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Synthesis of Alumina-Coated SiC Whiskers for Production of SiC Whisker-Reinforced Alumina Composite Materials

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(M.S. Thesis)

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Synthesis of Alumina-Coated SiC Whiskers for Production of SiC Whisker-Reinforced Alumina Composite Materials

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by

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Abstract

Thick coatings of hydrated basic aluminum sulfate, an alumina precursor, were precipitated on the surfaces of SiC whiskers from an aqueous solution. These coatings were then thermally decomposed to obtain alumina coatings on the SiC whiskers. Both high aspect ratio as-received SiC whiskers and reduced aspect ratio whiskers were used as core particles in the coating process. SiC content in the composite powders was controlled by either varying the amount of SiC whiskers that were added to the original coating solution, or by using multiple coating steps on the original SiC core particles. Coated whiskers were characterized before and after calcination using Scanning Electron Microscopy and X-Ray Diffraction. Samples of these composite powders were hot-pressed at 1600°C and 35 MPA pressure to obtain dense SiC whisker-reinforced alumina composite materials. Polished surfaces of these composites were observed using optical microscopy and SEM to qualitatively analyze whisker distribution in the matrix and residual porosity in the material. In all composites

using reduced aspect ratio whiskers, whisker distribution was uniform throughout the material, and residual porosity was very low. Fracture surfaces of some materials were observed in SEM, showing that a limited amount of whisker pull-out had occurred.

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1 Introduction

1.1 Goals

The use of ceramic composite materials in commercial applications is currently being hampered by conflicting requirements. Large volume fractions of reinforcing phase must be used to obtain materials with the most useful mechanical properties. This is especially true for fracture toughness, which seems to increase with reinforcing phase volume fraction in whisker-reinforced ceramic composites[1-3]. The presence of large whisker volume fractions in a green composite body, however, presents a serious hindrance to densification[3]. This is because ceramic whisker contacts increase with increasing volume fraction, and these contacts, when extensive enough, form a "network" which resists shrinkage due to the refractory nature of the whisker material. This problem is intensified as the average aspect ratio of the whiskers is increased.

Pressureless sintering of whisker-reinforced ceramic composites to near-full density is therefore difficult when using even low whisker volume fractions, and impossible if the whisker contents are greater than about 15 volume%. Tiegs and Becher obtained nearly fully dense composites (>95% theoretical density) using pressureless sintering and about 10 vol.% SiC whiskers, but hot-pressing generally must be used to obtain composites with greater than 10% whiskers and closed porosity[3]. As the whisker content in the composites is increased further, more severe hot-pressing conditions of temperature and pressure are necessary to obtain closed porosity. Table 1 shows conditions necessary to obtain dense alumina-SiC composites from previous studies. The ability to produce ceramic composites with

closed porosity by free sintering is a sufficient goal because hot isostatic pressing can then be used to obtain near-theoretical density composites.

Another major problem in composite processing is the difficulty of producing these materials with a homogeneous distribution of both phases throughout the microstructure of the body[5]. Regions of excess reinforcing phase in the body may not densify as well as the rest of the body, and regions of excess matrix phase will not provide as much crack energy dissipation as the bulk of the material. Both of these inhomogeneities will diminish the mechanical performance of the material, so uniform distribution of both phases within the composite is important during processing.

By introducing the matrix phase as a coating on individual particles of the reinforcing phase of the material not only will the distribution of both phases be more uniform, but contacts between the reinforcing particles can be greatly reduced or eliminated. This will allow sintering of the composites to very high densities using relatively mild conditions of temperature and pressure. An ideal green composite body would consist of individual reinforcing particles, each coated with enough matrix phase so that densification of the body would occur just by sintering the matrix phase coatings to high densities. A simple model of this process is shown in Figure 2.

1.2 Precipitation of Ceramic Precursors

Current research in the production of ceramic powders has concentrated on the precipitation of nearly spherical powders using several chemical processing methods[6-13]. Alkoxide hydrolysis, solvent

removal, precursor decomposition, and precursor solubility manipulation have been used to obtain alumina particles with varying degrees of success[18]. In all cases, the homogeneous precipitation and subsequent growth of ceramic or ceramic precursor particles in solution has been the goal of the research. Homogeneous precipitation requires very "clean" starting solutions because dirt particles will become sites for heterogeneous precipitation which will occur before the desired homogeneous precipitation. If the reinforcing phase particles such as SiC powder particles or whiskers are added to these starting solutions, the process can be controlled so that the alumina precursor precipitates heterogeneously on the surface of the core SiC particles and homogeneous precipitation of excess alumina particles is minimized.

One method for producing nearly spherical alumina particles that has been very successful is the manipulation of the solubility of aluminum sulfate in an aqueous solution. A quantity of urea or formamide is dissolved in a solution containing dissolved aluminum sulfate and a dispersant. This solution is heated to 90-100°C for an extended period of time, during which the urea decomposes, causing the release of ammonium ions and hydroxide ions uniformly throughout the solution. The urea decomposition reaction is given as: $(H_2N)_2CO + H_2O + 2H_3O^+ \rightarrow CO_2 + 2H_2O + 2NH_4^+$.[17] According to Blendell et al., the introduction of hydroxide ions causes a gradual increase in solution pH. This pH change causes the solubility of aluminum hydrolysis products to decrease.[31] Once the concentration of hydrated basic aluminum sulfate (HBAlS), the ultimate product of aluminum cation hydrolysis, exceeds its solubility limit by a certain amount,

known as the homogeneous nucleation limit, small nuclei of HBAlS precipitate. This precipitation depletes the Al^{3+} cations present in the solution (see Figure 3). The depletion of Al^{3+} cations will cause the concentration of dissolved HBAlS to decrease below the homogeneous nucleation limit, but then more HBAlS will grow on the existing nuclei until the concentration of dissolved HBAlS drops below the solubility limit at the current solution pH. Several early studies were done on this method for producing HBAlS particles[14-15]. HBAlS particles can be thermally decomposed to form alumina particles. This method was developed more recently by Brace and Matijevic[16], and then by Cornilsen and Reed[17]. The method to be described in this thesis was based on the work done by Blendell, Bowen, and Coble[18].

1.3 Precipitation of Precursors as Coatings

Several ceramic precipitation methods have been modified to produce thin coatings of ceramics or ceramic precursors on various core particles[19-24]. Kratohvil and Matijevic have modified an alumina precursor precipitation method to produce thin, uniform aluminum (hydrous) oxide coatings on several different core particles[19]. The use of the precipitation method described by Blendell et al. to produce SiC particles with thick alumina coatings requires only simple modifications. SiC core particles are dispersed in the aqueous solution of urea and aluminum sulfate prior to heating. As the pH changes during heating, and the concentration of aluminum species exceeds the solubility limit, before excess HBAlS precipitates homogeneously, it will be depleted from solution by heterogeneous precipitation on the SiC core particle surfaces (see Figure 3). If the pH increase occurs slowly enough, precipitation of the HBAlS on

the SiC surfaces will deplete enough of the Al^{3+} cations from solution to avoid any homogeneous precipitation. Since the pH change in solution depends on the rate of urea decomposition, which in turn depends on the temperature of the solution, careful temperature control is critical to obtaining a uniform, thick coating of alumina on the SiC particles.

Hydrated basic aluminum sulfate coatings on SiC particles must be thermally decomposed to produce alumina-coated SiC before these particles are sintered. The decomposition behavior of spherical HBAlS particles was studied in detail by Sacks, Tseng, and Lee[25], and in less detail by other authors. The large weight loss that occurs during the decomposition of HBAlS to form alumina results in a porous alumina which is slightly more difficult to sinter to high densities than a dense alumina coating would be, and the evolution of gaseous waste during the decomposition of the HBAlS requires that the decomposition and sintering steps be performed separately. Once decomposed, though, the coated particles can be processed as other, more common ceramic powders. In fact, since the two phases of the composite are "attached," sedimentation processing methods such as centifugal casting and slip casting can be used without causing phase separation. Phase separation can be a problem when processing powder mixtures because of the different particle sizes and densities that the two different phases normally have[26].

1.4 Whisker Aspect Ratios

Regardless of the processing method used to produce alumina-SiC whisker composite materials, the fraction of SiC whiskers that can be added to the alumina matrix while still obtaining near full densities

is limited by the average aspect ratios of the whiskers. Milewski's work has shown that whiskers with high average aspect ratios (>40) such as those SiC whiskers that are presently available commercially, have very large specific bulk volumes[27]. Because of this, only small volume fractions of as-received SiC whiskers can be included in a composite if high densities are to be achieved without causing whisker damage during densification of the matrix phase. Therefore it is also necessary to reduce the average aspect ratios of SiC whiskers obtained commercially before they are coated with the alumina matrix material. This problem must be balanced against the problem of reducing the composite's fracture toughness when the whisker aspect ratio is reduced[4]. Furthermore, care must be taken so that during the whisker size reduction, unwanted fine particulates are not produced because these drastically increase the specific surface area of the SiC particles used for coating. Since the coating-processing method is most beneficial when all SiC surfaces have a thick alumina coating, too high a specific surface area may reduce the efficiency of the coating process, and therefore the sintering process as well.

2 Experimental Procedure

2.1 Whisker Aspect Ratio Reduction

As-received American Matrix SiC whiskers have average aspect ratios that are too large to obtain high final densities in a composite. These whiskers were ground in a 500ml plastic rolling mill containing Zirconia milling balls (2.5mm diameter) for 24 hours at 165 RPM to reduce the average aspect ratio of the whisker batch. The ground whiskers were suspended in ethanol using a small quantity of

Polyvinylpyrrolidone (PVP) K30, a polymeric dispersant, and allowed to settle for 10 minutes. The remaining supernatant, containing fine SiC particles produced during the milling, was removed and discarded. The solid obtained was then dried to obtain reduced aspect ratio whiskers (RARW).

2.2 Production of Coated Whiskers

The process of coating individual SiC particles with the alumina matrix phase precursor was accomplished in a simple flat-bottomed boiling flask with a condenser to prevent excessive loss of water over the period of time necessary for good control of the precipitation of the alumina precursor. An aqueous solution of .01M aluminum sulfate and 12 g/l urea, containing 2.5-5g/l SiC reduced aspect ratio whiskers and .5-1 g/l PVP K30 was obtained by first dividing the distilled water to be used in half, and dissolving the AlS and urea in one half of the water. The dispersant was dissolved in the remaining water, and then the whiskers were added to this, dispersing them thoroughly using an ultrasonic probe for several minutes to break up all agglomerates. This dispersion was allowed to settle for 5 minutes, after which the water containing the suspended whiskers was added to a boiling flask, followed by the water containing the dissolved AlS and urea. The mixture was stirred magnetically in the boiling flask which was partially immersed in oil on a stirring hot plate. A water-cooled condenser was then attached to the mouth of the flask.

The temperature of the mixture was slowly increased over a period of several hours until the processing temperature of 95°C was achieved. This temperature was held for 20 hours. Vigorous stirring must be maintained over this period to prevent settling of the SiC

core particles. After the 20 hour coating period, the heat source was removed and the coated particles were allowed to settle. The supernatant was removed and discarded. The remaining solids were soaked in an ammonium hydroxide solution to remove adsorbed sulfate ions from the coating process. Water was removed from the solid obtained using three acetone rinses and then air drying. This produces a freely flowing powder of SiC whiskers coated with an alumina precursor. In order to decompose the alumina precursor and obtain alumina-coated whiskers, the powder was calcined in static air at 850°C for several hours. Coated powder specimens before and after calcination were characterized using Fourier Transform Infrared Spectrometry (FTIR), X-Ray Diffraction and Scanning Electron Microscopy (SEM). FTIR samples were prepared by mixing a small quantity of the powders with potassium bromide and pressing thin pellets of these mixtures in a steel die. Powder X-Ray Diffraction patterns were obtained in a diffractometer using Cu Kα radiation with a range of 2θ=20 to 100 degrees.

2.3 Densification of Coated Whiskers

Loose alumina-coated SiC whiskers were loaded into a graphite die lined with graphite foil and hot-pressed using a 35 MPa load applied during the heat-up of the furnace. The samples were heated to 1600°C for 1 hour, after which the load was released and the furnace was cooled. Hot-pressed pellets were cut and polished using diamond wheels and diamond paste down to 1μm and the polished surfaces were observed using an optical microscope and a Scanning Electron Microscope. Fracture surfaces of broken pellets were also observed using SEM.

3 Results and Analysis

3.1 Coating Optimization

Optimization of the procedure for coating SiC particles with the alumina precursor required a series of many coating experiments, varying one of many parameters for each experiment until acceptable coatings were obtained. Figure 4 shows as-received American Matrix SiC whiskers and SiC whiskers after ball-milling (reduced aspect ratio whiskers, RARW). For early coating optimization experiments, as-received whiskers were used. Figure 5a shows an example of unacceptable coating results, with a large fraction of whiskers left uncoated and a large amount of excess free alumina precursor particles. Figure 5b shows optimal coating results on as-received SiC whiskers, with very few uncoated whiskers and a negligible amount of free alumina precursor particles. This powder sample was obtained using 5g/l SiC whiskers and 1g/l PVP K30 as a dispersant. It was found that variation of the concentrations of the dissolved species provided little control of the alumina precursor coating thicknesses and morphologies, yielding unacceptable results. This is because the chemistry of the coating process is not yet fully understood, and this understanding will be necessary for successful variation of the concentrations of the dissolved species which does not involve time-consuming trial and error variations of these concentrations. Therefore control of coating thickness and morphology is achieved most effectively by varying the amount of SiC whiskers that are dispersed in the original coating solution.

As previously mentioned, early coating experiments were conducted using as-received SiC whiskers. Figure 6a shows SiC reduced aspect ratio whiskers coated using the same concentrations as those used for the results shown in Figure 5b with as-received whiskers. Grinding causes an increase in specific surface area of whisker samples, so RARW will show a greater fraction of uncoated whiskers than as-received whiskers after the coating procedure is completed. Figure 6 shows coating results on RARW using various whisker additions to the original coating solution. With decreasing SiC RARW addition, less surface area is available for coating by the alumina precursor, and so resulting coatings on SiC particles will be thicker and the fraction of uncoated whiskers will decrease, but the amount of excess alumina precursor that is precipitated as free particles will also increase. Part of the excess precursor can be removed by sedimentation, but an appreciable amount of these particles will remain in the final powder samples.

Another way of increasing the amount of alumina that is added to a quantity of SiC whiskers is to use a sample of coated and calcined whiskers as core particles in a second coating procedure. This results in whiskers with a thick coating of alumina, which appear as oblong particles, as shown in Figure 7, using both as-received SiC whiskers and SiC RARW as original core particles. Optimally, each particle is a small composite "package" containing one SiC whisker and a quantity of porous alumina. These particles can be sintered to produce composites on a larger scale, with a lower final SiC whisker volume fraction than for sintered once-coated whiskers.

Measurement of the pH of the coating solution was carried out at various stages during the coating process in order to compare our results with those of previous authors. It was found that the pH of the coating solution containing all components prior to heating was about pH=3.5-4.0. During heating, the pH of the solution decreased to a final pH=3.0. These pH values differ from those reported earlier for a process used to precipitate spherical basic aluminum sulfate hydrate particles using concentrations of dissolved species that are similar to those used in this study[18]. It is possible that the precipitation of the alumina precursor on SiC whiskers involves a different chemical mechanism than that which occurred in the previous study but it is improbable that the presence of SiC whiskers in the coating solution affected the solution pH to an appreciable degree.

3.2 Calcination of Powders

Calcination of alumina precursor coated SiC whiskers to produce alumina coated SiC whiskers causes little noticeable change in particle appearance. Figure 8 shows coated and calcined as-received SiC whiskers. This can be compared to Figure 5b to notice any change in particle morphology due to calcination. The porous nature of the coating on the particles allows the large amount of weight loss that occurs during calcination without shrinkage of the coating which might cause it to break up and flake off of the whiskers. X-Ray Diffraction spectra for the composite powders were obtained before and after calcination in order to attempt to identify the phase(s) produced by this coating method. FTIR spectra were obtained before and after calcination for comparison with a previous study by Sacks et al.[25] X-Ray Diffraction patterns are shown in Figure 9, and FTIR spectra are

shown in Figure 10.

3.3 Composite Densification

Figure 1 shows residual porosity in a hot-pressed alumina-SiC whisker composite at points where whisker contacts were left in the green body. The lack of a uniform distribution of the component phases on a microstructural scale is the cause of this residual porosity. For this reason, the phase distribution in dense bodies produced using composite powders was evaluated. Loose powder samples of alumina coated SiC whiskers with various compositions were loaded in a graphite die and hot-pressed. Polished surfaces of the pellets that were obtained this way were examined using optical microscopy to evaluate resulting whisker distributions in the alumina matrices. Typical optical micrographs are shown in Figures 11-13. Figure 11 shows the polished surface of a composite obtained by hot-pressing once-coated as-received SiC whiskers. Powder samples shown in Figure 6 using reduced aspect ratio whiskers were hot-pressed to obtain composite surfaces shown in Figure 12. Twice-coated whisker powder samples (Figure 7) were also hot-pressed, and typical polished surfaces are shown in Figure 13. Whisker volume fraction variations can be noticed qualitatively from these figures.

Quantitative analysis of SiC whisker volume fraction in the composite pellets was not possible in this study for a number of reasons. X-Ray Analysis in the SEM was used to determine SiC volume fractions in the polished surfaces, but because whisker orientation occurred during hot-pressing, the SiC fractions that were calculated from polished surfaces perpendicular to the hot-pressing direction will be higher than for the bulk of the material. These numbers can

be used for purposes of comparison, though, and they are included in Table 2. Density values for the composite pellets that were obtained using Archimedes' Principle in toluene are also included in Table 2. For fully dense composites, the density of the pellet can be used to calculate its phase composition by assuming that the density of SiC is 3.21 g/cc and the density of Al_2O_3 is 3.96 g/cc. SEM was also used to obtain a qualitative analysis of the residual porosity in each of these composite pellets (surfaces shown in Figures 14-16). Residual porosity in all composite pellets was very low except for the material produced using once-coated as-received SiC whiskers, which contained a large amount of residual porosity.

3.4 Fracture Surfaces

An accurate evaluation of the mechanical properties of composites produced using this method has yet to be completed, so a more qualitative analysis of the mechanisms of fracture that occur in this material was conducted. Composite pellets containing about 40 volume% SiC RARW were broken so that the resulting fracture surfaces could be observed. Typical fracture surfaces are shown in Figure 17. Figure 17d shows a higher magnification view of a hole where limited whisker pull-out has occured. SiC whiskers generally become hexagonal in cross-section during densification, making them easily recognizable in a composite fracture surface.

4 Discussion

4.1 Whisker Coating Process Mechanism

The characterization of coated particles was done primarily to determine the mechanism that occurs during the coating process.

Values of pH measured in the coating solutions during the coating process indicate that the explanation offered by Blendell et al. was not valid for this study. The pH did not increase in the solution, as it does in an aqueous solution of urea heated to 95°C over a period of several hours.[14,18] This indicates that the hydroxide ions introduced to the solution by the decomposition of urea participate more directly in the precipitation of the alumina precursor. The insolubility of aluminum hydroxide (alone in water $K_{sp}=2\cdot10^{-32}$) also makes it seem unlikely that dissolved aluminum sulfate, which should dissociate to release Al^{3+} ions, could exist in solution with hydroxide ions without the formation of a precipitate. A decrease in solution pH during the coating process is also an indication that hydrolysis of aluminum ions has occurred.[16] Earlier studies on this precipitation method provide results which are more in agreement with the results obtained here.[14-17] A theory on the chemical mechanism for precipitate formation was developed using these references and conversations with several chemists.[28]

When aluminum sulfate is dissolved in water, Al^{3+} and $(SO_4)^{2-}$ ions are present in solution. In water with a neutral pH, hydroxide (OH^-) ions and hydrogen (H^+) ions are present in equal concentrations in solvating water surrounding the Al^{3+} cations. Some of the hydroxide ions from the water may combine with dissolved Al^{3+} in some proportion to form complexes, $Al(OH)_x^{(3-x)+}$. This would result in a slight excess of H^+ ions in solution which would cause a fairly acidic solution pH. The hydrolysis of Al^{3+} cations is even more favorable at increased temperatures, and so when the temperature of the solution is increased, the pH decreases to an even lower value before urea

decomposition has any effect on the solution pH. The complex is still in solution, and the introduction of more hydroxide ions to the solution via the decomposition of dissolved urea allows the formation of $Al(OH)_3$, which is insoluble in water and so it precipitates out of solution. The slow rate of urea decomposition during heating results in a slow rate of $Al(OH)_3$ formation and allows precipitation of this alumina precursor in a controlled manner. During precipitation of the $Al(OH)_3$, continual urea decomposition buffers the solution, which maintains the pH value it had at the onset of precipitation. Actually, the solid which precipitates from solution is probably more complex than simply aluminum hydroxide because of the presence of a high concentration of sulfate ions in the coating solution, some of which bind, either chemically via coordination with hydroxo-aluminum complexes, or physically, by adsorption, to the aluminum-based solid which precipitates. A more thorough chemical analysis of this solid will be necessary to obtain definitive results and to prove or disprove this theory.

X-Ray Diffraction results for coated whisker powders prior to calcination, shown in Figure 9a, assist in the identification of the composition of the whisker coating. Several peaks could be assigned to the SiC core material. Two basic aluminum sulfate hydrate compounds (card #12-0144 $Al_6O_9SO_3 \cdot xH_2O$ and card #36-0540 $3Al_2O_3 \cdot 4SO_3 \cdot 8H_2O$) provided good matches with many of the remaining peaks, but several peaks could not be identified. It was concluded from this analysis that the composition of the coating material prior to calcination consisted of a basic aluminum sulfate hydrate compound that was a mixture of the two shown above, that is, with a total Al to

S ratio that is probably between 1.5 and 6.0. This can be compared with the Al to S ratio of .67 for the aluminum sulfate compound originally dissolved in the coating solution. These ratios agree well with previous studies.[14,16,18] It is possible that the composition of the precipitating compound depends on the ratio of Al^{3+} to $(SO_4)^{2-}$ ions present in the coating solution. This ratio decreases as the precipitation continues, so it would be logical to assume that the $Al_6O_9SO_3 \cdot xH_2O$ compound is the first solid that precipitates, and the $3Al_2O_3 \cdot 4SO_3 \cdot 8H_2O$ compound begins to precipitate later, once the Al to S ratio of the coating solution decreases sufficiently.

The diffraction pattern obtained for the coated whiskers indicated that the coating was crystalline in nature due to the sharp diffraction peaks. Diffraction patterns for powders that were soaked in an ammonia-water solutions to remove adsorbed sulfate ions are essentially identical to those obtained prior to the sulfate removal soak. Spherical particles obtained by Sacks et al. using a similar process for homogeneous precipitation of alumina precursor particles had amorphous diffraction patterns, possibly caused by slight differences in the method by which the solids were precipitated.[25]

Fourier Transform Infrared Spectra for coated whisker samples before and after calcination, shown in Figure 10, were compared to those obtained by Sacks et al.[25] Spectra obtained in this study were weak because the cores of almost all particles in the KBr disc are SiC, which probably does not allow any transmission of infrared radiation due to its high density. Despite this problem, spectra appear similar to those from the previous study over the wave number range studied here. Their analysis will not be discussed in detail,

but this analysis indicated the presence of molecular water, sulfates, and probably Al-O bonds in the coated whiskers prior to calcination. This analysis was done as a supplement to the X-Ray Diffraction study, and no separate conclusions could be drawn from it.

Figures 5-7 illustrate the effect of variation of SiC whisker addition to the original coating solutions. Results shown here confirm that the whisker surface area available for precipitation has an effect not only on the thickness of coating on the SiC, but also on the amount of excess alumina precursor particles that are precipitated. The use of a double-coating procedure appears to be a more successful means of obtaining thick coatings on SiC whiskers than simply decreasing the SiC addition to the original coating solution which would produce too great a quantity of excess alumina precursor, as is shown in Figure 6d.

4.2 Decomposition of Whisker Coatings

Calcination of whiskers coated with the alumina precursor material prior to densification of the powders was necessary so that gaseous species produced by the decomposition of the coating could be removed without impeding the densification process. During decomposition hopefully all residual sulfates and water of hydration will be removed, leaving a coating that consists only of Al_2O_3. This was achieved in earlier studies and so a similar calcination temperature was used to calcine these coated whiskers. X-Ray Diffraction results for powders after calcination, shown in Figure 9b, indicate that basic aluminum sulfate hydrate compounds are no longer present in the composite powders. Several of the peaks can be assigned to the SiC phase present in the whiskers used as core

particles, and almost all of the remaining peaks can be assigned to the phase Γ-Al_2O_3 (card #10-0425). It is probable that other alumina phases are present in the coating due to the calcination temperature of 850°C that was used, and other studies have shown that the coating can be completely transformed to α-Al_2O_3 with calcination of the powders to 1200°C.[18,25] The Γ-Al_2O_3 phase is a "transition" phase during the transformation to α-Al_2O_3. Peaks on the diffraction pattern for the calcined powders which correspond to the transition alumina phase peaks are rather broad. This could be explained by the presence of other alumina phases in the coating which have very similar diffraction patterns to the Γ-Alumina phase or by the composition of the coating of tiny crystallites of alumina.

Fourier Transform Infrared spectra obtained for coated and calcined SiC whiskers are also similar to the spectra obtained by Sacks et al. over the wave number range of this analysis. Their analysis indicated that though there was still some sulfate absorption, it had decreased significantly.[25] Again, FTIR analysis provided no new conclusions for this study.

A large weight loss of about 41% accompanied the decomposition of the coated whisker samples containing about 40 volume% SiC whiskers. With only a small shrinkage accompanying this decomposition, the coating itself becomes very porous in nature, with no significant change in appearance of the particles. The lack of any significant change in particle morphology during calcination is an indication that sulfate ions do not constitute a large part of the alumina precursor. The loss of an appreciable amount of sulfate groups during calcination would cause significant structural

rearrangement in the coating, probably resulting in grain growth and shrinkage of the coating. This supports the belief that aluminum hydroxide is predominant over aluminum sulfate in the precursor material. With calcination of the coating to higher temperatures some grain growth within the coating might be expected to occur, but with only limited densification, until much higher temperatures are reached where sintering of alumina can occur.[18,25]

4.3 Composite Densification

Samples of composite powders were hot-pressed so that densification behavior and whisker distribution in resulting composites could be compared to the aspect ratio and volume fraction of whiskers used as core particles in the coating process. It was also done to compare densification conditions necessary for dense composite fabrication to previous studies. Whisker distributions in composites produced using densification of alumina-coated SiC whiskers can be qualitatively evaluated from Figures 11-13. In all composites that contain reduced aspect ratio whiskers, the distribution of whiskers in the alumina matrix was uniform on the microscopic level shown in these figures, and was also uniform on a more macroscopic level observed using lower magnification observation in an optical microscope. There were no noticeable regions of whisker clusters or regions of matrix phase excess throughout the polished surfaces of the composite pellets. Figures 11-13 show polished surfaces that were perpendicular to the hot-pressing direction of the pellet. Observation of polished surfaces parallel to the hot-pressing direction indicated that whisker orientation had occured during densification, but whisker distribution was uniform in these surfaces

as well. These observations indicate that the coating process was successful not only in producing thick coatings on a very large percentage of the whisker core particles, but also in minimizing the quantity of excess alumina particles that were produced during the process.

Composite pellets produced using as-received SiC whiskers as core particles for the alumina coating also showed good whisker distribution on the macroscopic level, with no observable regions of whisker clusters or alumina excess, but the high aspect ratios of these whiskers prevented optimal separation of the whiskers on a microscopic level. There is evidence that a great deal of whisker damage had occured during densification, and some whiskers had lined up with other whiskers to allow maximum packing during densification. Whisker contacts could not be completely eliminated during hot-pressing, as is evident by the large amount of residual porosity in the composite polished surface. Because as-received whiskers with high average aspect ratios have such high specific bulk volumes, elimination of whisker contacts in the green body does not necessarily guarantee the prevention of whisker contacts during densification. The quantity of alumina matrix material included in the composite may be still lower than the amount that would be mathematically necessary for fully dense composites using whiskers with such high aspect ratios. Twice-coated as-received whiskers do not show the same problems as once-coated whiskers because the quantity of alumina used in the composite is much higher in these materials.

Polished surface observation using Scanning Electron Microscopy was done to augment the previous micrographs by showing residual

porosity in the composites more clearly. Figures 14-16 show typical regions from the polished surfaces for each of the systems studied. Composite pellets obtained using reduced aspect ratio whiskers show little or no residual porosity in these pellets, with the porosity decreasing with decreasing whisker content. The use of whiskers with reduced average aspect ratios obviously aided in densification of the composites, as is evident from observation of Figure 14, which shows a relatively porous surface from a composite produced using as-received whiskers. Once again, twice-coated whiskers showed little residual porosity because of the greater alumina fraction used in the composite powders. Results of densification experiments using the powders from this study are promising because high densities were achieved using densification conditions which are more mild than those from previous studies (Table 1).

4.4 Fracture of Composites

SEM Micrographs of fracture surfaces obtained by breaking composite pellets which contain about 40 volume% SiC reduced aspect ratio whiskers (Figure 17) were obtained for a qualitative analysis of the mechanisms of fracture which occur in such a composite. Observation of these fracture surfaces indicates that a limited amount of whisker pull-out has occurred. The irregular surfaces of SiC whiskers that were used in this study cause the whiskers to be mechanically "keyed" in the alumina matrix after densification, a problem that is exacerbated by the residual compression of the whiskers by the matrix. This prevents the whiskers from pulling out of the matrix to a larger degree during fracture, and probably prevents the fracture toughness values for the material from reaching

the levels that could be obtained by using whiskers which retain a smooth surface after composite densification. When large SiC volume fractions are used in an alumina matrix composite, residual stresses in the composite after densification may negate some toughening influence that whisker additions have on such a material. Such stresses are caused by the difference in thermal expansion coefficients for the component phases. Lowering the sintering temperature of the composite is thus not only advantageous economically, but it probably also enhances the mechanical properties of the composite. This is because residual stresses caused by thermal expansion mismatch will be reduced when using a lower peak sintering temperature. Thorough mechanical property evaluations of the composite materials will be necessary to determine if residual stresses reduce the usefulness of these materials. If this does happen, the advantages and disadvantages of SiC whisker additions to alumina matrices must be balanced so that a material with optimal properties is obtained.

4.5 Summary

A successful method for producing thick coatings of an alumina precursor on SiC whiskers has been developed using heterogeneous precipitation of the precursor on the whisker surfaces from an aqueous solution. These coatings can be calcined to produce whiskers with a thick coating of alumina. Variation of SiC whisker addition to the original coating solution to act as core particles for the precipitation provides control of SiC content in the composite powder. Composite powder samples using both as-received SiC whiskers and reduced aspect ratio whiskers were hot-pressed to produce dense

composites with uniform distribution of whiskers throughout the matrix. Conditions of temperature and pressure necessary to produce these dense composites were less severe than those used in earlier studies. Residual porosity in composite pellets was lower when reduced aspect ratio whiskers were used than when as-received whiskers with higher average aspect ratios were used because of differences in specific bulk volumes of the whiskers. Fracture surfaces of resulting composites show indications that limited whisker pull-out has occurred. This is an original composite fabrication process which controls the distribution of the component phases of the composite, thereby affecting microstructural homogeneity and necessary densification conditions of the composite.

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APPENDIX

Equipment List

Chemicals: Aluminum Sulfate: Fisher Scientific, Inc.
Fair Lawn, NJ

Urea: J.T. Baker Chemical Co.
Phillipsburg, NJ

SiC Whiskers: American Matrix, Inc.
Knoxville, TN

Dispersant: PVP K30 GAF Chemical Co.
Wayne, NJ

FTIR: Analect RFX-30 FTIR Spectrometer
Analect Instruments, Irvine, CA

X-Ray Diffractometer: Siemens Krystalloflex

SEM: International Scientific Instruments, Inc., Santa Clara, CA
WB-6 and DS-130 SEM's

SEM X-Ray: EG and G Ortec System 5000, Oak Ridge, TN

Hot-Press: Thermal Technologies, Inc., Concord, NH

Optical Microscope: Nikon Epiphot-TME
Nippon Kogaku K.K.

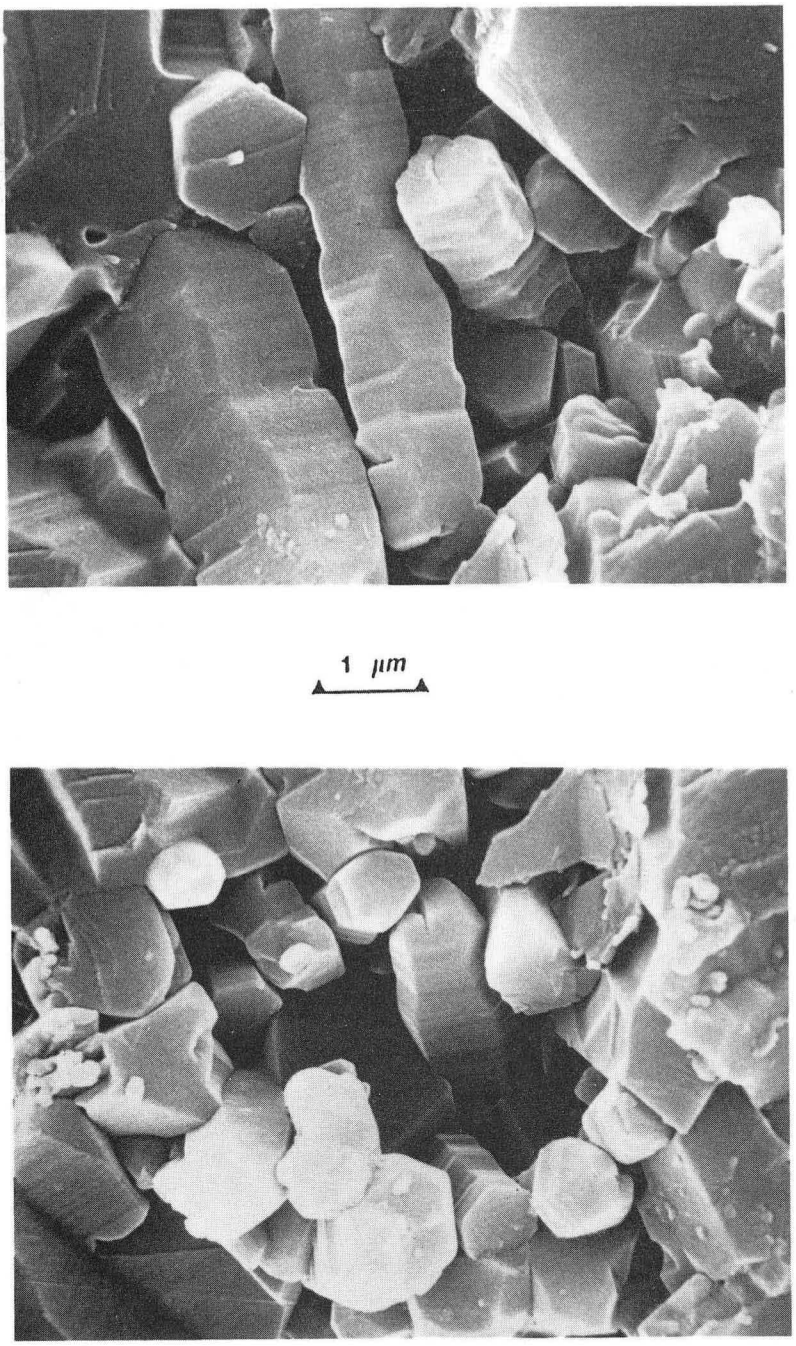
Table 1: Densification conditions used in previous studies for production of SiC whisker-reinforced Alumina matrix composite materials.

Author	Temperature	Pressure	Whisker Content	% Theoretical Density
Porter et al.[2]	1500°C	24 MPa	15 wt.%	fully dense
Homeny et al.[29]	1900°C	31.2 MPa	30 vol.%	fully dense
Tiegs et al.[3]	1700-1800°C	pressureless (with additives)	10 vol.%	≥95%
Becher et al.[5]	1850°C	not mentioned	20 vol.%	fully dense
Sacks et al.[26]	1600°C	pressureless	15 vol.% 30 vol.%	83% 80%
Wei et al.[1]	1850°C	41 MPa 41 MPa 41 MPa	20 vol.% 30 vol.% 40 vol.%	99.9% 99.9% 99.9%
Baek et al.[4]	1800°C	34.5 MPa	20 vol.%	not given
Iio et al.[30]	1850°C	not mentioned	30 wt.% 40 wt.%	>99% 98%

Table 2: Compositions and residual porosities of hot-pressed pellets.

Sample	A	B	C	D	E	F	G
Powder Shown in Figure	5b	6a	6b	6c	6d	7a	7b
Pellet Shown in Figures	11 14	12a 15a	12b 15b	12c 15c	12d 15d	13a 16a	13b 16b
Pellet Density (g/cc)	3.70	3.71	3.76	3.76	3.80	3.86	3.89
from surfaces perpendicular to the hot-pressing direction:							
SiC Volume%	50.1	45.9	41.7	40.7	32.5	21.8	23.3
Al_2O_3 Volume%	49.9	54.1	58.3	59.3	67.5	78.2	76.7
Relative Density (Fig.14-16)	por	lp	nfd	fd	nfd	nfd	fd

por= porous (closed porosity) lp= low residual porosity
nfd= nearly fully dense fd= fully dense



XBB 894-3289A

Figure 1: Residual porosity in a hot-pressed Alumina matrix-SiC whisker composite at points of contact among several whiskers. (bar=1μm)

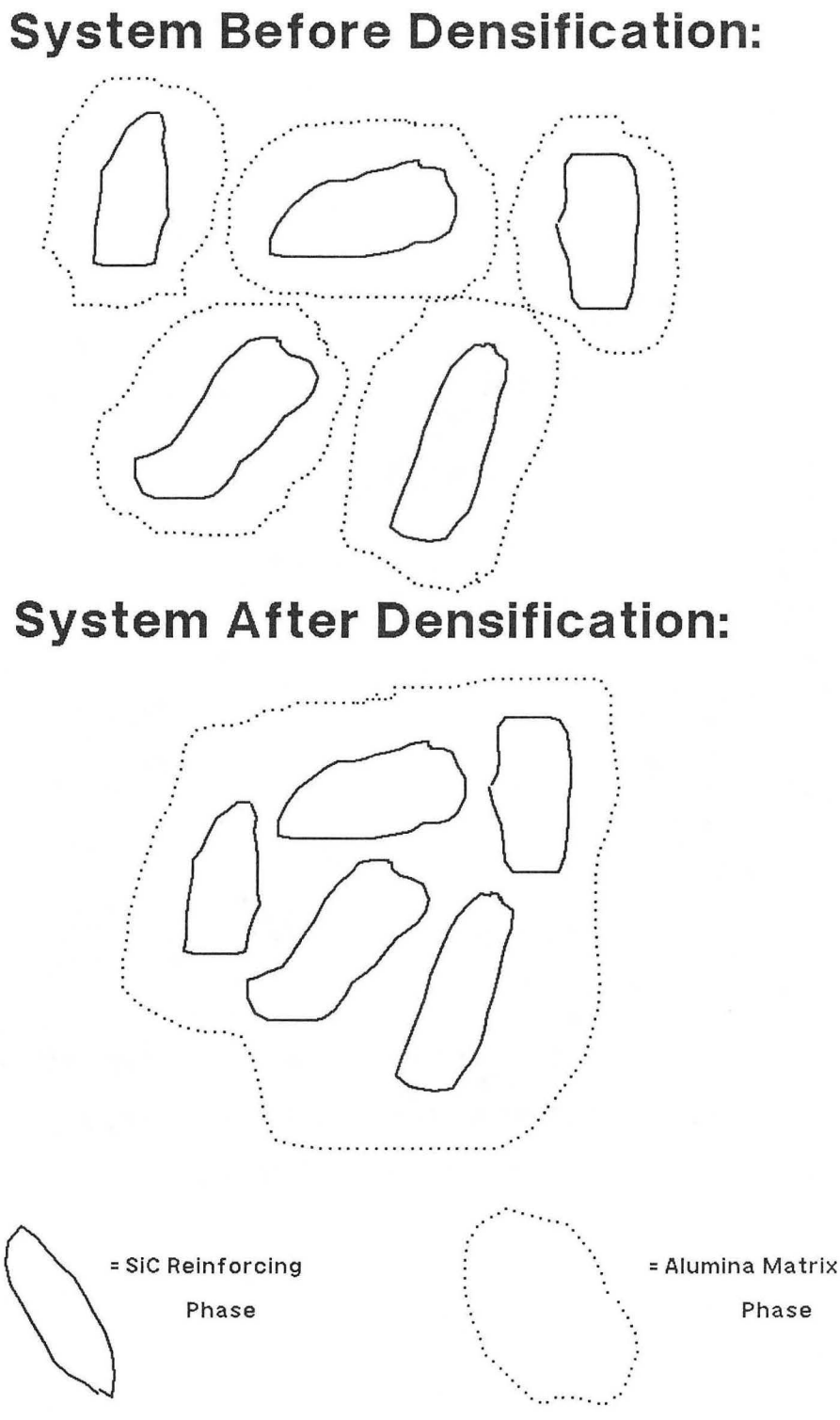


Figure 2: Model of composite fabrication method used to eliminate whisker contacts and provide uniform reinforcing phase distribution throughout the matrix.

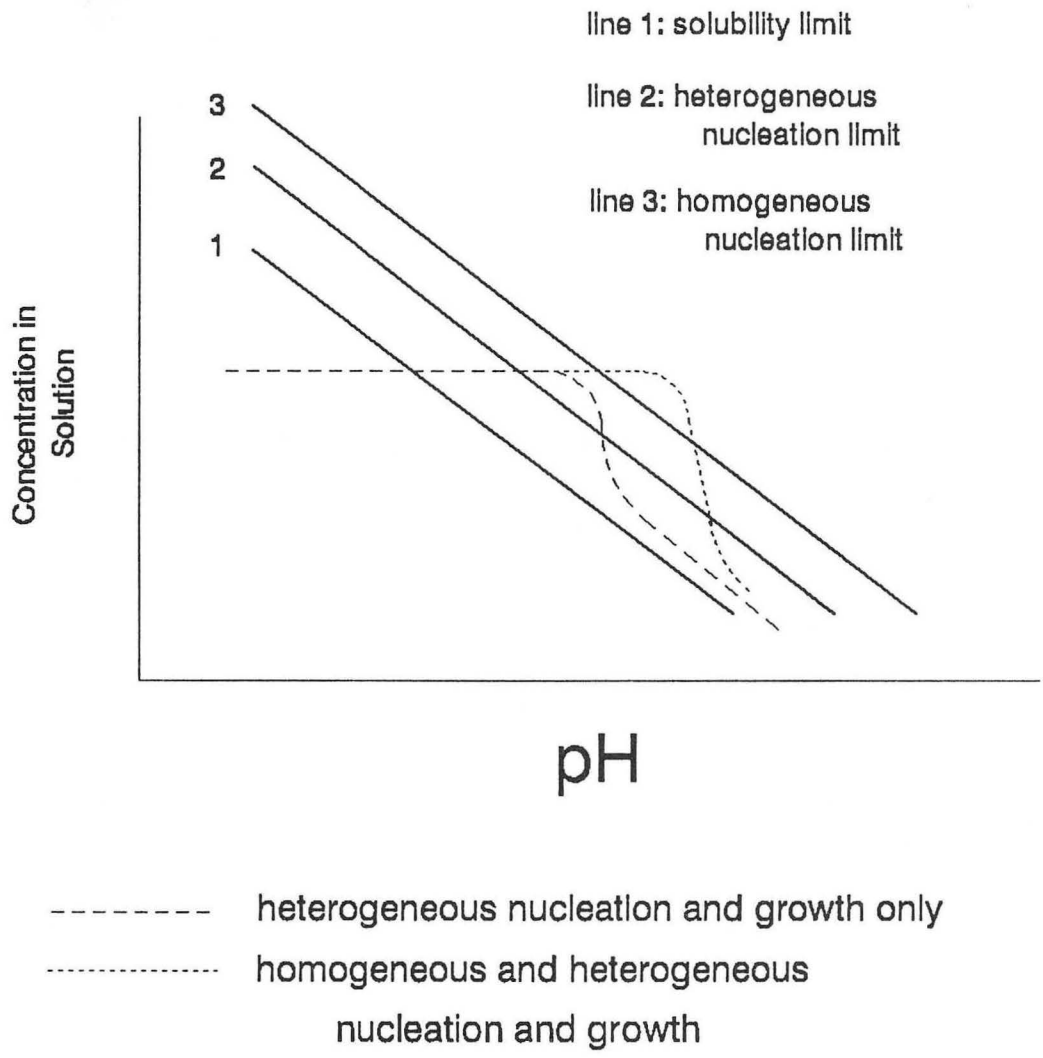
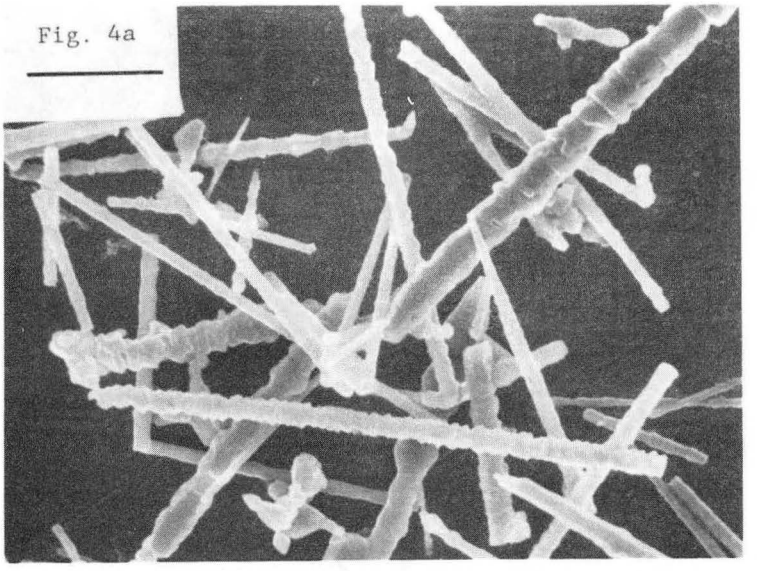
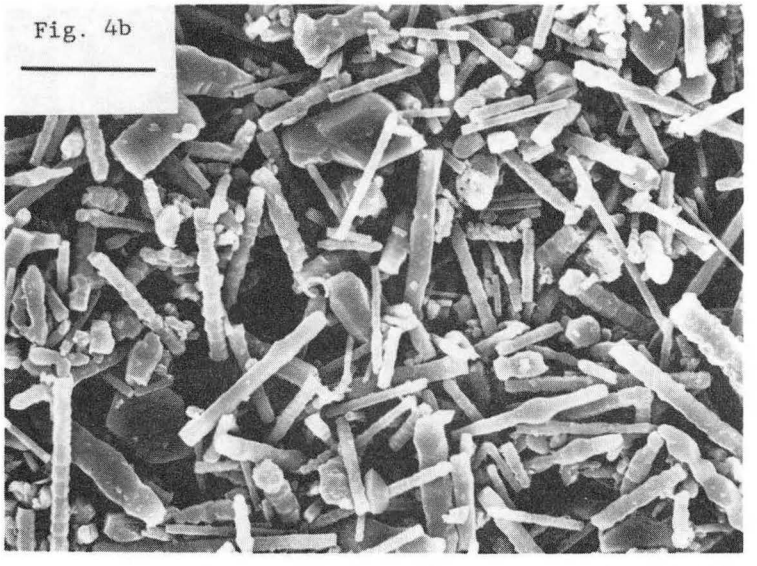


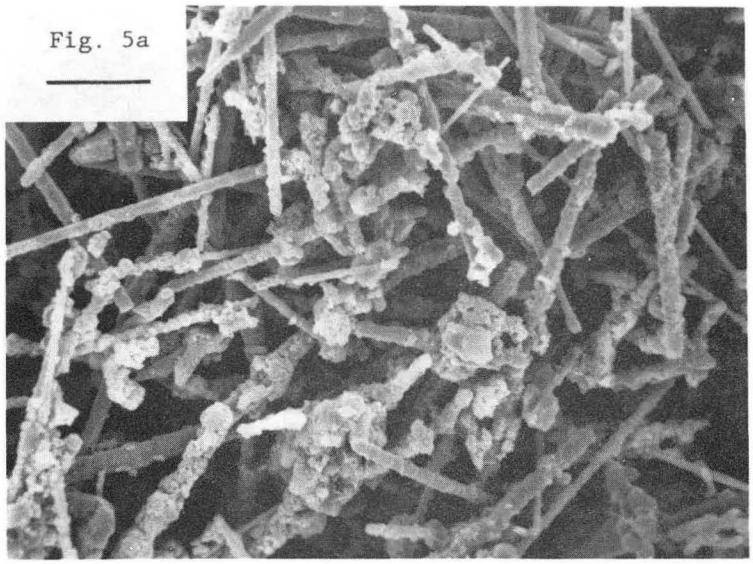
Figure 3: Modified LaMer Diagram showing nucleation and growth behavior of a precipitate from solution with increasing solution pH (from Blendell et al.[18]).

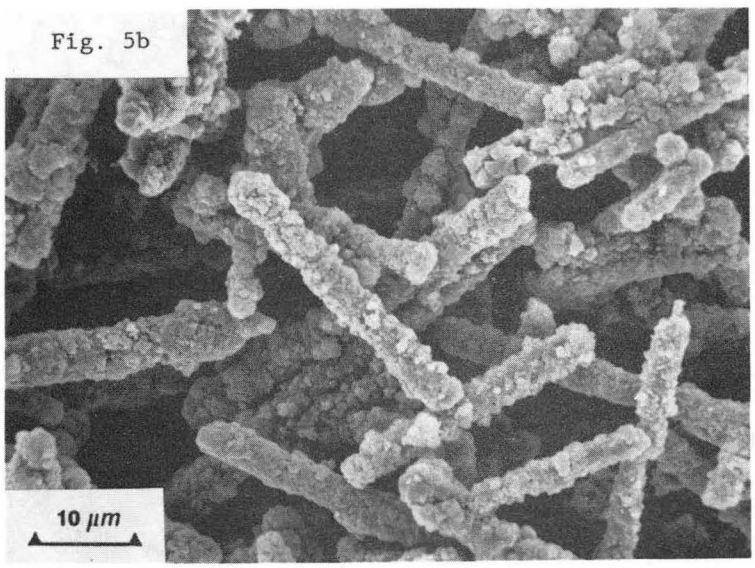




XBB 890-9500

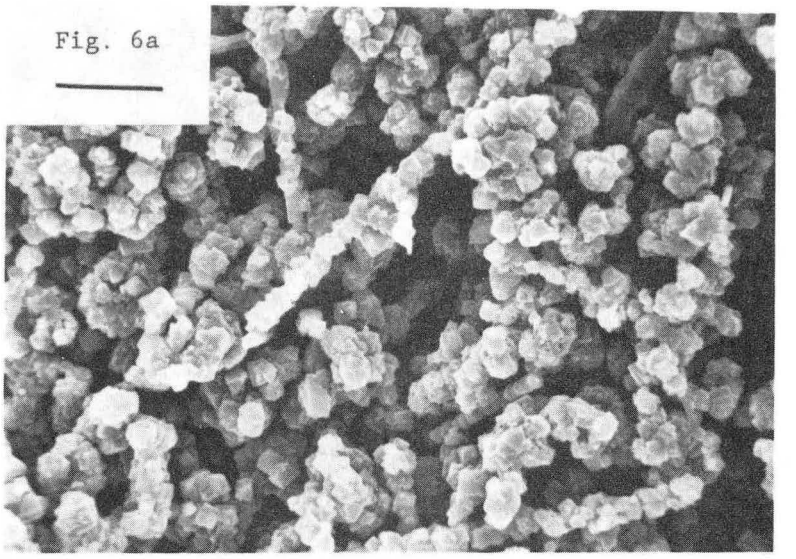
Figure 4: SiC Whiskers used in coating experiments. (a) As-received SiC whiskers (b) Reduced Aspect Ratio Whiskers (RARW). (bar=10μm)

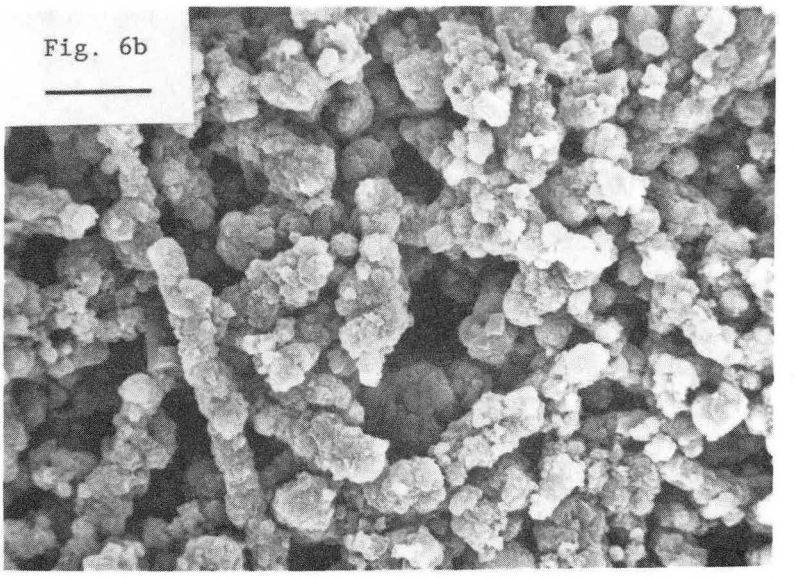




XBB 890-9499

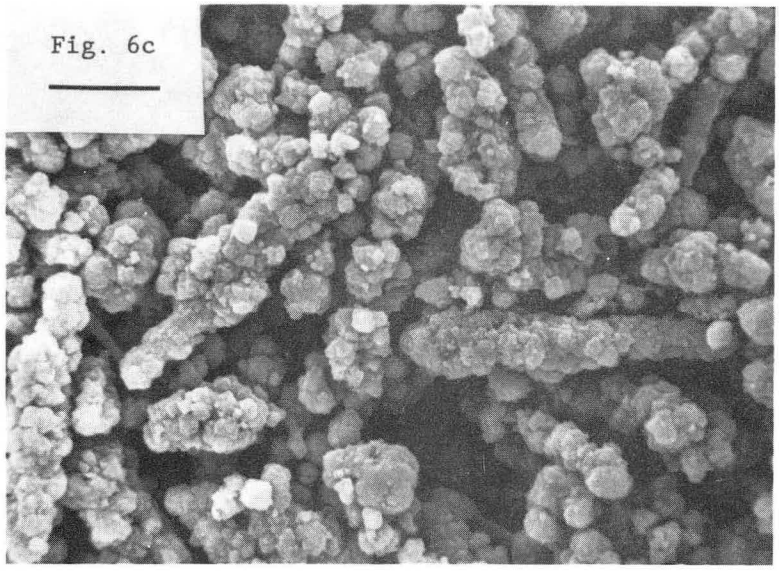
Figure 5: Coating results on as-received SiC whiskers.
(a) Unacceptable coating results (b) Optimal coating results.
(bar=10μm)





XBB 890-8420B

Figure 6: Coating results on RARW with decreasing SiC addition to the original coating solution containing .01M Aluminum Sulfate and 12g/l Urea. (a) 5.00 g/l RARW (b) 4.28 g/l RARW.



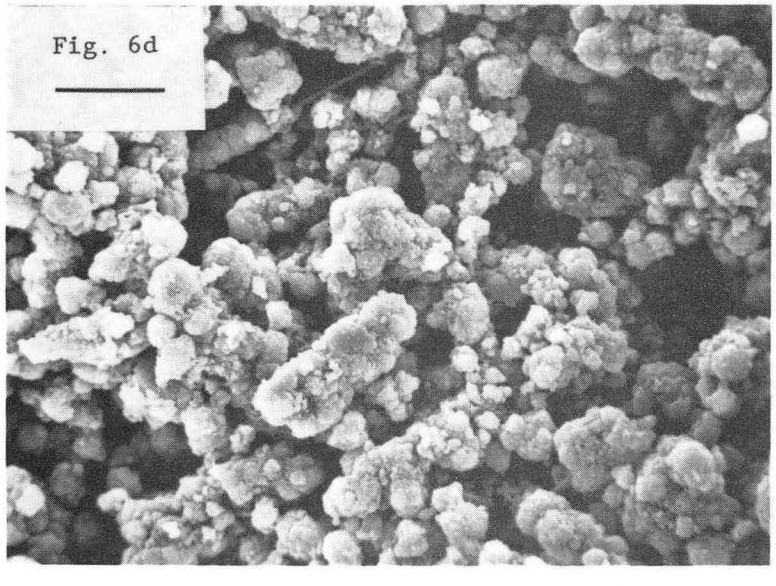


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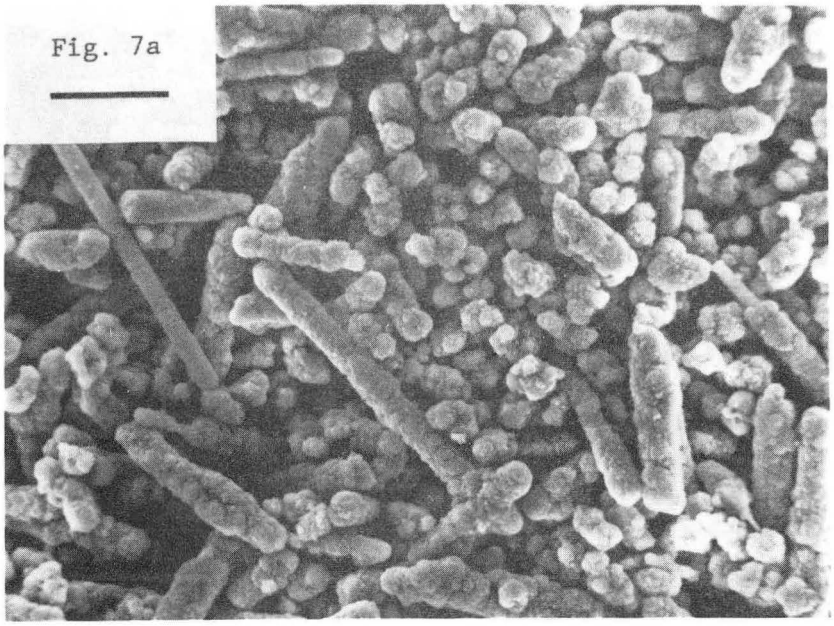
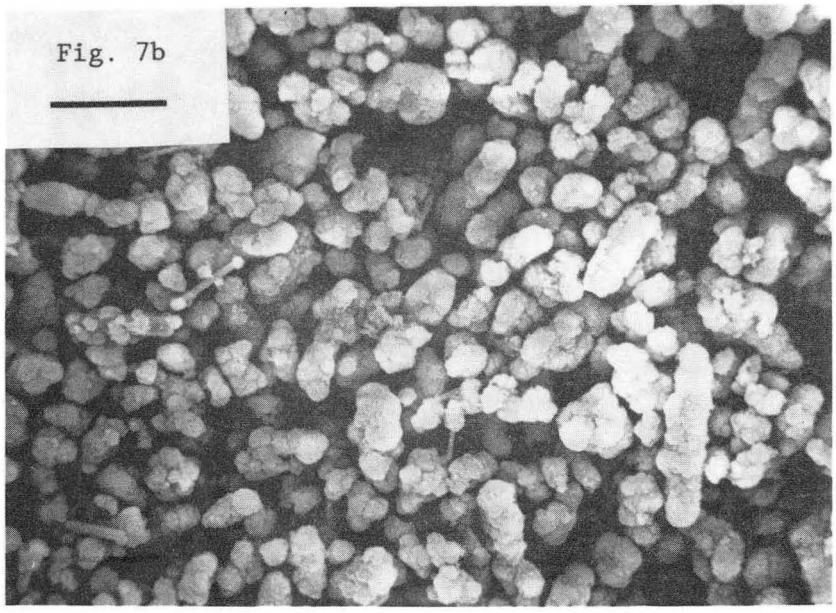
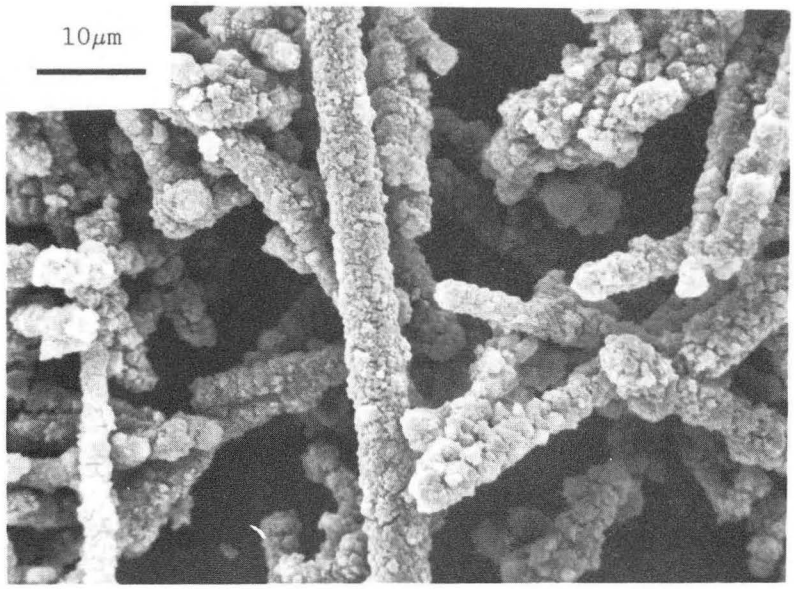
Figure 6 (continued):
(c) 3.57 g/l RARW (d) 2.85 g/l RARW. (bar=10μm)

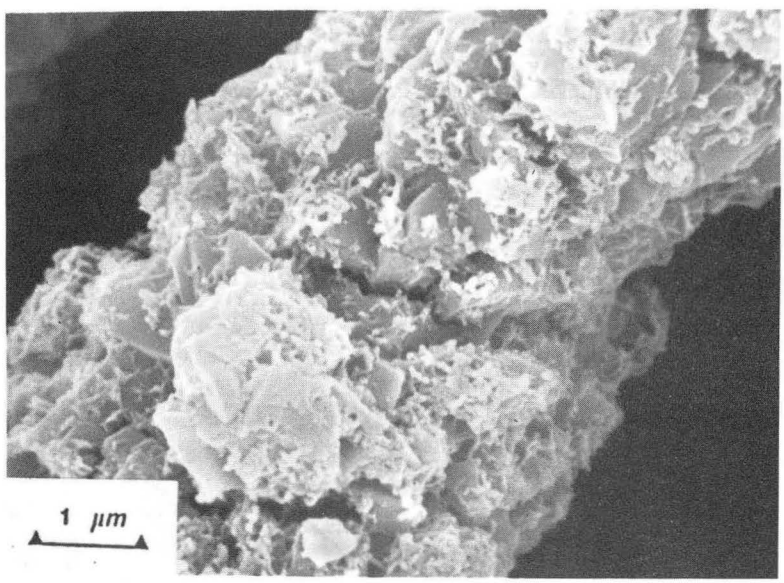




XBB 890-9498

Figure 7: Twice-coated SiC whiskers. (a) As-received SiC whiskers (b) Reduced Aspect Ratio Whiskers (RARW). (bar=20μm)





XBB 894-3286A

Figure 8: Coated and calcined as-received SiC whiskers for comparison with Figure 5b (2 magnifications).

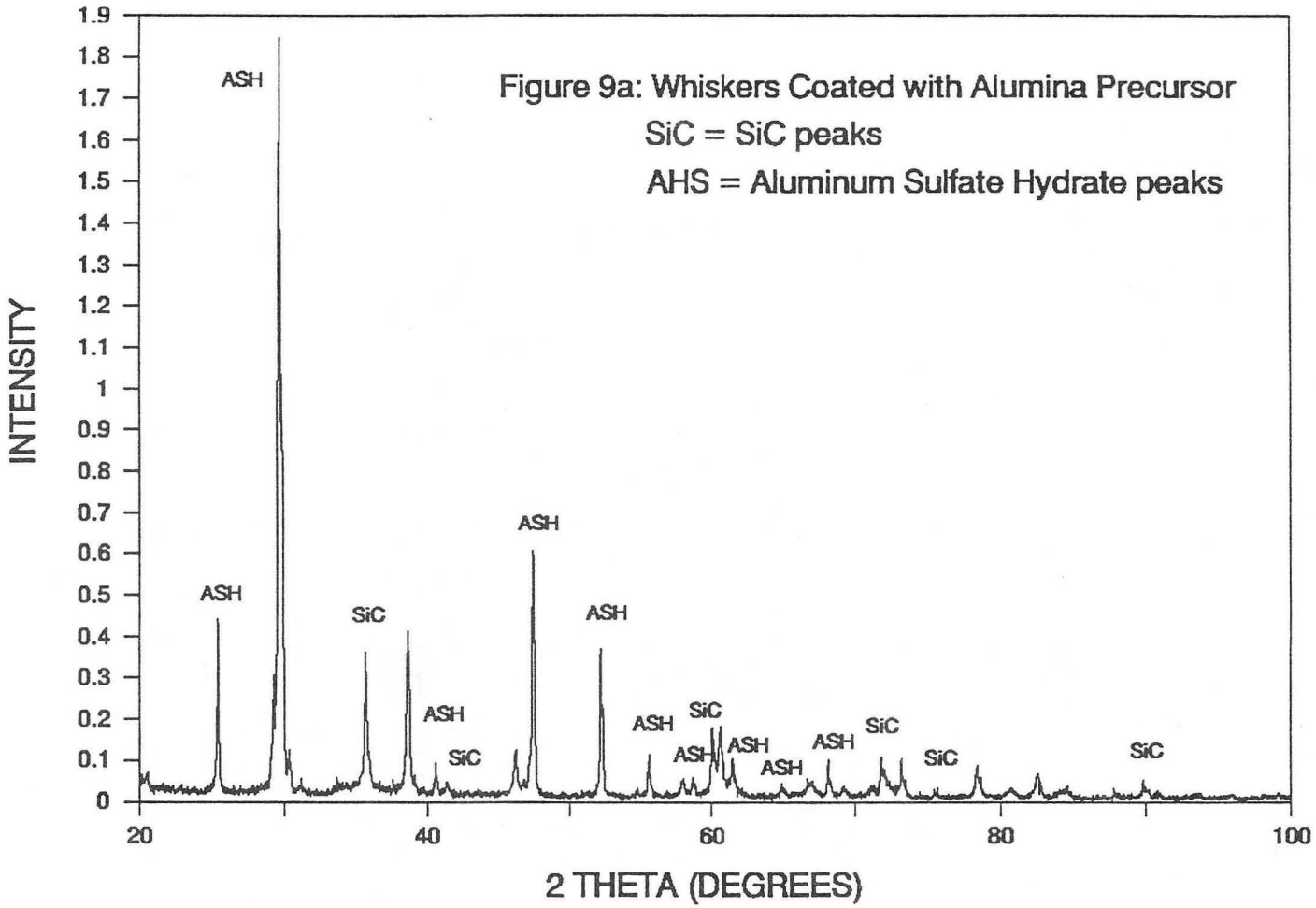


Figure 9: X-Ray Diffraction Patterns for coated whiskers.
(a) Whiskers coated with Alumina precursor.

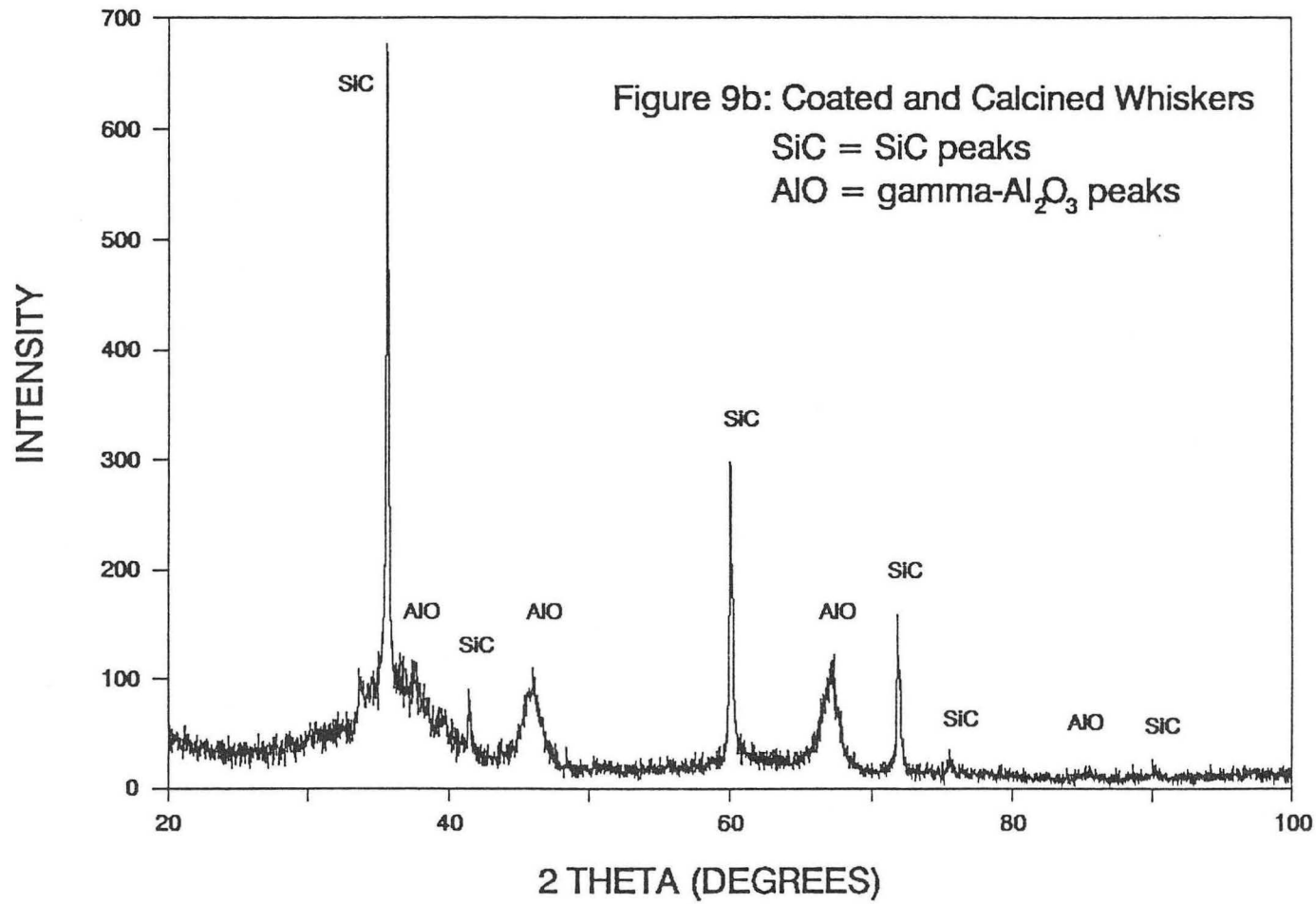


Figure 9 (continued): (b) Whiskers with coating after calcination.

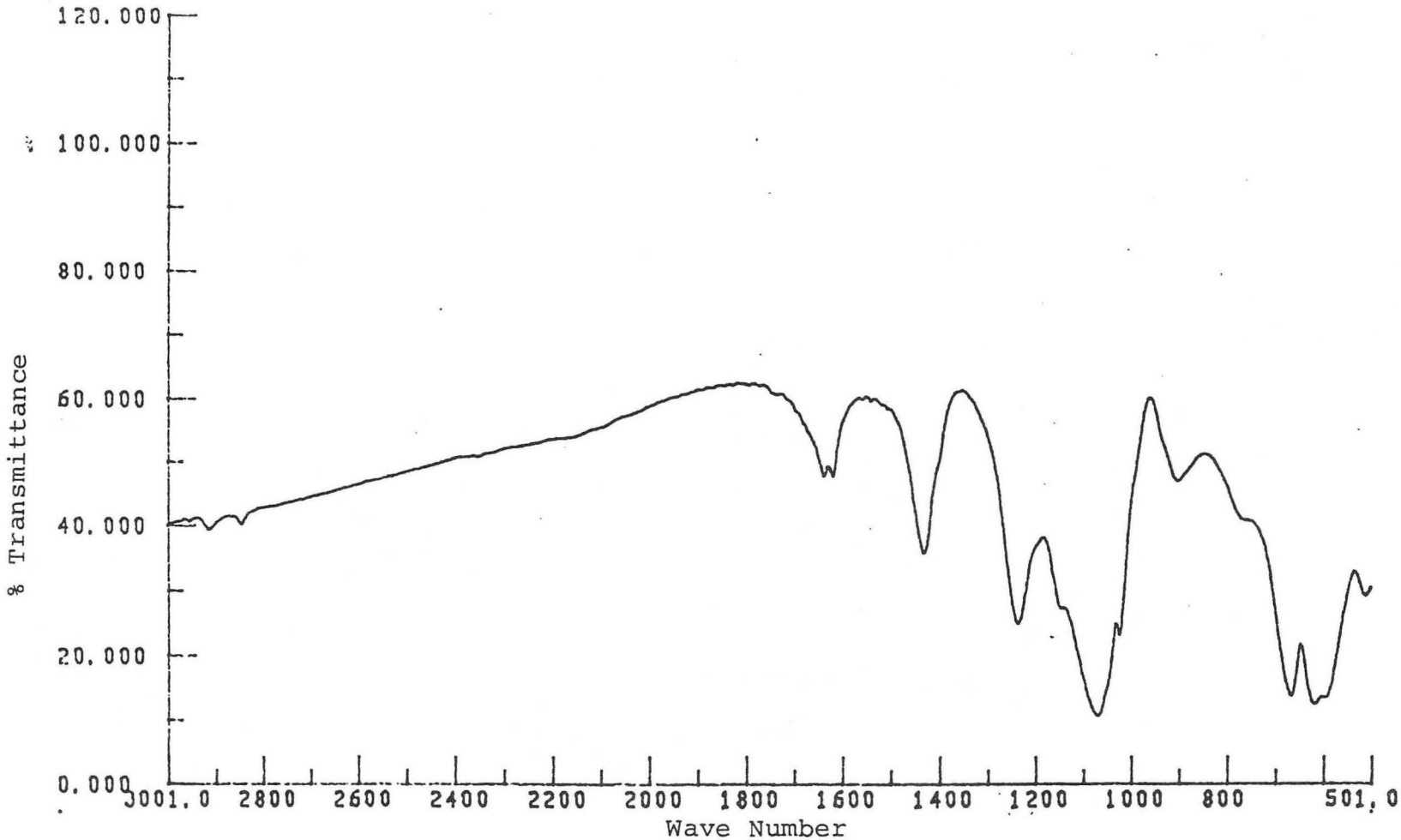


Figure 10: Fourier Transform Infrared Spectra for coated whiskers.
(a) Whiskers coated with Alumina precursor.

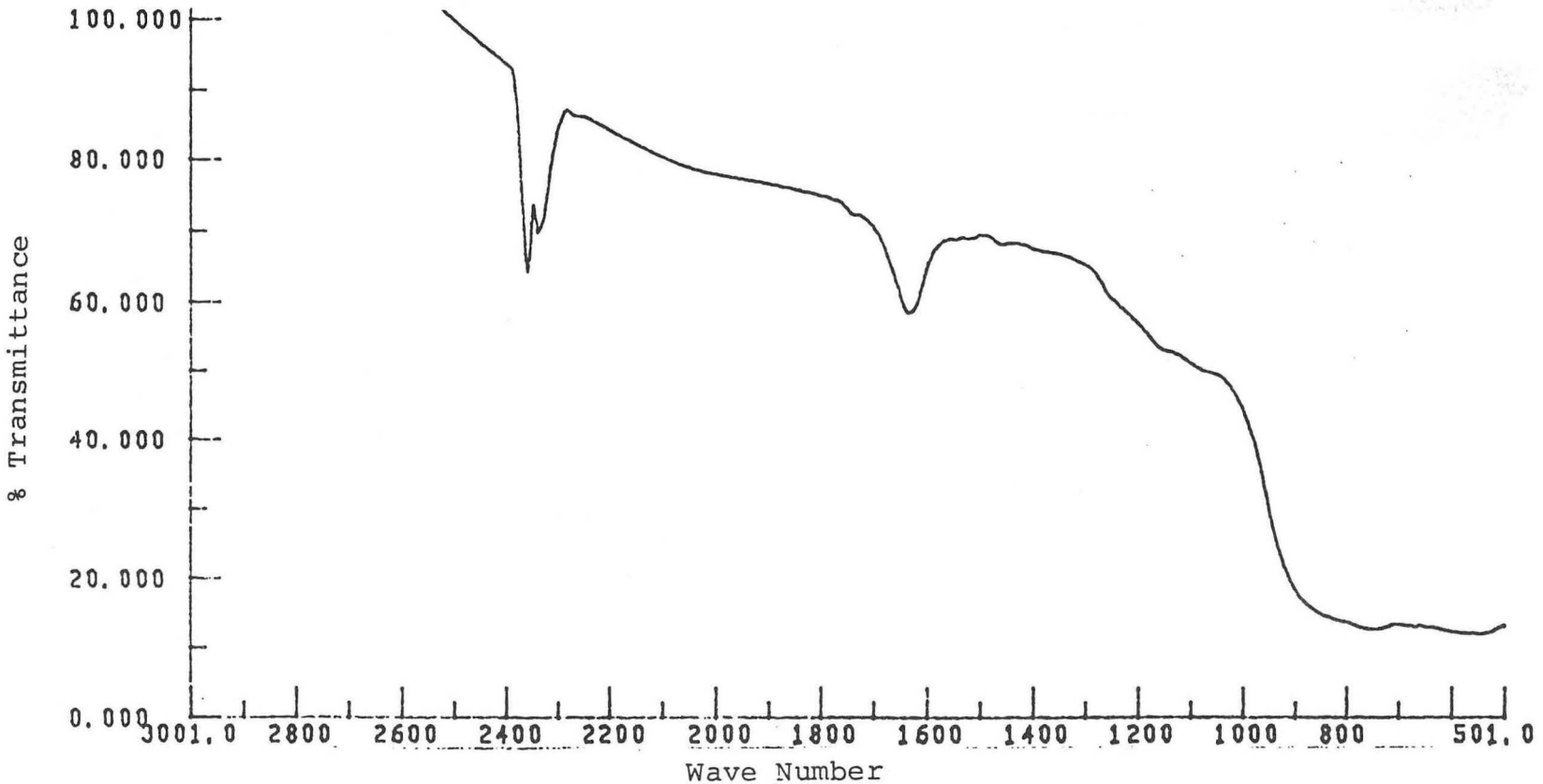
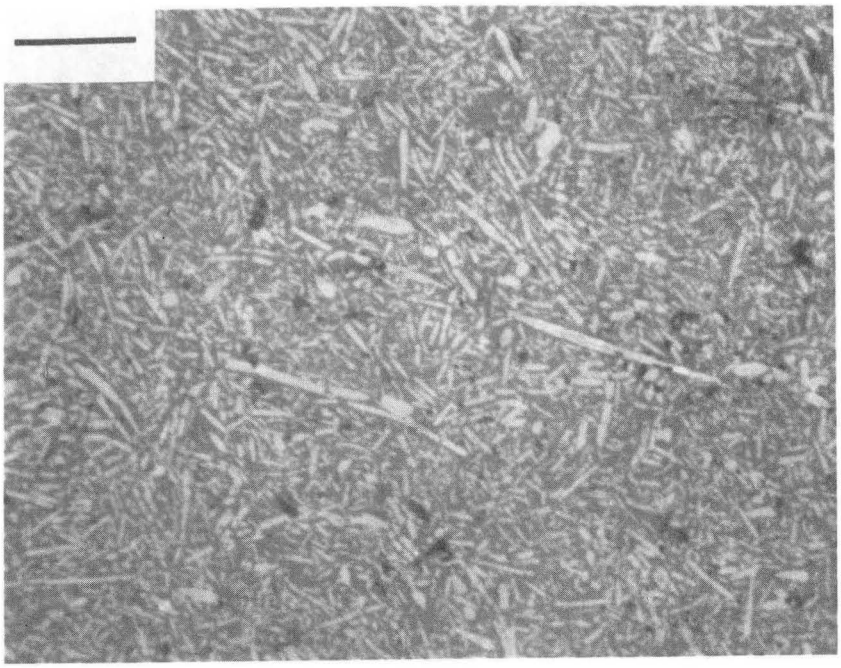
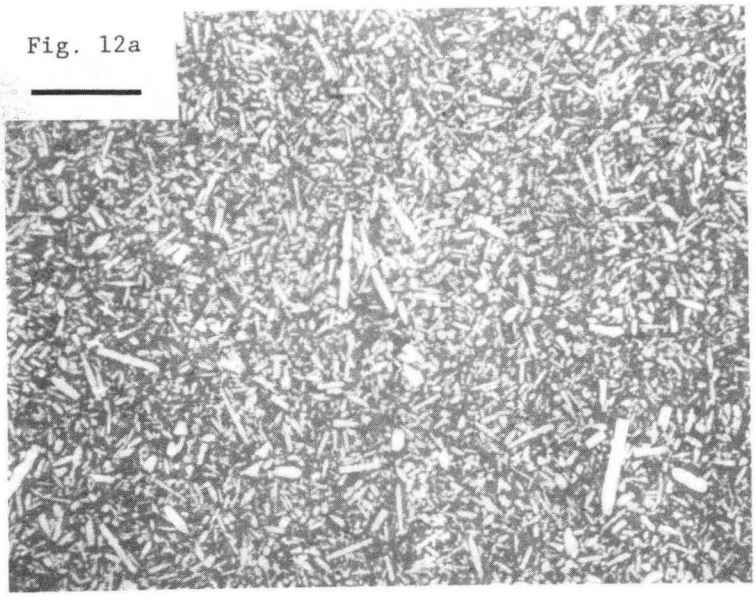


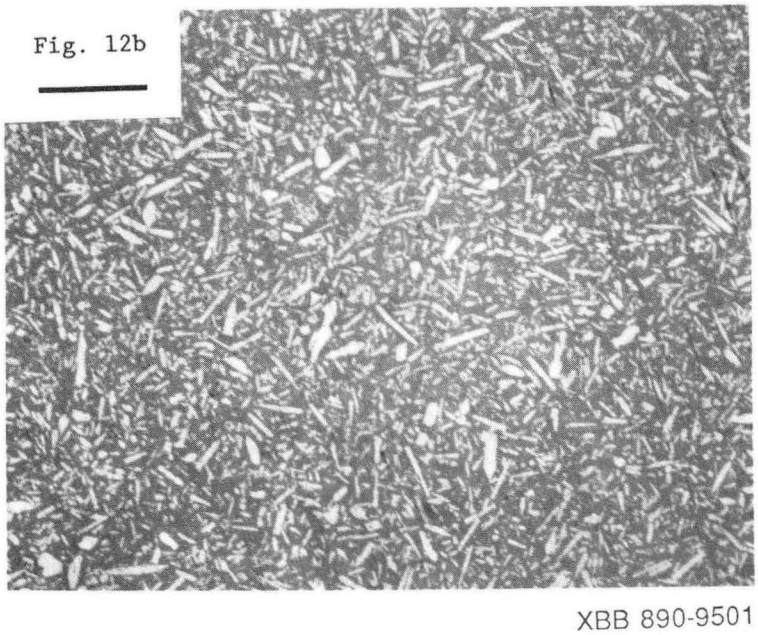
Figure 10 (continued): (b) Whiskers with coating after calcination.



XBB 890-9508

Figure 11: Optical micrograph of a polished surface of a composite pellet obtained using once-coated as-received SiC whiskers. (bar=40μm)





XBB 890-9501

Figure 12: Optical micrographs of polished surfaces of composite pellets obtained using once-coated RARW, shown in Figure 6. (a) Fig. 6a (highest whisker addition) (b) Fig. 6b. (bar=40μm)

Fig. 12c

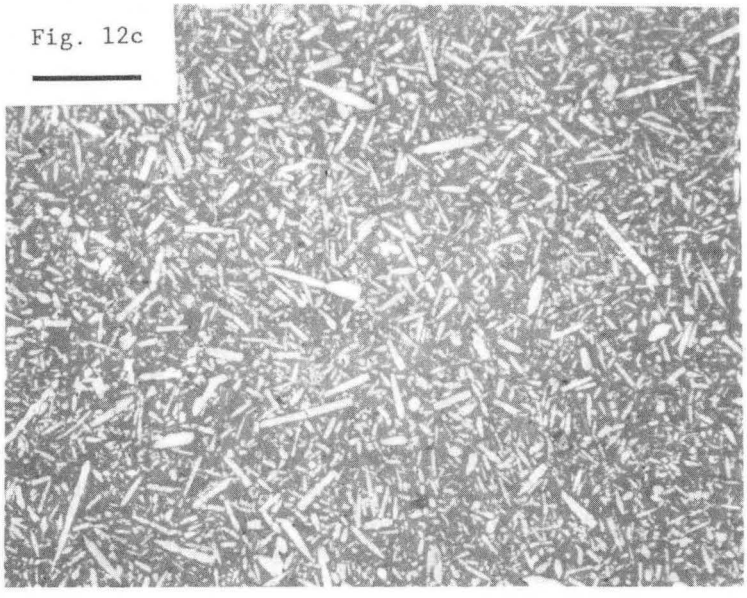
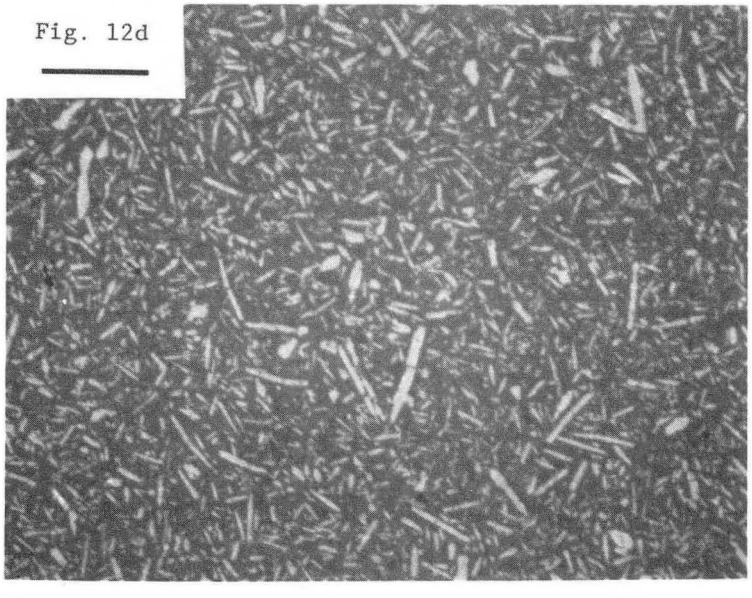


Fig. 12d



XBB 890-9502

Figure 12 (continued):
(c) Fig. 6c (d) Fig. 6d (lowest whisker addition). (bar=40μm)

Fig. 13a

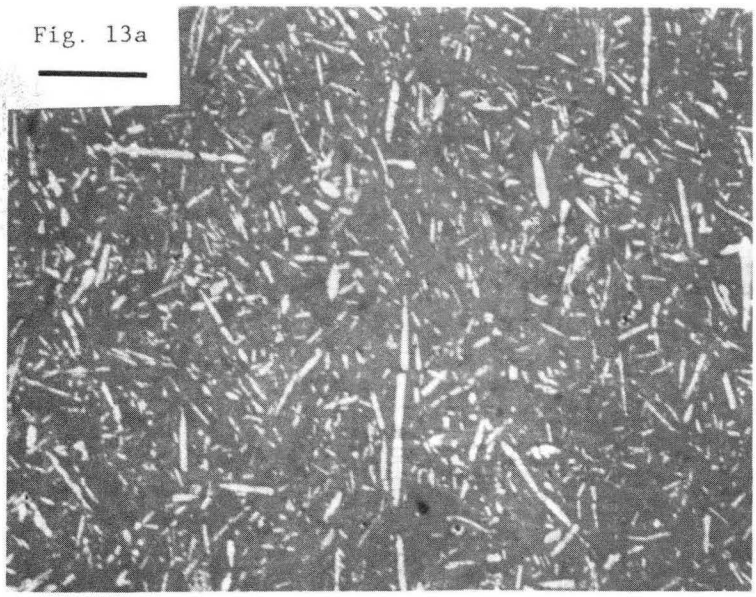
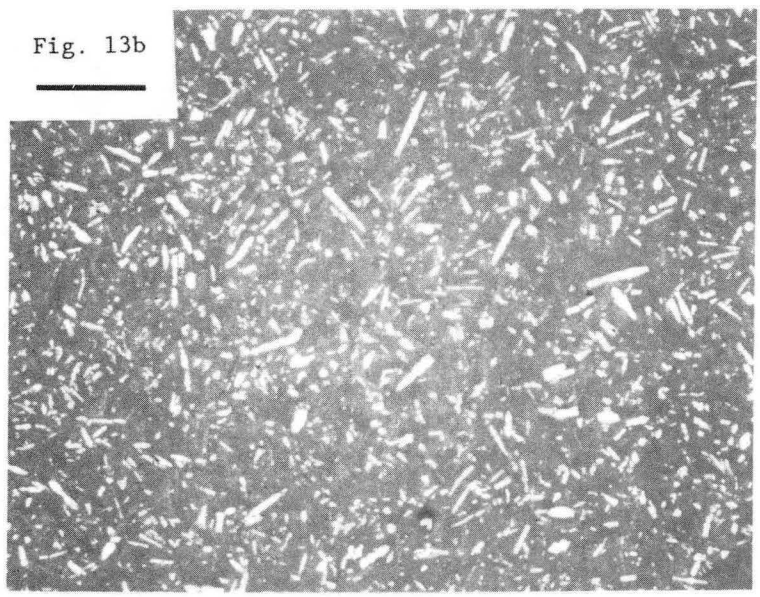
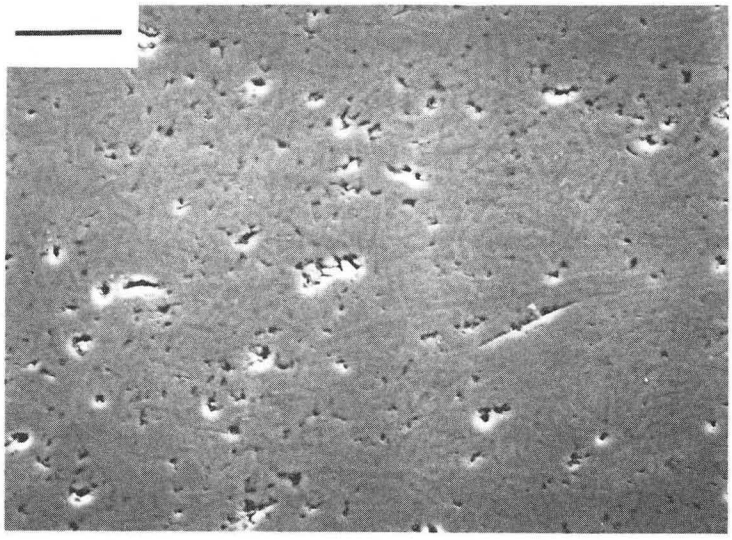


Fig. 13b



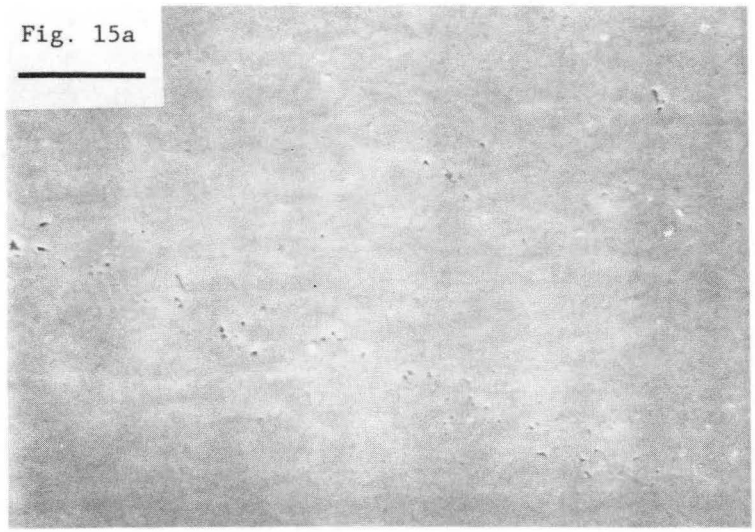
XBB 890-9503

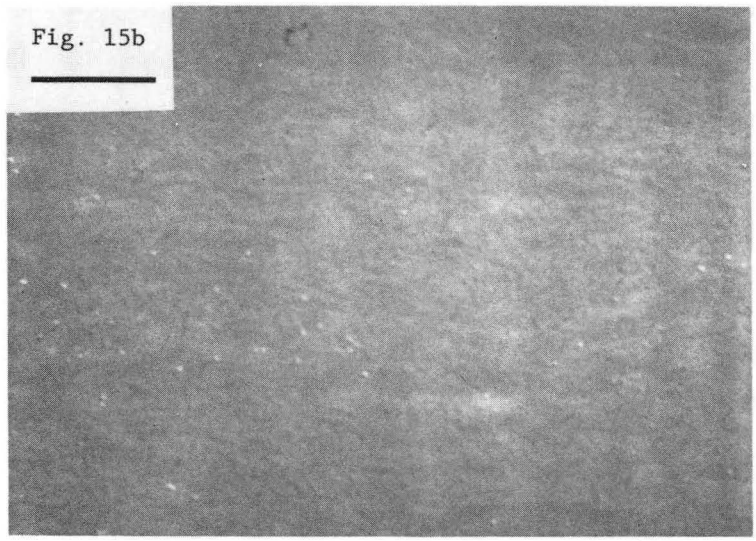
Figure 13: Optical micrographs of composite pellets obtained using twice-coated whiskers. (a) As-received SiC whiskers (b) SiC RARW. (bar=40μm)



XBB 890-9507

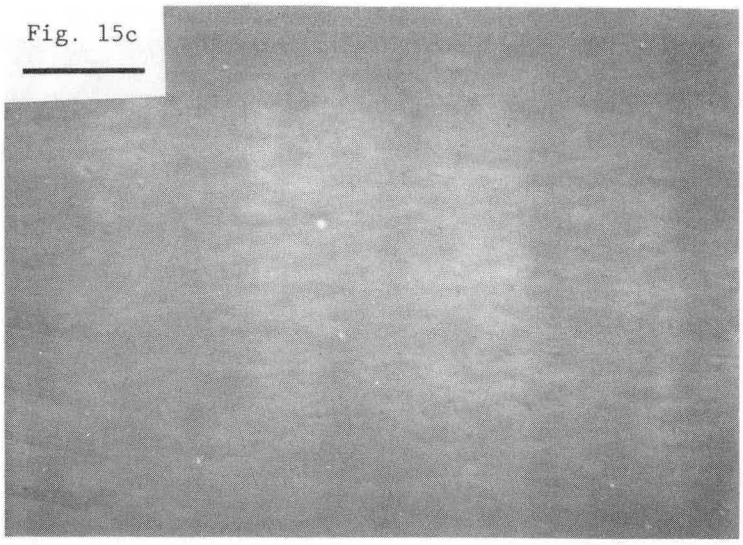
Figure 14: SEM micrograph of a polished surface of a composite pellet obtained using once-coated as-received SiC whiskers. (bar=20μm)

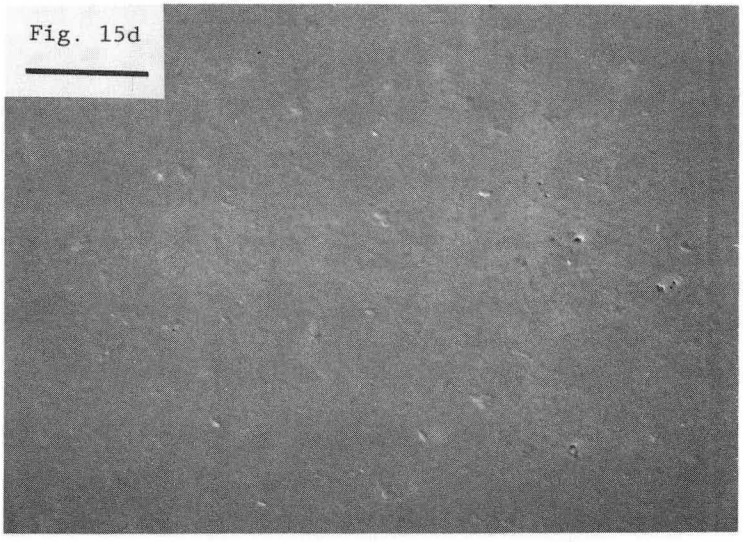




XBB 890-9504

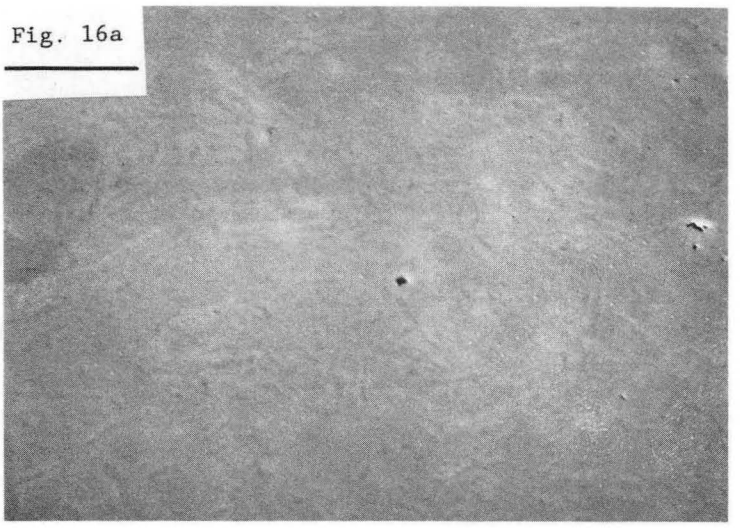
Figure 15: SEM micrographs of polished surfaces of composite pellets obtained using once-coated RARW, shown in Figure 6. (a) Fig. 6a (highest whisker addition) (b) Fig. 6b. (bar=20μm)

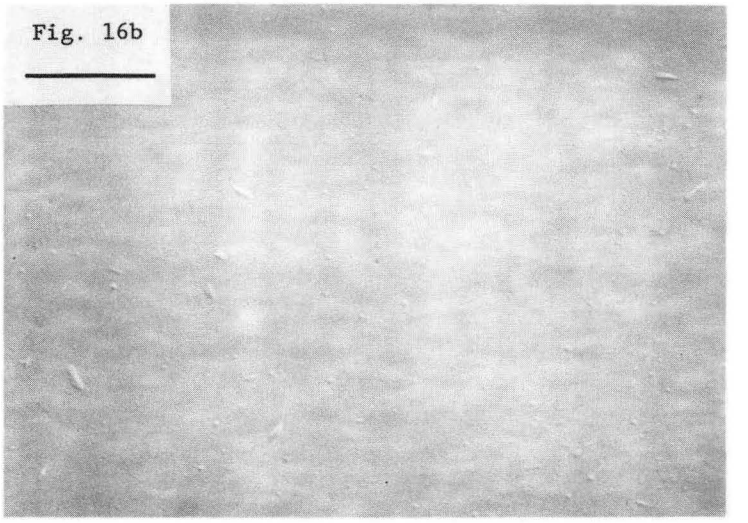




XBB 890-9505

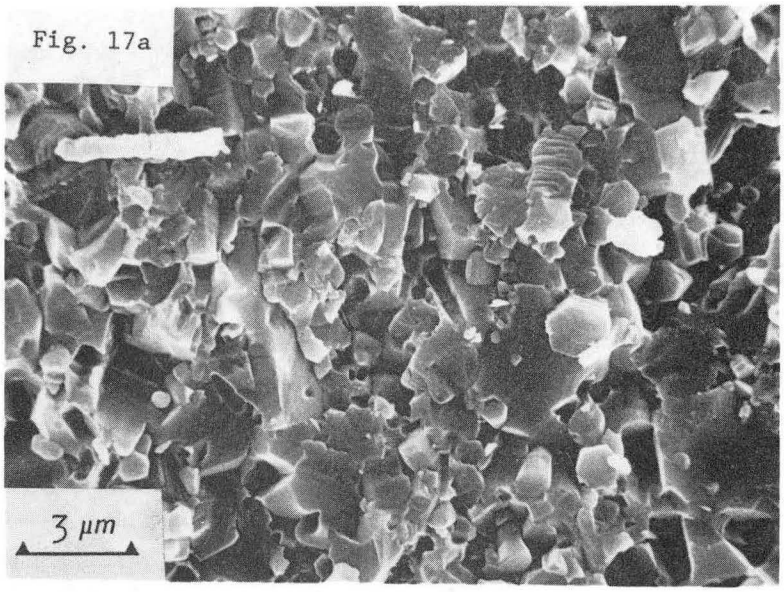
Figure 15 (continued):
(c) Fig. 6c (d) Fig. 6d (lowest whisker addition). (bar=20μm)

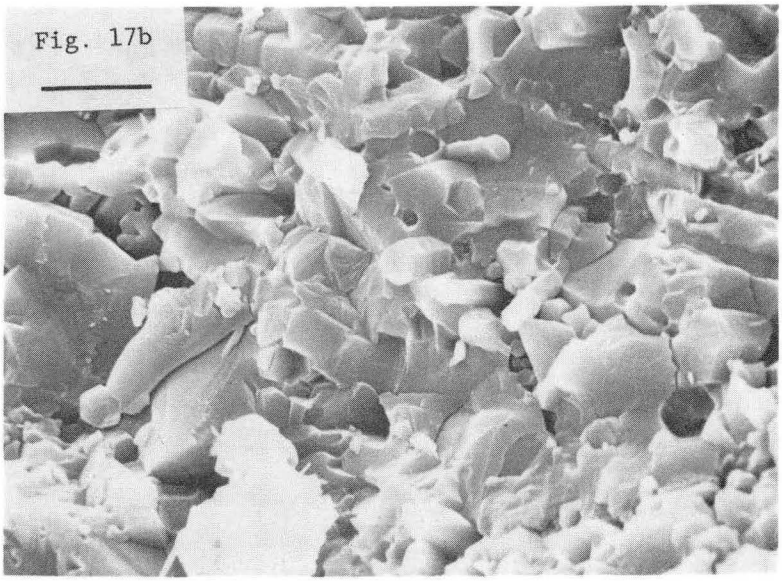




XBB 890-9506

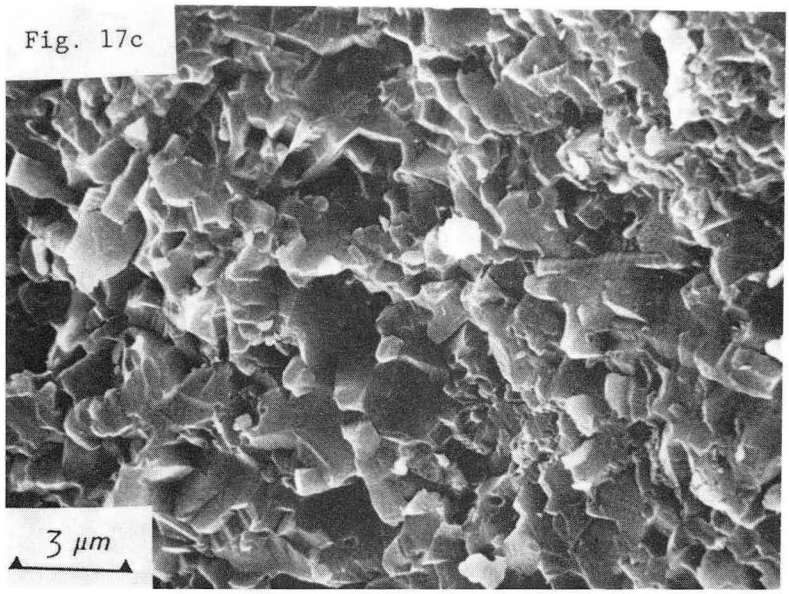
Figure 16: SEM micrographs of composite pellets obtained using twice-coated whiskers. (a) As-received SiC whiskers (b) SiC RARW. (bar=20μm)

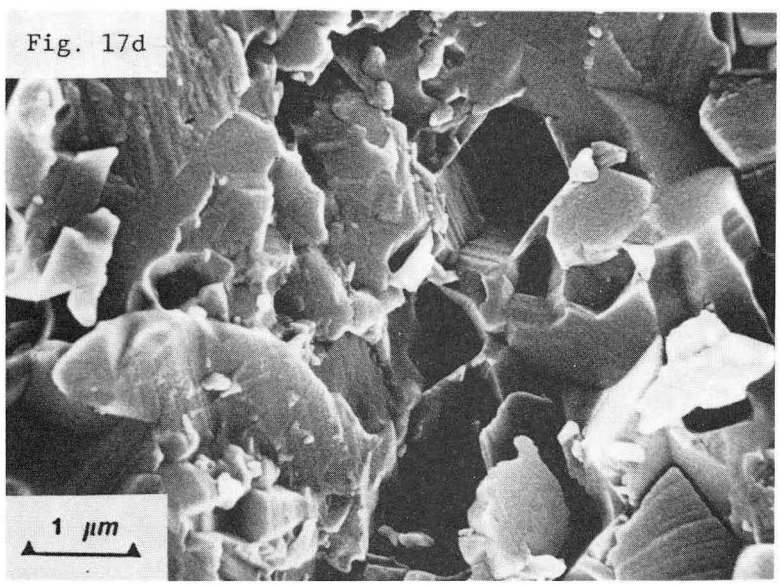




XBB 894-3284C

Figure 17: SEM micrographs of fracture surfaces of composite pellets obtained using coated whisker samples with 45 volume% SiC whiskers. (a), (b). (bar=3μm)





XBB 894-3288C

Figure 17 (continued):
(c) (bar=3μm) (d) higher magnification view of whisker pull-out hole. (bar=1μm)

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