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Author

Cao, J.J.

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J.J. Cao, Y. He, W.J. MoberlyChan, and L.C. De Jonghe
Materials Sciences Division

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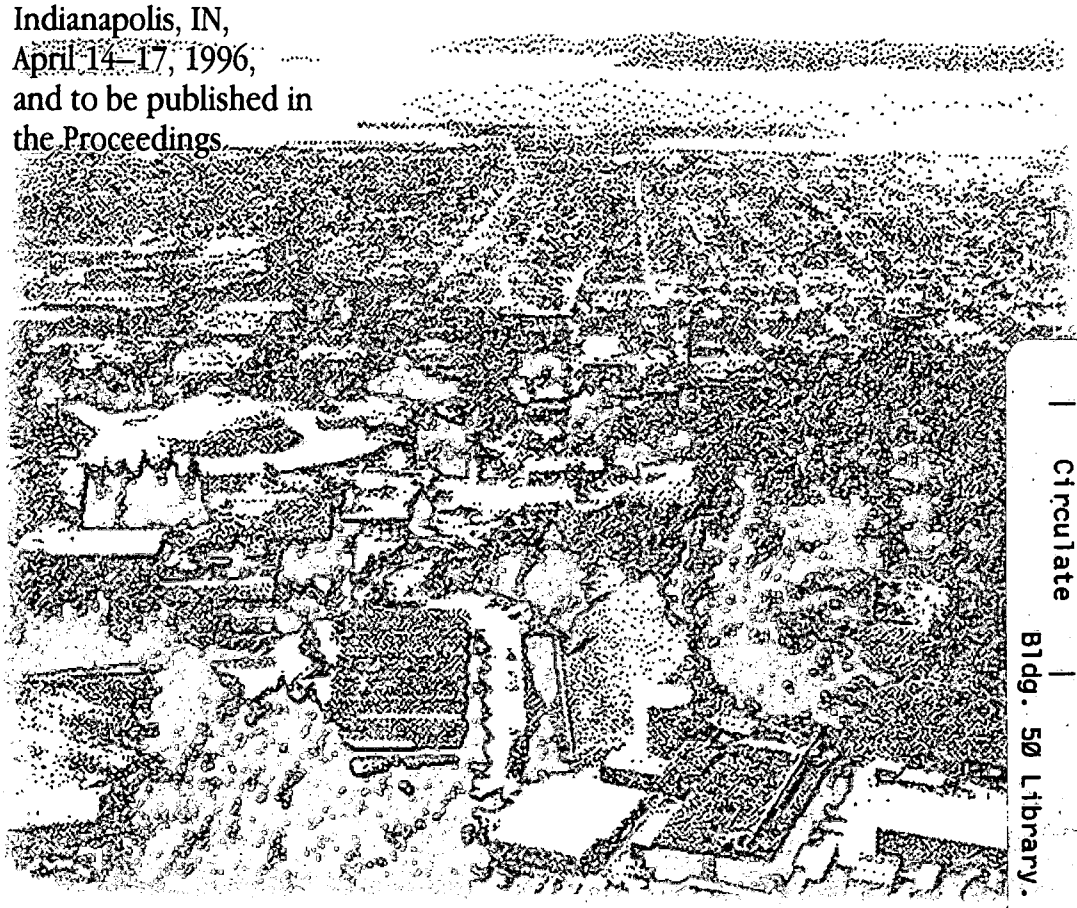

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Joe J. Cao, Y. He, W. J. MoberlyChan, and L. C. De Jonghe

Department of Materials Science and Mineral Engineering
University of California

and

Materials Science Division
Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720

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Joe J. Cao, Y. He, W. J. MoberlyChan, and L. C. De Jonghe

Materials Science Division, Lawrence Berkeley National Laboratory, and Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720

Silicon carbide composites were fabricated through the incorporation of alumina-coated SiC platelets into a SiC matrix. Mechanical properties were evaluated in direct comparison with a commercial Hexoloy SiC. The fracture toughness of the composite, with a fine grained β-SiC matrix, was twice that of the commercial material. The alumina-coating on the platelets provided a weak interface to promote crack deflection and platelet bridging, as well as easing densification of the composites. On the other hand, a three-fold increase in fracture toughness (9.1 MPa$\sqrt{m}$) of an *in situ* toughened monolithic SiC was achieved by processing at higher temperatures, promoting the β-to-α phase transformation and forming a microstructure containing high-aspect-ration plate-shaped grains. Efforts were made to combine the effects of coated-platelets reinforcement and *in situ* toughening in the matrix. Moderate high toughness (8 MPa$\sqrt{m}$) was achieved by coupled toughening. The contribution of matrix-grain-bridging, however, was limited by the processing temperature at which the oxide coating was stable.

1. INTRODUCTION

Silicon carbide ceramics generally exhibit high strength at elevated temperatures with excellent creep and oxidation resistance, good thermal conductivity, low thermal expansion, superior hardness, and high elastic modulus. But the widespread application of SiC as a structural material has been hindered by its low fracture toughness (K_C ~ 2-3 MPa$\sqrt{m}$). The incorporation of reinforcement particulate to enhance toughness was effective and raised the fracture toughness to ~ 6 MPa$\sqrt{m}$, although the choice of toughening phase in a SiC matrix was generally limited to TiB_2 [1] and TiC [2,3] due to the severe sintering conditions. High temperature stability and chemical compatibility of the reinforcement with SiC are necessary requirements. The thermal expansion coefficient mismatch between TiB_2 or TiC and the matrix SiC generates a compressive hoop stress and a tensile radial stress around the particles, causing crack deflection and an increment in fracture toughness. At elevated temperatures,

however, the internal stresses are relieved, with a corresponding degradation of the mechanical properties [4].

The apparent chemical compatibility and matching thermal expansion of α-SiC platelets made them an ideal reinforcing phase in a SiC matrix. Furthermore, an alumina coating on the platelets prior to fabrication of the composites provided a barrier to protect the integrity of the platelets during sintering and also achieved a weak interphase between the platelets and the matrix, thereby raising the fracture toughness of the composites by promoting crack deflection and bridging.[5]

In recent years, *in situ* toughened SiC ceramics have received considerable attention [6-12]. For example, SiC materials, processed under carefully controlled atmospheres with additions of substantial amounts of Al_2O_3 [6-8] or Al_2O_3 + Y_2O_3 [9-11] additives, exhibited heterogeneous microstructures and reached a fracture toughness nearly twice that of conventional B and C-doped SiC, such as commercial Hexoloy. More recently, an ultra-high-toughness monolithic SiC was developed at the Lawrence Berkeley National Laboratory using aluminum metal, boron, and carbon in relatively low concentrations as sintering aids (designated as ABC-SiC, referring to the sintering additives) [12].

In this paper, we report experimental studies on a SiC composite reinforced by oxide-coated SiC platelets in a fine-grained matrix, an *in situ* toughened monolithic SiC, and composites with a self-toughened matrix. The combined toughening effects of platelet reinforcement and matrix-grain-bridging are discussed.

2. EXPERIMENTAL PROCEDURES

2.1 Alumina-Coating on SiC Platelets

The α-SiC platelets (Third Millennium Technologies, -400 mesh grade) were coated using a slurry-coating technique [13]. A small amount of polymeric dispersant (PVP K30, GAF Chemical Corporation) was dissolved at room temperature in distilled water prior to the addition of SiC platelets. An aqueous solution of hydrated aluminum sulfate (crystals, Fisher Scientific) and urea (Mallinckrodt) was mixed with the suspended platelets in a flat-bottom distilling flask. The slurry contained 0.1 M hydrated aluminum sulfate, 0.2M urea 10g/L platelets, and 0.75g/L PVP K30. The mixture was vigorously stirred using a mechanical stirrer, capped with a water-cooled reflux condenser, and slowly heated to 92°C and held for 24 hours. The platelets were coated with a hydrated basic aluminum sulfate by heterogeneous precipitation. After annealing in an inert gas at 880°C for 6 hours, the coatings were converted to crystalline alumina.

2.2 Fabrication of SiC Monoliths

Submicron size β-SiC powder (BSC-21, Ferro) was mixed in toluene with 3 wt% metallic aluminum powder (H-3, Valimet, CA), 0.6wt% boron (high purity, sub-micron particle size, Callery Chemical Co., PA), and 4 wt% apiezon wax (which was found to yield ~50% carbon upon pyrolysis). The slurry was ultrasonically agitated for 5 minutes, and stir-dried in air. The mixture was then re-ground in a mortar and pestle and screened through a 200 mesh sieve. After cold die-compression at 35 MPa, the green compacts of 38 mm in diameter were hot pressed in graphite dies lined with graphite foil, at temperatures between 1700°C and 1900°C, for 1 hour, at 50 MPa, under flowing argon.

2.3 Production of SiC Composites

The β-SiC powders with sintering additives for the matrix were prepared as described in section 2.2. Twenty five weight percent of alumina-coated α-SiC platelets were then mixed with the β-SiC powders, and cold compacted into 38 mm diameter discs at a uniaxial pressure of 35 MPa. The composites were hot pressed at 1700°C to 1900°C for 1 hour.

2.4 Mechanical Testing

Beams of 3 x 3 x 28 mm were cut from the hot pressed SiC billets. The tensile surfaces were polished to a 1μ diamond finish, and indented using a Knoop indenter at a load of 12.5 kg. The indentation crack was made parallel to the hot pressing direction and perpendicular to the long axis of the beam. The beams were tested under four-point bending with an outer span of 25.4 mm and an inner span of 9.5 mm, at a crosshead speed of 0.05 mm/min. During bending, the crack experienced the sum of the applied and the residual stress intensities. Stable crack growth proceeded until instability was reached. The initial half-penny shaped crack developed into a semi-elliptical shape at instability. The ratio of short axis to the long axis of the critical crack was consistently found to be ~0.65 [12]. The fracture toughness was determined from the relation:

$$K_C = Y\sigma\sqrt{a} \qquad (1)$$

where σ is the fracture stress, *a* is the crack depth at instability, measured on the fracture surface using a scanning electron microscope (SEM), and *Y* is a crack geometry constant. For an ideal half-penny-shaped surface crack, the crack-geometry constant is 2/Öp. Taking into account the shape of the crack and a free surface correction, *Y* = 1.18 x 1.12 x 2 / Öp = 1.5. As the residual stress from the indentation was significantly reduced after stable crack extension, it was ignored in equation (1). To assure the measured toughness results, a commercial Hexoloy

SiC (Hexoloy SA, Carborundum, Niagara Falls, NY) was also tested under identical conditions for comparison.

3. RESULTS AND DISCUSSION

3.1 Alumina-coating on SiC platelets

Successful coating required careful control of the processing parameters, including the reaction temperature (reaction kinetics), concentrations of constituents, and surface area of the platelets. Controlled heterogeneous precipitation on the platelet surface was necessary and homogeneous precipitation had to be avoided. A model based on reaction kinetics was developed and used as a guide to reach the optimal coating conditions. Detailed descriptions of the coating model can be found elsewhere [14]; here we only discuss the basic ideas. Fig. 1 shows a map that is divided into four regions by the solid lines *a* and *b*, corresponding to the critical salt concentration [P_{comp}] to achieve complete coating and the critical concentration [P_{crit}] to have homogeneous precipitation, respectively. Line *c* gives an example of the relative concentration of the solution-complex versus parameter AK_2. In regions I and III, the concentration of the pre- precipitation solution-complex [P] exceeded the critical value [P_{crit}], and therefore homogeneous nucleation occurred. In region IV, incomplete coating resulted. Region II was ideal to achieve complete coating while avoiding homogeneous precipitation.

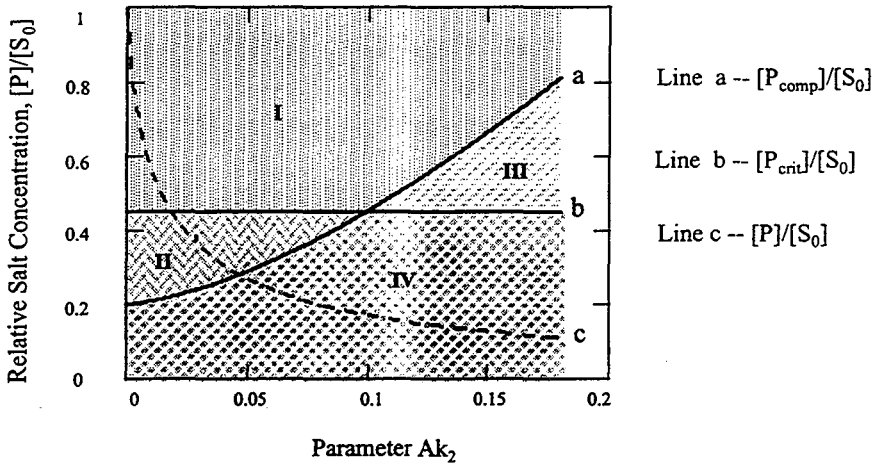

Fig. 1 A coating process map based on kinetics calculations. Where [S_0] is the initial concentration of the dissolved salt, [U_0] is the initial concentration of urea, [P] is the maximum concentration of the pre-precipitation solution-complex corresponding to [S_0] and [U_0], [P_{crit}] is the critical value of [P] above which homogeneous precipitation occurs, [P_{comp}] is the minimum [P] to achieve complete coating, A is the total surface area of the platelets, and k_2 is a rate constant.

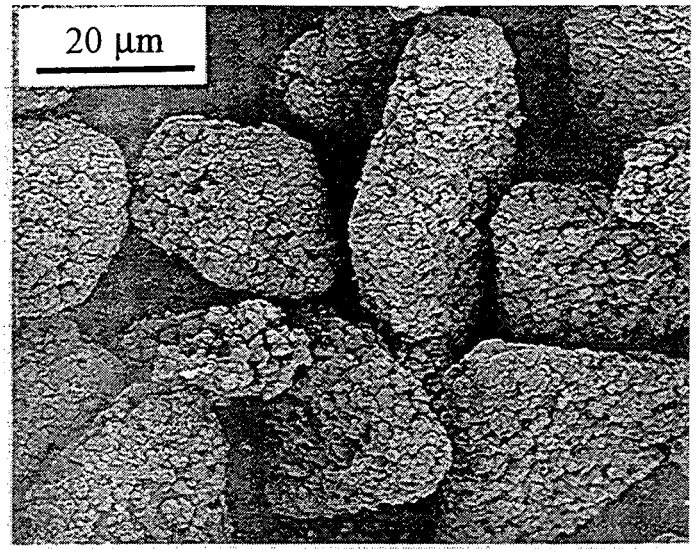

Fig. 2 SEM micrograph of alumina-coated SiC platelets. The coated platelets were used as reinforcement in SiC composites.

With the help of the map, one could more effectively tune the coating process. The microstructural development of the coating of alumina precursor has been described elsewhere [5]. Figure 2 shows an SEM micrograph of alumina-coated platelets after calcination. The coating presents a good coverage on the platelets and has a thickness of 1 to 2 μm.

3.2 Coated SiC Platelets in a Fine-Grained SiC Matrix

SiC composites with 25 wt% of alumina-coated SiC platelets (approximately 20 vol% of SiC platelets) were hot pressed to nearly full density at 1700°C for 1 hour. The polished surfaces of the composite were examined by optical and scanning electron microscopy. Figure 3 shows two polished perpendicular surfaces of the composite. The bright areas are the alumina coatings that continuously surround the platelets. During hot pressing, the platelets had rotated and preferentially aligned in a plane perpendicular to the hot pressing direction. Similar observation on preferential orientation of platelets was reported in an alumina-matrix composite [15].

The current sintering additives of a combination of Al, B, and C had effectively promoted densification of the composite. This processing temperature of 1700°C is very low for SiC matrix composites. Previous work on particulate TiC and TiB_2 reinforced SiC were hot pressed at temperatures upwards 2100°C [1-4]. Densification of a composite with a large volume fraction of reinforcement phase can be hindered by the percolation of the second phase. The oxide coating prevented the platelets from physically contacting each other. In addition, creep of the oxide coating during hot pressing eased sliding of the platelets relative to

each other. The low processing temperature suppressed the $\beta \rightarrow \alpha$ phase transformation in the matrix and ensured a fine-grained microstructure. Transmission electron microscopy revealed all β-phase, mostly equiaxed grains ranging from submicron to 2 microns in the matrix [16].

The coatings were also essential to protect the integrity of the platelets. A composite using uncoated platelets suffered from abnormal growth of the platelets, which introduced large internal flaws. As a result, the composite with uncoated platelets exhibited poor strength.

The measured fracture toughness results are listed in Table 1 and further illustrated in Fig. 4. The alumina-coated platelets reinforced SiC composite showed a 50% increase in the fracture toughness over that of the monolithic material. Please note that the toughness of the composite is twice that of the commercial SiC. On fractographs, the coated-platelets were noticed to interact with the crack, resulting in more tortuous fracture surfaces. A composite with uncoated platelets, however, showed minimal increase in toughness compared to that of the monolithic SiC (Table 1).

Table 1. Fracture Toughness of Monolithic ABC-SiC and Alumina-Coated SiC_P / SiC Composite Materials

Material	Hot Pressing Conditions	Fracture Toughness (MPa$\sqrt{m}$)
Commercial Hexoloy SiC	*	2.9
Composite with uncoated platelets	1700°C/1h	5.1
Monolithic ABC-SiC	1700°C/1h	4.2
"	1780°C/1h	5.9
"	1840°C/1h	8.9
"	1900°C/1h	9.1
Composite with coated platelets	1700°C/1h	6.3
"	1780°C/1h	7.7
"	1840°C/1h	7.9
"	1900°C/1h	8.0

3.3 *In Situ* Toughened ABC-SiC

A near fully dense ABC-SiC with a very fine microstructure (mean grain size ~ 1 mm) was obtained by hot pressing at 1700°C for 1 hour. By hot pressing at higher temperatures, the b-to-a phase transformation took place, which promoted the formation of plate-shaped grains. Fig. 5 shows an SEM micrograph of a heavily etched ABC-SiC processed at 1900°C for 4 hours, where the plate-shaped SiC grains have very high aspect ratios.

The fracture toughness of the monolithic materials are shown in Table 1 and Fig. 4. When the hot pressing temperature increased from 1700°C to 1900°C, the fracture toughness increased from 4.3 to 9.1 MPa$\sqrt{m}$. The latter value is over 3 times higher compared to that of Hexoloy SiC. These toughness values, determined from the controlled surface flaw method, were consistent with more precise measurements made using fatigue pre-cracked compact tension specimens. For example, the steady-state toughness of the material hot pressed at 1900°C was measured as 9.1 MPa$\sqrt{m}$; the fracture toughness of Hexoloy SiC was determined to be 2.5 MPa$\sqrt{m}$ using pre-cracked DC(T) specimens [16].

Toughening in the ABC-SiC materials was primary attributed to grain bridging and subsequent grain pullout. With very fine grains (for example, after hot pressing at 1700°C), toughening from grain bridging and pullout was minimal. After hot pressing at higher temperatures (*e.g.*, at 1900°C), growth of the plate-like grains with increased aspect ratio highly enhanced the effect of grain bridging, resulting in a significant improvement in fracture toughness. Fig. 6a shows intact plate-shaped grains in the crack wake spanning across the opposite faces of the crack, providing significant resistance to the crack from further opening. In contrast, the crack path in Hexoloy is quite straight, showing no evidence of any bridging ligaments (Fig. 6b). A semi-quantitative analysis on toughening mechanisms and studies on cyclic fatigue behavior in the *in situ* toughened ABC-SiC have been reported elsewhere [17].

3.4 Coated SiC Platelets in a Self-Toughened Matrix

In an attempt to combine the toughening effects from platelet reinforcement and matrix-grain-bridging, alumina-coated SiC platelets/SiC composites were processed at temperatures ranging from 1700°C to 1900°C. When the hot pressing temperature was below ~1800°C, the composites exhibited higher toughness than the corresponding monolithic materials (Fig. 4). Fig. 7 shows fracture surfaces of a composite processed at 1780°C. The platelets provided sites for crack deflection and participated in pullout to a certain degree (Fig. 7a). At the same time, the matrix fractured intergranularly and the matrix-grains were pulled out (Fig. 7b). The overall toughness of the composite is a simple additive combination of the platelet reinforcement and matrix-grain-bridging in energy terms [18,19], and can be described as

$$K_C = [E^c(J^0 + \Delta J^{gb} + \Delta J^{pr})]^{1/2} \qquad (2)$$

where E^c is the elastic modulus of the composite, J^0 is the energy consumption by lattice bond rupture, ΔJ^{gb} is the energy consumed by matrix grain bridging, and ΔJ^{pr} is the energy by platelet reinforcement.

From the expression (2), a better composite toughness is expected in a toughened matrix with highly elongated grains. The composites hot pressed at temperatures above ~ 1800°C, however, showed lower toughness than the corresponding monolithic materials. Three reasons could be envisioned. First, the presence of the reinforcing platelets inhibited growth of the elongated grains in the matrix. Thus, grain-bridging in the matrix was less effective compared to the *in situ* toughened monolithic SiC under the same hot pressing conditions. Becher [18] showed that the added SiC whiskers in an Si_3N_4 composite worked as effective grain-growth inhibitors. Second, the high processing temperature influenced the stability of the alumina coating on the platelets. The higher the sintering temperature, the larger the alumina grain size in the coating. The large grain size would enhance grain boundary grooving and pin-hole formation. Thus the alumina coating might become isolated islands instead of a continuous barrier. We had observed in an yttria-coated SiC platelet / SiC composite that a uniform yttria-coating changed to a granular morphology [16]. Finally, at temperatures > 1800°C, the alumina-coating might have been degraded due to a chemical reaction between alumina and SiC as was suggested by a thermodynamic calculation [20].

4. CONCLUSIONS

SiC platelets were coated with alumina using a slurry coating technique. The coated platelets were then used to fabricate SiC composites by hot pressing at temperatures ranging from 1700°C to 1900°C. The alumina-coating prevented direct contact of the platelets and eased densification of the composites. A composite with a fine-grained matrix exhibited a fracture toughness 50% higher than the monolithic material processed under the same conditions. Combined toughening from matrix-grain-bridging and coated-platelets reinforcement resulted in a toughness of 8 MPa$\sqrt{m}$, representing a two and half-fold increase in toughness over the commercial Hexoloy SiC. Tailoring the microstructure of the composite to promote coupled-toughening, however, was limited by the stability of the alumina-coating at the densification temperature of the composites. In fact, an *in situ* toughened monolithic SiC showed the highest fracture toughness of 9.1 MPa$\sqrt{m}$.

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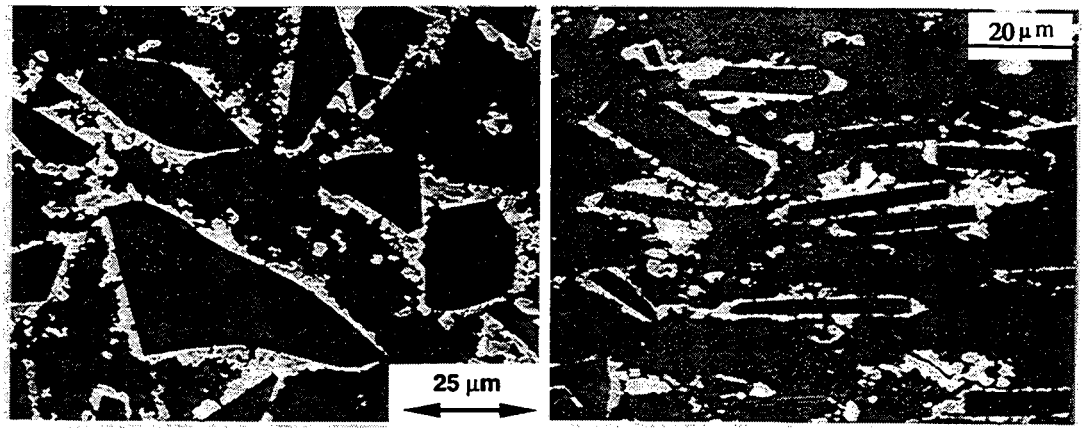

Figure 3 SEM micrographs of polished surfaces of a SiC composite hot pressed at 1700°C: a) of a surface perpendicular to the hot pressing direction and b) of a surface parallel to the hot pressing direction. The composite is near fully dense. The alumina-coating provided a continuous barrier to protect the integrity of the platelets and a weak interphase.

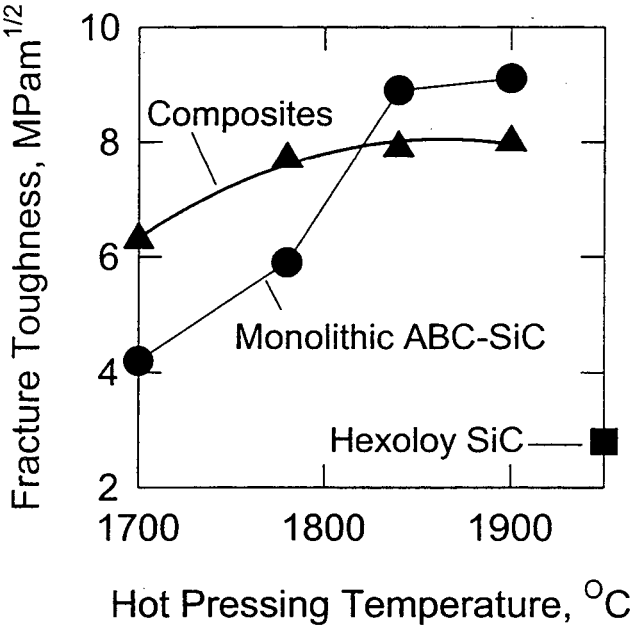

Fig. 4 Fracture toughness of monolithic ABC-SiC and alumina-coated SiC platelets reinforced SiC composites hot pressed at various temperatures. The toughness of a commercial Hexoloy SiC, measured under identical conditions, is also shown for comparison.

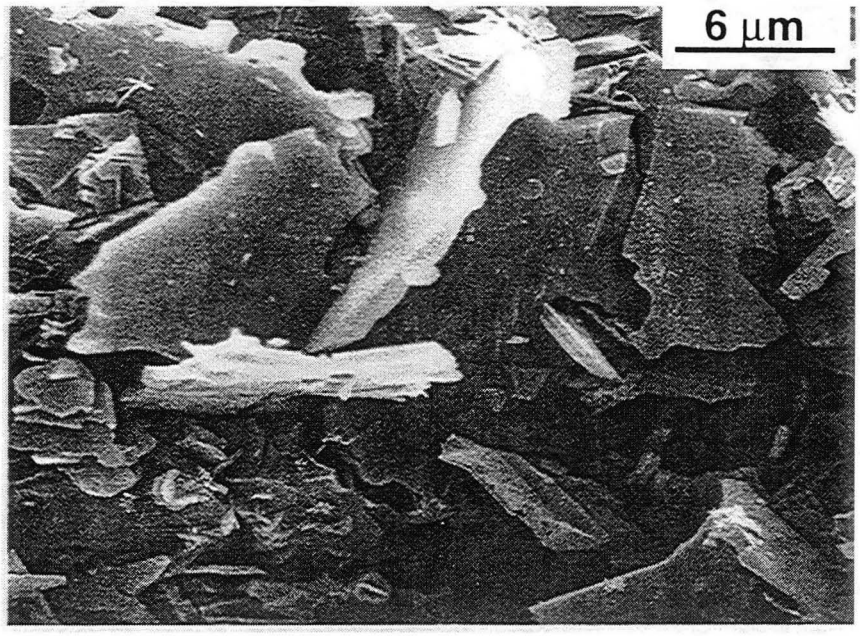

Fig. 5 SEM micrograph of an heavily etched ABC-SiC hot pressed at 1900°C for 4 hours. Notice the high-aspect-ratio plate-shaped SiC grains.

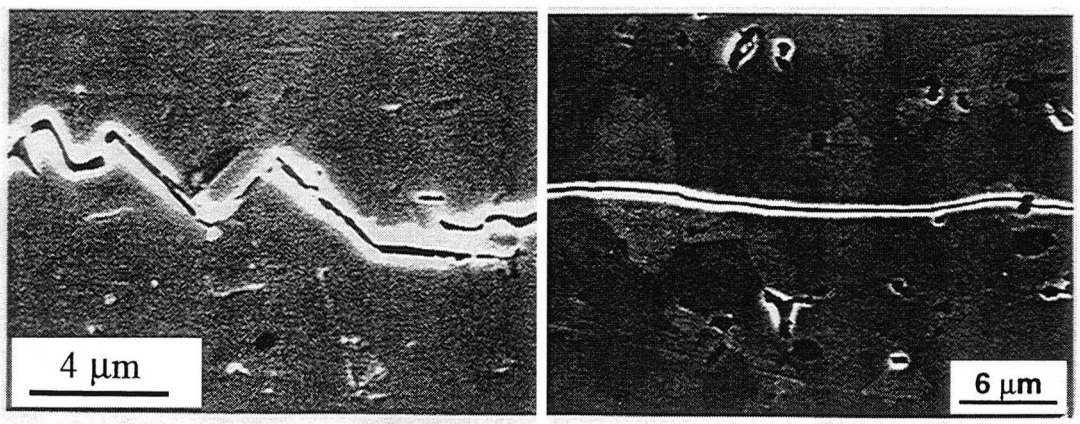

Fig. 6 Crack profiles in the ABC-SiC hot pressed at 1900°C where platelet-shaped grains bridged the crack faces (a) and in a commercial Hexoloy SiC where a straight crack broke the grains transgranularly (b).

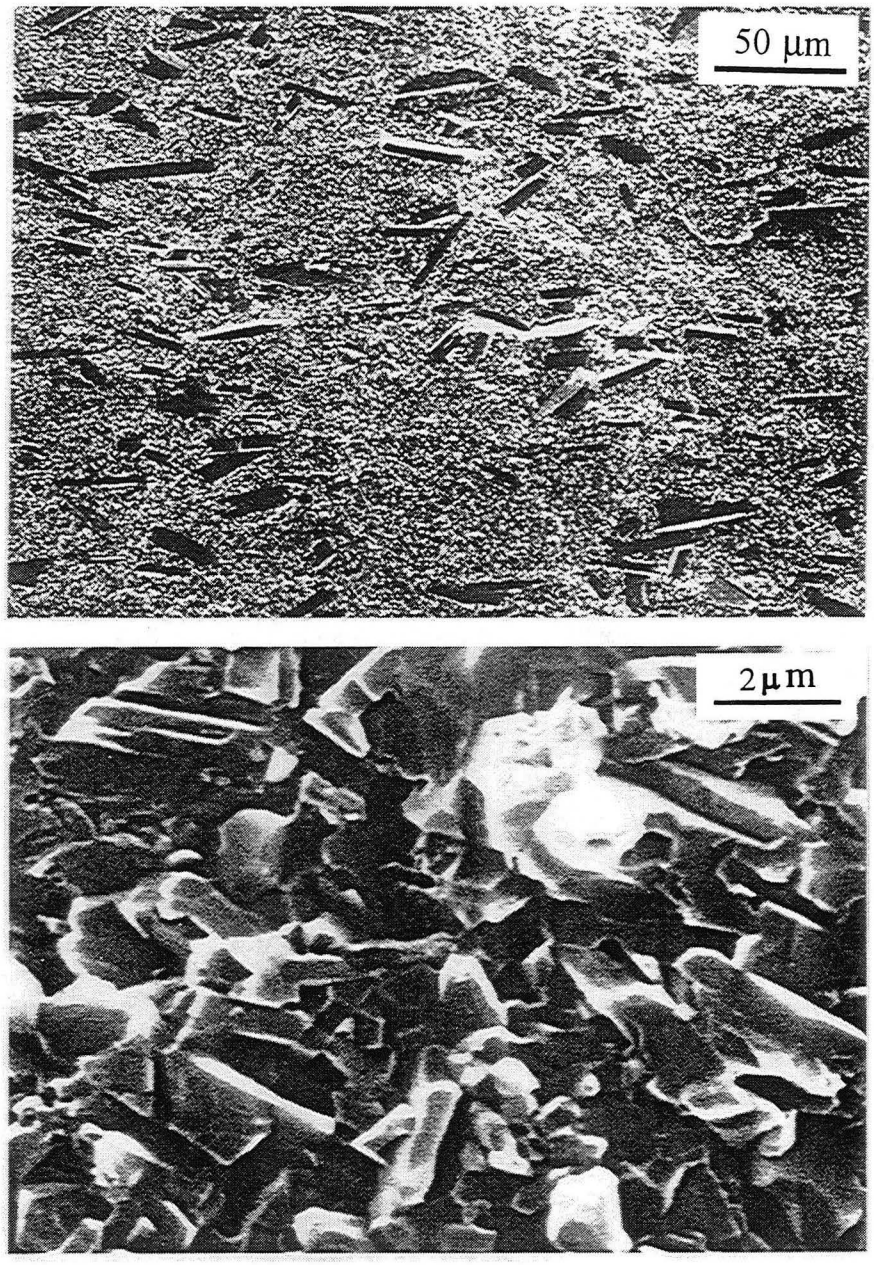

Fig. 7 Fractograph of an alumina-coated SiC platelet / SiC composite hot pressed at 1780°C for 1 hour. Crack deflection and some pullout occurred at the platelets (a) and intergranular fracture of the matrix grains provided matrix-grain-bridging (b).

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Ernest Orlando Lawrence Berkeley National Laboratory
One Cyclotron Road | Berkeley, California 94720

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