle size distribution (μm)	
d_{90}	37
d_{50}	14
d_{10}	7·8
Aspect ratio	8–10

fine, H. C. Starck) and alumina (A16SG, Alcoa) were used as sintering additives. The main properties of the powders used are shown in Table 1, while Table 2 shows the properties of the platelets.

Special binders for thermoplastic forming of ceramics were developed. For hot moulding a binder consisting of paraffin 54/56 (Wintershall), Genamine 18 R 100 D (Hoechst) and beeswax was used. Feedstocks for injection moulding and thermoplastic extrusion were manufactured based on polyethylene (LD), paraffin, wax and surfactants.

2.2 Forming techniques

Thermoplastic slips for hot moulding were manufactured by mixing the powders with the binder in a heated ball mill at a temperature of 100°C. The rheological properties of the thermoplastic slips were determined using a shear-stress-controlled rotation viscosimeter (UM/MC, Physica). Feedstocks for injection moulding and thermoplastic extrusion were prepared in a vacuum sigma-blades kneader (Linden) at a temperature of 130°C. For the characterization of moulding compounds a torque rheometer (Rheocord 90/Rheomix 600, Haake) was used.

Hot moulding (low-pressure injection moulding) was used to manufacture test bars, tubes, rings, discs and balls (Fig. 1). Hot moulding was realized on a hot moulding machine (KSE 2, Somtec) at a temperature of 95°C and a pressure of 5 MPa. For injection moulding of test bars (6 × 7 × 70 mm) an injection moulding machine (Allrounder

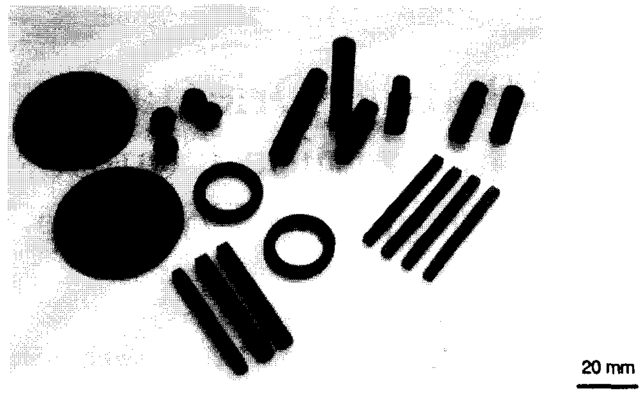

Fig. 1. Sintered SiC platelet/SiC ceramic parts with different shapes made by thermoplastic forming techniques.

370 C, Arburg) was used. The feedstock was also extruded at 130°C to produce tubes of dimensions 9 × 12 mm. For thermoplastic extrusion a twin-screw extruder (TW 100, Haake) was used. Stabilization of extruded tubes was achieved by cooling with compressed air.

Debinding of green ceramic parts was realized by thermal dewaxing at a temperature up to 270°C in a porous powder bed, followed by free-standing debinding of the parts up to 450°C in air.

Sintering of debinded ceramics was carried out in argon atmosphere at 1950°C in a furnace (FSW 315/400-2200, KCE).

2.3 Characterization

The bulk densities were determined using the immersion technique. The relative density was calculated by dividing the sintering density by the theoretical density of the powder blends. The sintered test bars were finished and chamfered. Flexural strength was measured using a three-point bend fixture (40 mm span) with a crosshead speed of 0·5 mm min^{-1} at room temperature. The fracture toughness was determined by the single-edge notched bend (SENB) method (200 μm notch). For each set 10 (flexural strength) or six (fracture toughness) samples were measured and the averaged values are reported.

The sintered ceramic parts were sectioned perpendicular and parallel to the flow direction of the mixture. After ceramographic preparation the microstructure was analysed by optical microscopy.

3 Results

3.1 Influence of SiC platelet content on rheological properties of thermoplastic moulding formulations

First it was necessary to clarify the influence of platelet content on the rheological properties of the thermoplastic moulding formulations, because

Table 3. Composition of thermoplastic SiC platelet/SiC hot moulding formulations

No.	*Solid phase content (wt%)*	*Composition*		*Platelet content (%)*
		SiC powder	*Oxide additive*	
1	78·95	90·09	9·91	0
2	79·78	85·59	9·41	5
3	80·54	81·53	8·97	9·5
4	81·28	77·75	8·55	13·7
5	82·08	74·14	8·16	17·7
6	83·44	67·93	7·47	24·6
7	86·06	57·39	6·31	36·3
8	83·00	57·39	6·31	36·3
9	80·20	57·39	6·31	36·3
10	78·61	57·39	6·31	36·3

their behaviour affects the opportunities for forming ceramic shapes. Therefore thermoplastic moulding formulations with different platelet contents were studied.

In Table 3 the compositions of the thermoplastic SiC platelet/SiC slips are shown. Beginning with a typical thermoplastic slip for manufacturing of liquid-phase-sintered silicon carbide (no. 1, Table 3), the platelet content was systematically increased and the rheological properties of slips were measured. The addition of platelets to the slip (Table 3, nos 1–7) increases the total solid phase content in the system, resulting in a higher viscosity. However, the viscosity of the composition decreases with increasing platelet content from 0 to 10% (Table 3, nos 1–3) as shown by the effect of the shear stress on the shear rate (Fig. 2). At first sight this result seems to be surprising but it can be explained by the effect of the lower specific surface of a powder blend with higher platelet content.

The thermoplastic slip with a platelet content of 50% was mixed with additional binder to decrease the solid content (Table 3, compositions 7–10, and Fig. 3). The effect of the solid content on the viscosity of the thermoplastic slips is shown in Fig. 4. It can be seen that the addition of SiC platelets to the thermoplastic slip of silicon carbide does not result in a higher viscosity. On the contrary, for the same rheological properties, the addition of platelets allows us to increase the solid content of the thermoplastic slip. In fact, the processing of platelet-containing thermoplastic slips was possible without any problems.

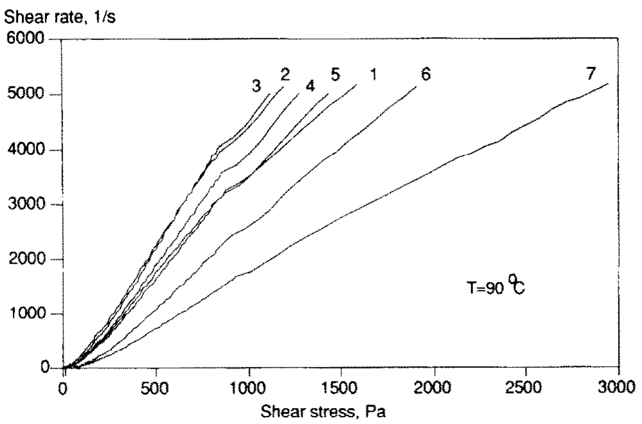

Fig. 2. Flow behaviour of thermoplastic SiC platelet/SiC hot moulding formulations.

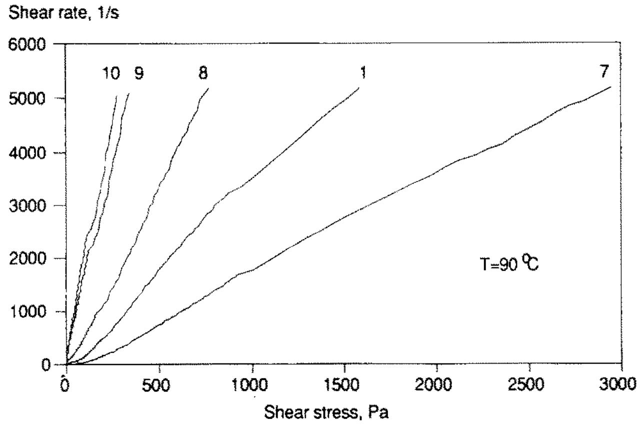

Fig. 3. Flow behaviour of thermoplastic SiC platelet/SiC hot moulding formulations.

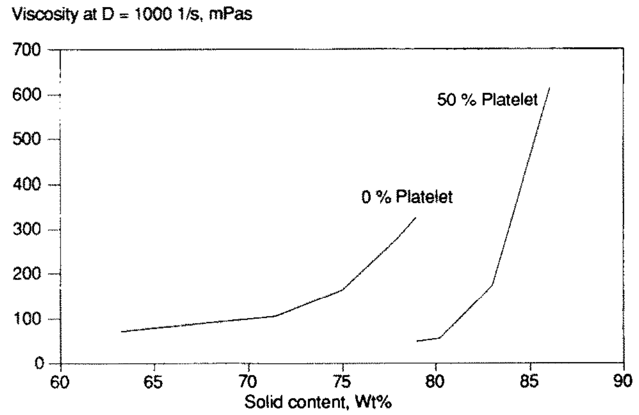

Fig. 4. Viscosity of thermoplastic slips without platelets and with a platelet content of 50%, as a function of the solid content.

3.2 Effect of forming technique on densification and material properties of SiC platelet/LPSSiC composites

Test bars with 10% SiC platelet content to SiC were manufactured by uniaxial dry pressing, by hot moulding and by injection moulding. The debinded samples were sintered at identical conditions, finished and characterized. The results are shown in Table 4.

In Figs 5–7 the microstructures of the sintered test bars manufactured by uniaxial dry pressing (Fig. 5), hot moulding (Fig. 6) and injection moulding (Fig. 7) are shown. All microstructures show a homogeneous distribution of the platelets in the bulk. However, in hot- and injection-moulded test

Table 4. Material properties of test bars made by different forming techniques (LPSSiC + 10% platelets)

	Dry pressing	*Hot moulding*	*Injection moulding*
Density (% of theoretical)	97·0 ± 0·3	96·6 ± 0·3	98·3 ± 0·1
Flexural strength (MPa) [three point bend]	424 ± 15	422 ± 68	497 ± 38
Fracture toughness (MPa $m^{1/2}$)	5·6 ± 0·4	not determined	6·2 ± 0·6

bars, especially in the longitudinal axis, an alignment of the platelets can be observed. This alignment in thermoplastically formed test bars prevents the formation of a platelet framework and results in higher sintering densities. The highest sintering density (> 98% of theoretical value) was achieved by injection moulding. A higher injection pressure seemed to result in more perfect alignment of the platelets in the injection-moulded test bar. The highest material properties of injection-moulded test bars (flexural strength 497 MPa) corresponds to the high density.

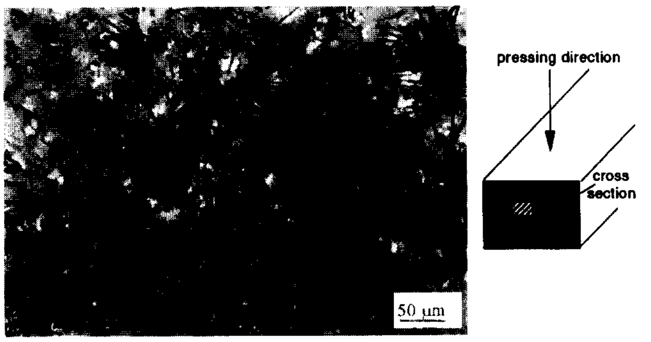

Fig. 5. Photomicrograph of a sintered dry-pressed test bar, original magnification 200:1 (dark field).

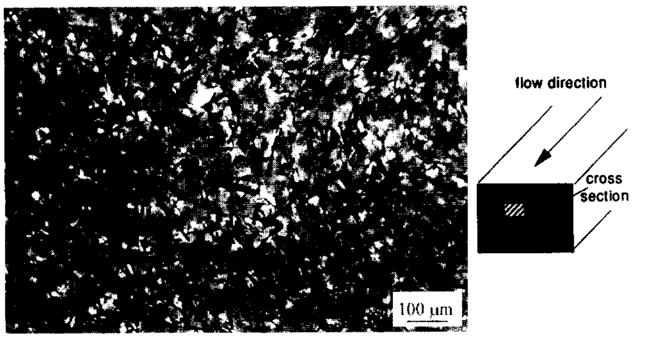

Fig. 6. Photomicrograph of a sintered hot-moulded test bar, original magnification 100:1 (dark field).

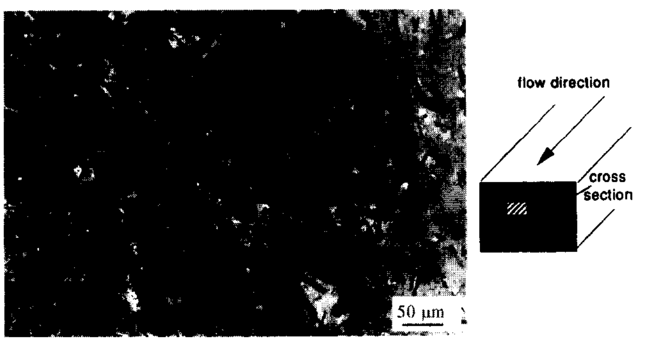

Fig. 7. Photomicrograph of a sintered injection-moulded test bar, original magnification 200:1 (dark field).

3.3 Effect of SiC platelet content on densification of hot-moulded ceramic parts with different geometry

Different shape geometries of ceramic parts were examined to study the influence of forming technique on the SiC platelet orientation in a liquid-phase-sintered SiC matrix. Thermoplastic hot moulding slips with platelet contents of 0, 5, 10 and 20% were prepared and formed to test bars, discs, tubes, rings and balls. After debinding and sintering the densities were determined. The results are shown in Fig. 8. Additionally, the sintering density of dry-pressed test bars is presented.

As a rule, the sintering densities of SiC platelet/SiC samples decreased with increasing SiC platelet content. The dry-pressed test bars with SiC platelet contents > 10% were limited to sintering densities of 95% (of theoretical density), whereas the density of hot-moulded test bars was improved even with an SiC platelet content of 20%. The highest sintering densities (97–98% of the theoretical value) with SiC platelet contents up to 20% were realized in hot-moulded discs.

It was supposed that the different densification behaviour of the hot-moulded part geometries

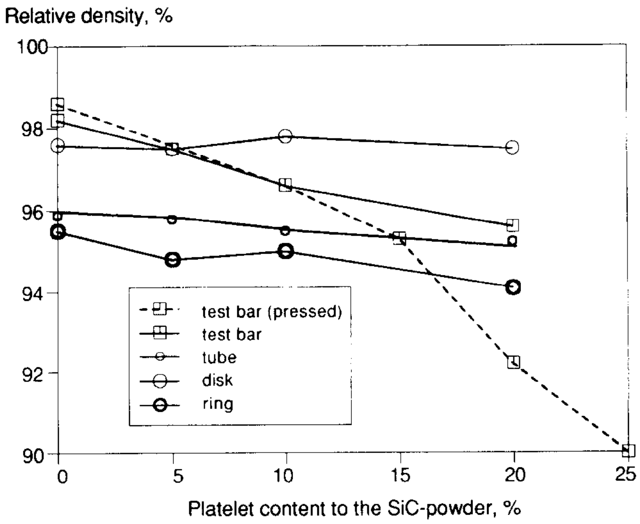

Fig. 8. Sintering density of SiC platelet/SiC composite samples as function of SiC platelet content, shape and forming technique (hot moulding and dry pressing).

examined is caused by the individual form filling processes. Therefore, the microstructure of SiC platelet/SiC composites with different shape geometry was studied.

3.4 SiC platelet alignment after sintering in thermoplastically formed parts with different shape geometry

Sintered discs, tubes, rings, bars and balls with 10% platelets were sectioned perpendicular and parallel to the flow direction of the thermoplastic mixture during forming. After polishing the microstructure was analysed by optical microscopy. The micrographs are shown in Figs 9–14.

For example, in Fig. 9 the microstructure of a sintered hot-moulded disc is presented. The comparison of photomicrographs parallel (a) and perpendicular (b) to the flow direction of the mixture shows the alignment of the platelets. The overview in Fig. 9(c) illustrates impressively the form filling process and the corresponding alignment of the platelets.

In a hot-moulded ring (Fig. 10) the platelets are perfectly aligned around the centre of the cross-section. Equally, the uniaxial flow direction during forming of tubes results in alignment of the platelets both during extrusion and hot moulding (Figs 11, 12 and 13). Figures 12 and 13 show again the comparison of sections parallel and perpendicular to the flow direction of the mixture in hot-moulded tubes.

However, the form filling process of a hot-moulded ball [Fig. 14(a)] is different. In this case a nearly isotropic platelet orientation results. This causes increased development of a platelet framework in the SiC matrix, as shown in a magnification [Fig. 14(b)], leading to lower sintering densities of the composite.

4 Conclusions

Corresponding to the flow of the mixture, an alignment of SiC platelets in a liquid-phase-sintered silicon carbide composite was observed. The alignment

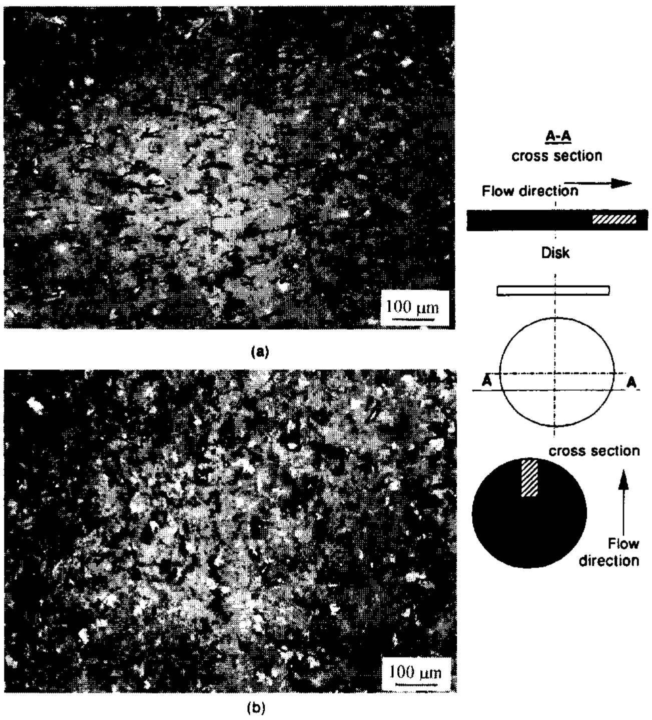

Fig. 9. Photomicrographs of a sintered hot-moulded disc, original magnification 100:1 (dark field), parallel (a) and perpendicular (b) to the flow direction. (c) Overview of form filling parallel to the flow direction, original magnification 50:1.

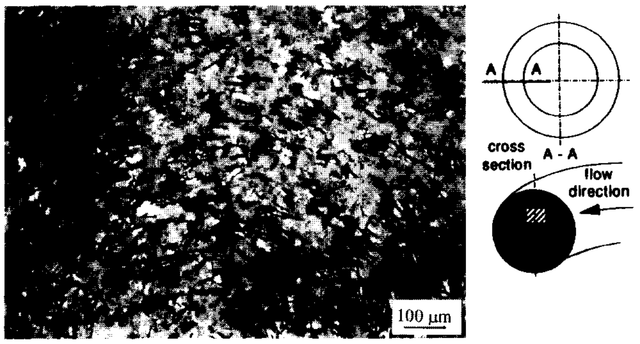

Fig. 10. Photomicrograph of a sintered hot-moulded ring, original magnification 100:1 (dark field).

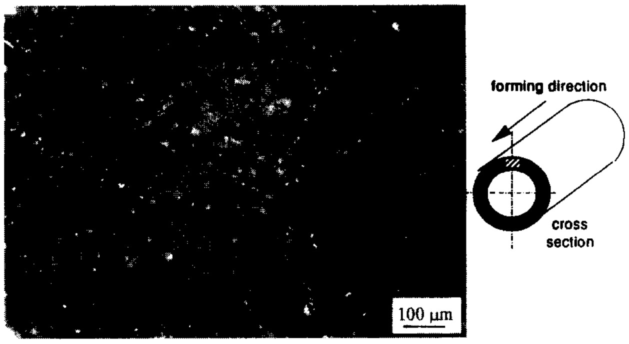

Fig. 11. Photomicrograph of a sintered extruded tube, original magnification 100:1 (dark field).

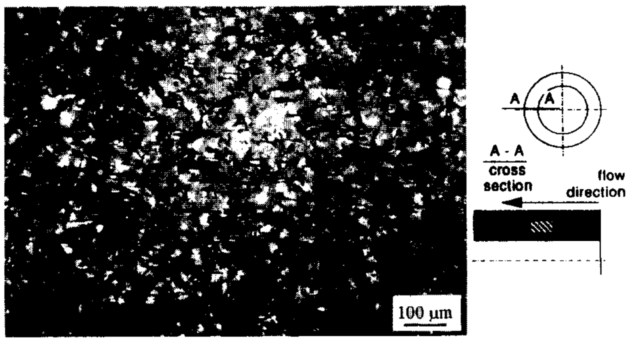

Fig. 12. Photomicrograph of a sintered hot-moulded tube parallel to the flow direction, original magnification 100:1 (dark field).

is influenced by the geometry of the ceramic parts. A perfect alignment of the SiC platelets improves the densification of the composite. The dry-pressed test bars with SiC platelet contents > 10% were limited to sintering densities of 95% (of theoretical), whereas the density of hot-moulded test bars was improved even with an SiC platelet content of 20%. The highest sintering densities (97–98% of the theoretical value) with SiC platelet contents up to 20 % were realized in hot-moulded discs. These results demonstrate the opportunity of making dense, platelet-reinforced composites by pressureless sintering.

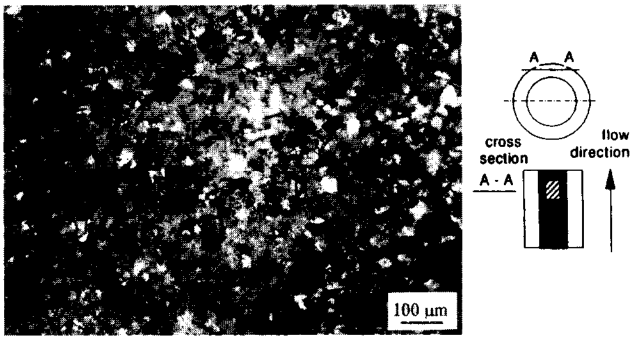

Fig. 13. Photomicrograph of a sintered hot-moulded tube perpendicular to the flow direction, original magnification 100:1 (dark field).

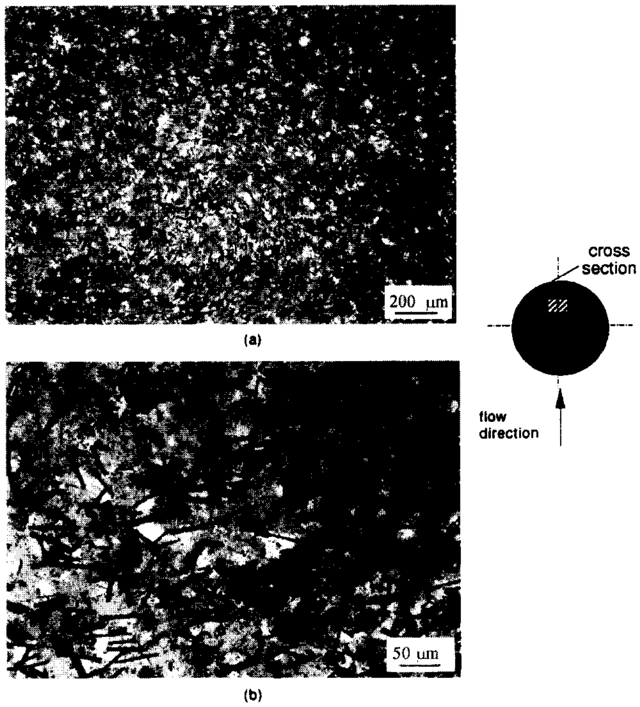

Fig. 14. Photomicrographs of a sintered hot-moulded ball, original magnification 50:1 (a) and 200:1 (b), dark field.

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