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Particulate Composites from Coated Powders*

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Abstract

A method is described for coating SiC whiskers with a thick layer of alumina to form homogeneous alumina matrix/silicon carbide whisker particulate composites. The method uses controlled heterogeneous precipitation in a relatively concentrated suspension of whiskers. The suspension-coated whiskers can be converted to a free-flowing powder after calcination. The processing parameters and the results of consolidation of the composite powder are reported. Nearly fully dense composites, containing over 40 vol.% whiskers, could be prepared.

Es wird ein Verfahren zum Beschichten von SiC-Whiskern mit Al_2O_3 vorgestellt, das es ermöglicht, homogene Al_2O_3-Matrix/SiC-Whisker Verbundwerkstoffe herzustellen. Das Verfahren beruht auf einer kontrollierten heterogenen Fällung in einer relativ konzentrierten Whiskersuspension. Durch die Kalzinierung bildet sich aus der Suspension beschichteter Whisker ein rieselfähiges Pulver. Die Verfahrensparameter und Ergebnisse der Sinterversuche dieser Pulver werden angegeben. Es konnten nahezu vollständig verdichtete Verbundwerkstoffe mit über 40 Vol.% Whiskeranteil hergestellt werden.

On décrit ici une méthode de recouvrement de whiskers de SiC par une couche épaisse d'alumine afin d'élaborer des composites particulaires homogènes à matrice alumine renforcée par whiskers de carbure de silicium. La méthode fait appel à la précipitation hétérogène contrôlée dans une suspension de whiskers relativement concentrée. Les whiskers recouverts par suspension peuvent être convertis, après calcination, en une poudre non agglomérée. On rapporte les paramètres d'élaboration et les résultats de la consolidation de la poudre composite. On obtient, de cette manière, des composites de densité proche de la densité maximale, à teneur en whiskers pouvant dépasser 40% volumiques.

1 Introduction

Densification of ceramic powder compacts is often limited by structural or chemical heterogeneities that lead to the development of irreparable sintering damage. These heterogeneities are inherent in technical powders and consist at least of a spread in particle sizes and a spacial variation of the compact's initial density. One approach to countering the problems caused by heterogeneities is striving to achieve an ideal system: monosized particles, uniformly packed.[1] This ideal condition can only be obtained with considerable effort, however. Even with monosized particles strictly uniform packing on the particle scale is difficult and corresponds to the fabrication of a single crystal. In practice, sufficiently homogeneous ceramics can be obtained from less restrictive prescriptions, provided the powders have a particle size distribution approaching that of the natural steady state distribution of a coarsening system.[2] In addition, special sintering schedules, such as limited pre-coarsening at low temperatures, may lead to additional improvements of microstructure by limiting sintering damage.[3]

Quite similar problems to those encountered in the production of single-phase ceramics arise in the

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fabrication of particulate composites. The powder/dispersed-phase system, however, in addition to the matrix structure, now contains the dispersed phase as a source of heterogeneity.[4] For example, network formation[5] and clustering of the dispersed phase not only limits densification severely but also produces defects from which failure, such as creep rupture, is initiated. Random mixing cannot yield cluster-free composites and, as shown by the work of Real & Goult,[6] for a volume fraction of 30% of an equiaxed dispersed phase, it can be expected that 50% of that phase would be present in clusters of 15 or more particles. The solution to the reduction of heterogeneities in the structure of the initial powder/dispersed-phase compact can be approached in a way equivalent to that for the single-phase material: monosized dispersed-phase particles distributed uniformly in the matrix. Uniformity of this type would, for example, eliminate the formation of dispersed-phase particle networks and allow easier fabrication of particulate composites with a higher second-phase content than has been obtained so far by pressureless sintering.[7]

The present paper reports on the preparation and use of alumina-coated SiC whiskers to produce a homogeneous ceramic composite. The fabrication and use of coated powders is well established in other technologies;[8] however, their use in the production of ceramic–ceramic composite systems, with few exceptions,[9,10] has so far been largely ignored. Part of the reason is that methods need to be developed to coat sub-micron particles with relatively thick layers of the matrix precursor, and that these methods must be economical. A number of solution coating methods have been reported, using dilute dispersion.[11,12] The method described here works with a concentrated suspension and can yield coated particles in quantity.

2 Principles of the Coating Process

A number of techniques have been used to prepare powders by chemical methods. For example, hydrolysis of alkoxides, solvent removal, precursor decomposition, and precursor solubility reduction have had varying degrees of success in producing uniform alumina or alumina precursor powders in the sub-micron size range. Several of these rely on homogeneous nucleation and growth and require solutions free of heterogeneous nucleation sites such as dirt particles. In the suspension-coating technique, it is precisely heterogeneous precipitation that is exploited and homogeneous nucleation that must be avoided. The process considerations have been described earlier[10] with the aid of a LaMer diagram, and indicated the need for a balance between the available surface area (i.e. the particle size and concentration) and the precipitation kinetics. Successful coating of particles in suspension therefore requires some trial and error for determining the proper concentration of particles and reactants under fixed reaction conditions.

While the application described here concerns the deposition of a single component coating, some comments can be made regarding the possibility of producing mixed component coatings. Referring to the schematic LaMer diagram,[13] Fig. 1a, single component coating by direct heterogeneous precipitation is possible if reaction conditions are kept

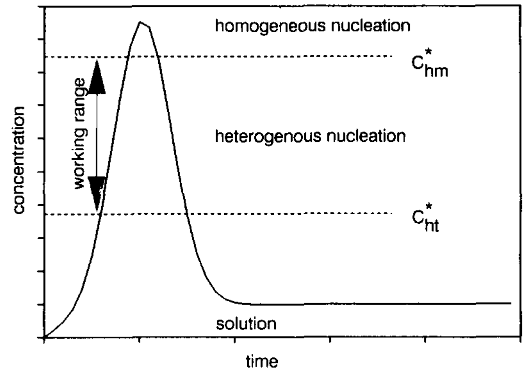


Fig. 1a. The diagram indicates the working range for single component coating powder by heterogeneous nucleation. The reaction conditions must be such that the concentration of the precipitate in the solution is above the critical supersaturation for heterogeneous nucleation, C^*_{ht}, but below the critical supersaturation for homogeneous nucleation in bulk liquid, C^*_{hm}; after Lamer.[13]

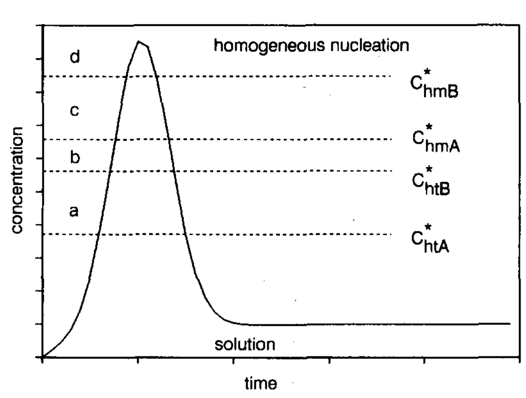


Fig. 1b. The diagram illustrates the difficulties associated with the heterogenous precipitation of a compound AB formed by co-precipitation of A and B. As the concentration of the precipitate rises A will deposit first in zone a, then AB would form in zone b. If the concentration rises further, to c, then A can precipitate homogeneously in the bulk solution, while AB is precipitating heterogeneously. The diagram is only schematic and assumes non-interaction between the processes. Various additional interactions may be postulated leading to different precipitation sequences that may result in chemical heterogeneity of the coatings.

in the zone between the homogeneous and the heterogeneous nucleation limits. For multicomponent coating, however, such a zone may not exist, as is schematically indicated in Fig. 1b for the formation of an AB coating, and sequential precipitation may result, leading to chemical heterogeneity. Instead of attempting to seek conditions for the formation of compound coatings by heterogeneities precipitation, it would then be more appropriate to induce rapid local co-precipitation, as e.g. obtained when strong, sudden local pH changes are produced by dripping a concentrated base from a burette into a solution, and to rely on heterocoagulation of the precipitate with the core particles. No systematic work in this direction has been reported, although it is likely that the methods used by Kim *et al.*[14] for coating silicon nitride with a YAG additive involved such heterocoagulation. In such a case, manipulation of the zeta potentials of the relevant particles becomes essential as well.

An additional factor in the successful coating of particles by heteroprecipitation is that these must remain isolated during coating so that the purpose of the methods is not defeated, and that the coating is sufficiently porous and of a fine particle size. It is then necessary to stir the slurry vigorously, and to include an appropriate dispersant. Unsatisfactory coatings may also result if the precipitation conditions are such that the precipitate coarsens significantly during processing. Such a case was found when attempts were made to coat SiC with ZnO. In this case, only the initial coating had the right microstructure, but continued coating was accompanied with strong coarsening, rendering the coated particles essentially non-sinterable (Brown, G., unpublished).

3 Coating of SiC Whiskers with Al_2O_3

One successful method for producing an alumina powder precursor is the controlled precipitation of hydrated basic aluminum sulfate (HBAS) from an aqueous solution. A quantity of urea is dissolved in an aluminum sulfate solution and a polymeric dispersant is added. The aluminum ions form hydration complexes $[Al(OH)_x^{(3-x)+}]$ with the hydroxyl ions of the water. Upon heating the solution to temperatures between 90 and 100°C the urea will decompose slowly and uniformly in the solution, and eventually provide sufficient hydroxyls to precipitate the insoluble HBAS. The precipitate can be converted to aluminum oxide by thermal decomposition. Using this process in the presence of the SiC whiskers can lead to exclusive heterogeneous precipitation on these whiskers and the formation of relatively thick coatings of HBAS. Careful control of the reaction temperature and the various concentrations of constituents are necessary for successful coating.

4 Experimental

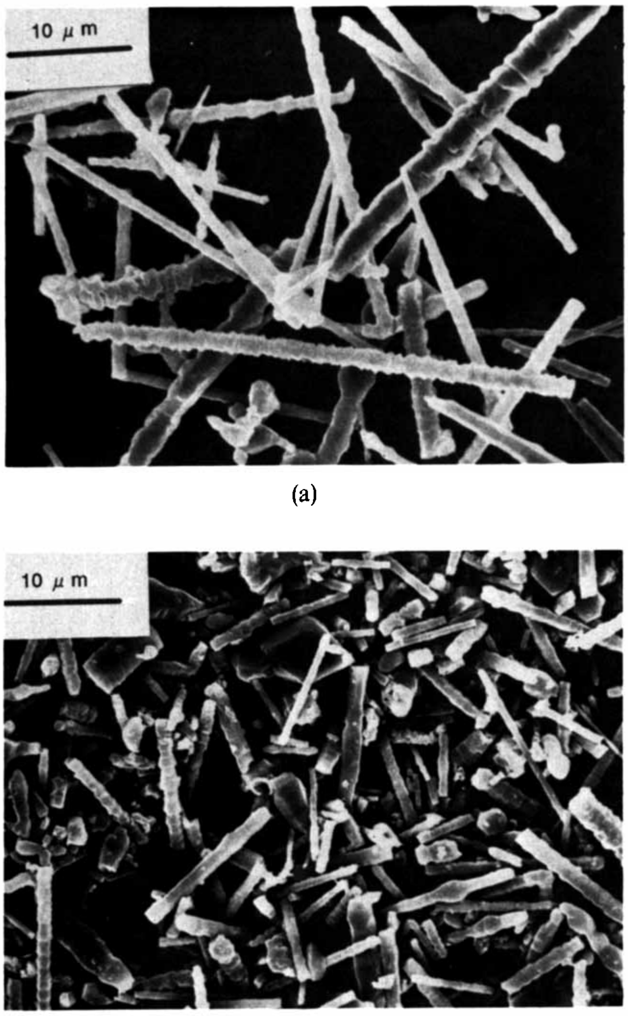
SiC whiskers were obtained from a commercial source, (American Matrix, Inc., Knoxville, TN). These whiskers had a diameter ranging between 0·3 and 3 μm and a wide aspect ratio distribution ranging up to 200 or more. The as-received whiskers were therefore reduced in size by milling, since it is known that much of the toughening of whiskers is retained for aspect ratios as low as 10.[7] The as-received whiskers were ground for 24 h in a rolling ball mill, using a polyethylene container and zirconia balls (2·5 mm diameter; Toya Soda USA, Inc., Atlanta, GA). The ground whiskers were suspended in ethanol with the aid of a polymeric dispersant (PVP K30; GAF Chemical Co., Wayne, NJ) and were allowed to settle for 10 min. The remaining supernatant was removed. Reduced aspect ratio whiskers (RARW) were obtained from the dried sediment, with an average aspect ratio of 10.

The SiC-RARW were coated by the HBAS alumina precursor by controlled heterogeneous precipitation. An aqueous solution was prepared containing 0·2M aluminum sulfate (AS) and 12 g/liter of urea. An aqueous dispersion of 10 g/liter of SiC-RARW with 2 g/liter of PVP K30 was ultrasonically agitated for several minutes and added to the sulfate solution in a 1:1 ratio. The mix was then magnetically stirred and heated slowly, over a period of 2 h, to the process temperature of 95°C. This condition was maintained under reflux for 24 h. Vigorous stirring was necessary to prevent the whiskers from settling or agglomerating. In the development of the optimal coating, it was found best to vary the available surface area by changing the concentration of particulates, rather than by modifying the reactant concentrations and the temperature. If insufficient particulates are present in the suspension, significant amounts of free HBAS can be found in the resultant powder; with too many particulates the available surface area should be varied by changing the concentration of particulates, rather than by modifying the reactant concentrations and the temperature. Following the coating, the suspension was cooled to room temperature and allowed to settle, after which the supernatant was discarded and the remaining slurry was washed with acetone and air-dried. The result is a free-flowing powder consisting of HBAS-coated SiC-RARW.

The powder resulting from the coating procedure was decomposed at 850°C in air for 2 h. During this calcination the HBAS coating converted to a porous alumina coating. Dense particulate composite specimens of the alumina-coated powders were obtained by hot pressing in a graphite die, with an applied load of 35 MPa at 1600°C in a graphite furnace under helium. Fracture surfaces and polished sections of these specimens were examined in the scanning electron microscope.

5 Results

Figure 2 shows the as-received whiskers and the RARW obtained after ball milling. Both types were used in coating and compaction experiments.



(a)

(b)

Fig. 2. (a) Micrograph of as-received whiskers of SiC; (b) micrograph of reduced aspect ratio whiskers.

Experimenting with process parameters indicated that varying the concentration of the dissolved species was less effective in optimizing the process than varying the concentration of the suspended whiskers. Figure 3 shows as-received whiskers after optimal coating that covers the whiskers entirely and leaves no free precipitates of HBAS. The entire experimental parameters matrix was not explored fully, and it is therefore likely that higher solids concentrations can be used, thereby increasing the economy of the method.

The thickness and density of the coating will determine the volume fraction of whiskers in the final densified product. This volume fraction may be estimated assuming complete precipitation of the HBAS on the available whisker surface area. The actual whisker content of the final product, while reproducible, does not correspond quantitatively to this assumption, since precipitation is not complete; it can be readily determined, however, from a volumetric density measurement of the hot pressed bodies and from the theoretical density of alumina and silicon carbide.

One way to obtain very thick coatings on the whiskers is to use coated and calcined whiskers again in a second coating process. This method was found to be more effective than changing the concentrations of the reactants, since the latter would range outside of the limits of concentrations necessary to obtain controlled heterogeneous precipitation. An example of a nearly fully dense, hot pressed composite with whisker contents of about 40 vol.% is shown in Fig. 4. No significant amount of fractured whiskers could be detected. It is noteworthy that whisker clustering, in contrast to what should be expected for random mixing, is completely absent.

The mechanical properties of the obtained composites have not yet been fully determined. Fracture surfaces, as shown in Fig. 5, indicate that some whisker pull-out had occurred, so that toughening by the dispersed phase may be active. Estimates of the toughness from indentation yielded a toughness around 6–8 MPa $m^{1/2}$ for a 40 vol.% composite. Further experiments on free sintering of RAR whiskers and platelets of SiC coated by the process described here, as well as their mechanical testing, will be reported on later. Initial experiments by Mitchell *et al.*[15] have shown that free sintering of the coated whiskers at volume fractions in excess of 30% is possible to densities in excess of 95% of theoretical. Attempts to densify mixtures of powders prepared from the pure HBAS precursor in which the same volume fraction of whiskers was mechanically mixed in, and for which the subsequent

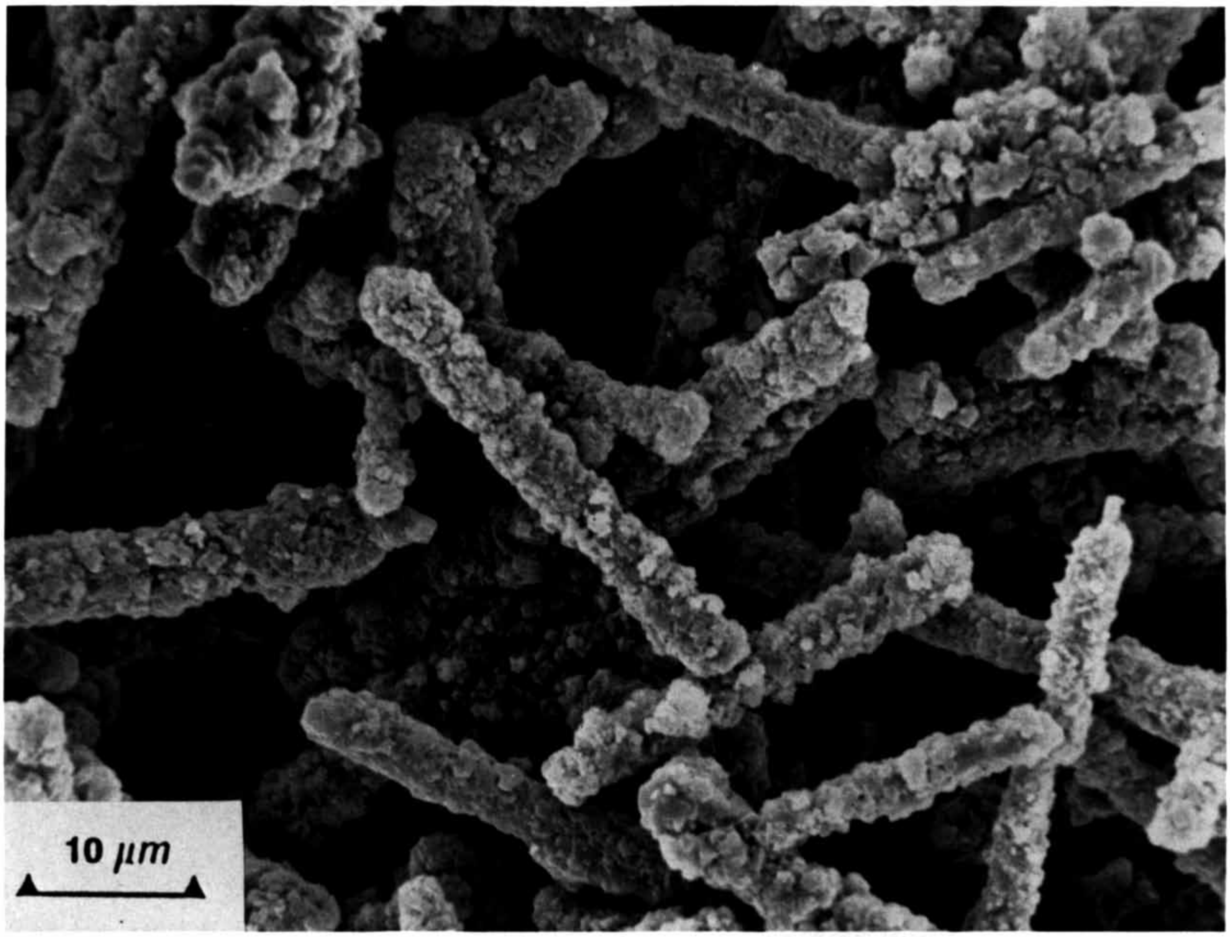


Fig. 3. Example of reduced aspect ratio whiskers after coating with the alumina precursor, hydrated basic aluminum sulfate (HBAS), and calcination to convert to aluminum oxide. Note that the coating is porous and of a fine particle size, allowing powder compaction and densification.

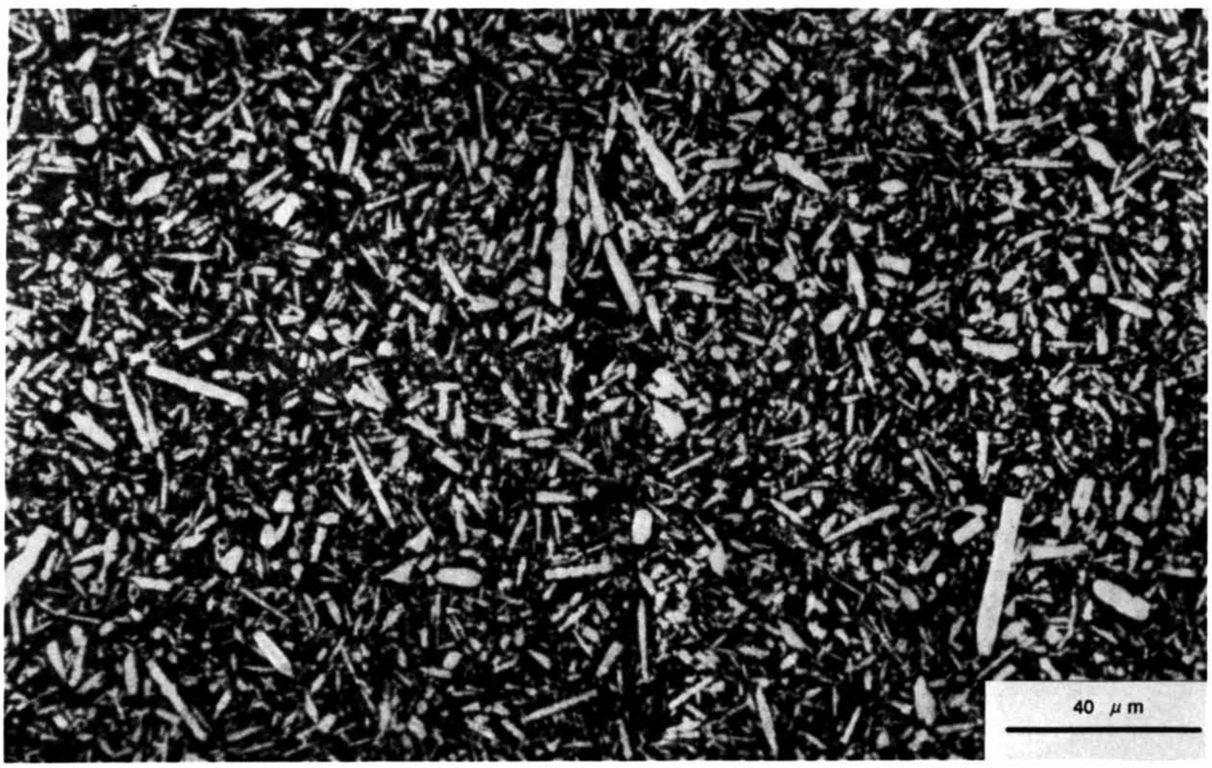


Fig. 4. Cross-section of a hot-pressed alumina/silicon carbide whisker composite with about 40 vol.% reduced aspect ratio whiskers. Note the absence of whisker clusters or whisker-depleted regions.

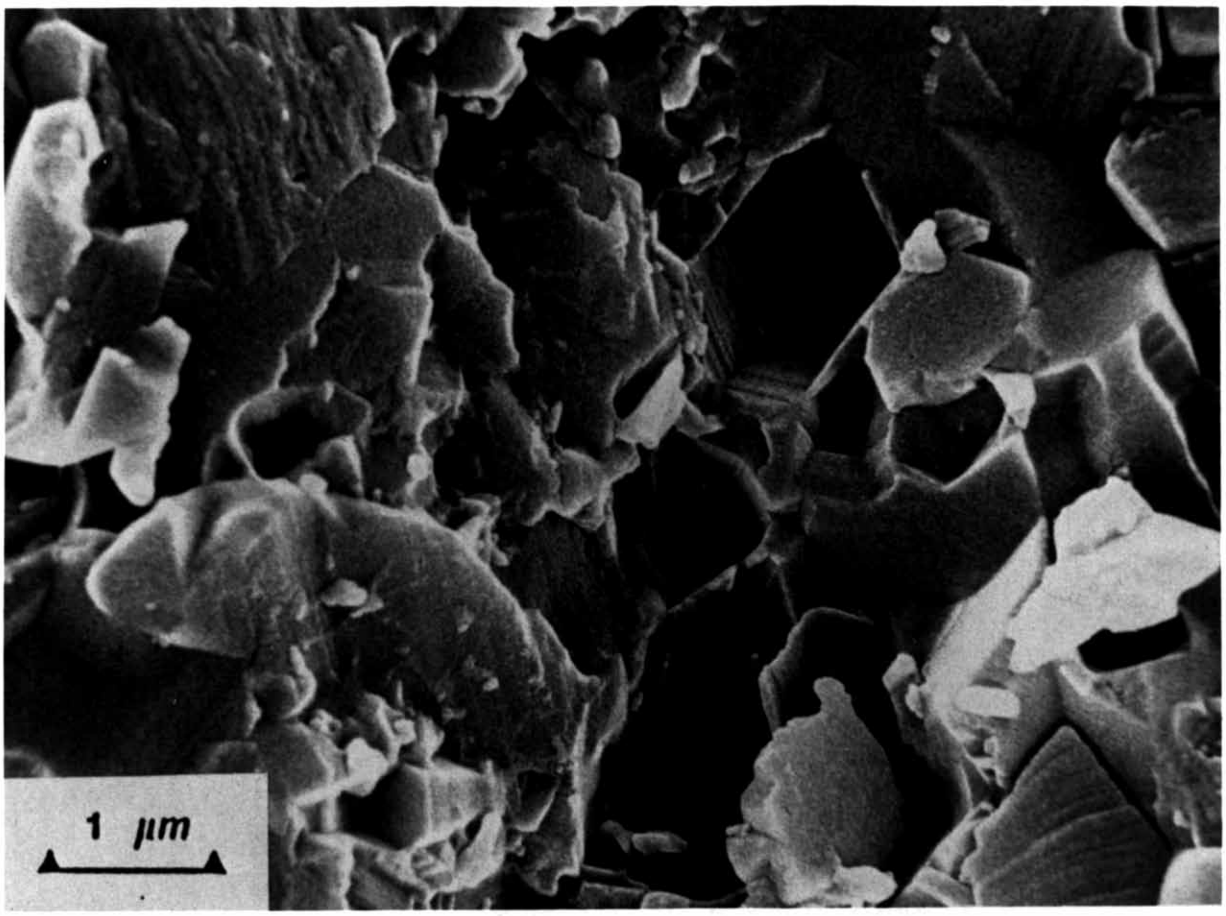
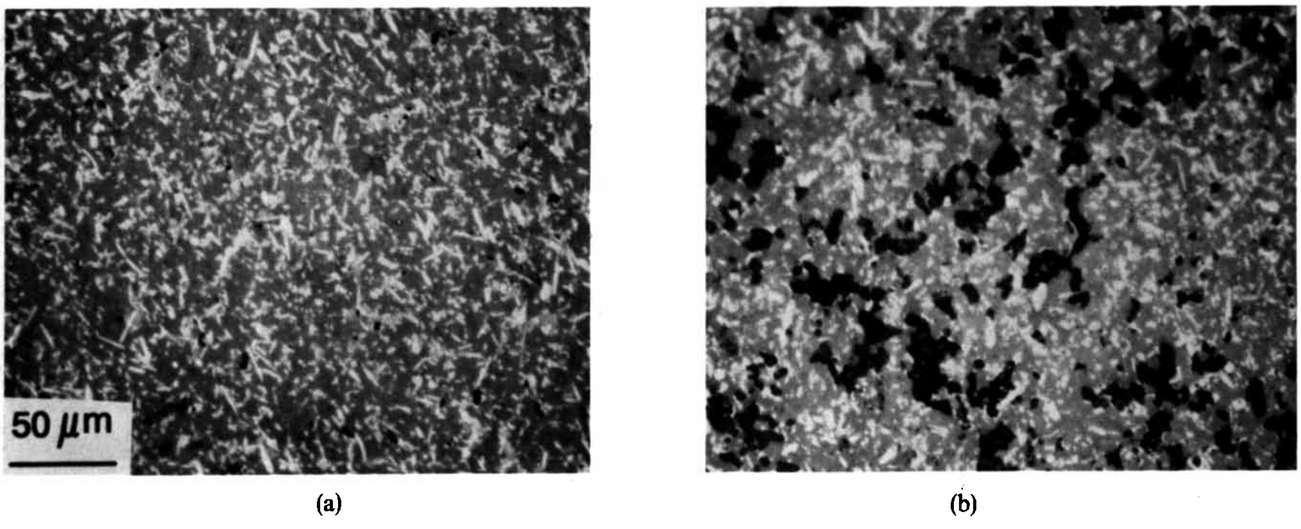


Fig. 5. Fracture surface of a hot-pressed, 40 vol.% Si-C-RARW composite. The micrograph shows some evidence of whisker pull-out.

processing was identical, yielded, by contrast, material that reached a density of only 75% and contained large pores, as shown in Fig. 6. While it is possible that the calcination procure introduce some silica through oxidation, which assisted in densification, these experiments demonstrated clearly the merit of using coated powders.

6 Conclusions

A method has been developed that produces silicon carbide whiskers coated with a thick layer of HBAS. This layer upon calcination converts to alumina and yields a free-flowing powder of coated whiskers. With the present experimental parameters, the



(a) (b)

Fig. 6. Comparison of free-sintered alumina/SiC-RARW composites, containing 30 vol.% of the SiC whiskers, (a) Micrograph of a composite prepared from coated powder; (b) micrograph of a composite prepared from mechanically mixed powder of SiC-RARW and alumina powder prepared separately by the same precipitation method.

procedure led to a coated powder that could be readily hot pressed to full density with a silicon carbide whisker content of about 45 vol.% in an alumina matrix. Recoating of the whiskers by an identical process after the first coating and calcination yielded, upon hot pressing, an alumina/SiC composite with about 25 vol.% whiskers.

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