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Extrusion of Alumina-Silicon Carbide Whisker Composites

M. A. Janney
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M. C. Vance

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M. A. Janney
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EXTRUSION OF ALUMINA-SILICON CARBIDE WHISKER COMPOSITES*

M. A. Janney, E. S. Bomar, and M. C. Vance

ABSTRACT

A method was developed to extrude tubes of alumina-silicon carbide whisker composites and the mechanical properties of extruded material were determined. Extruded parts had good strength (~300 MPa) and excellent thermal shock properties (ΔT_{crit} > 900°C). Extruded alumina-silicon carbide whisker composites represent a prime candidate for use as heat exchanger tubes.

INTRODUCTION

Recent studies[1,2] have shown that significant energy savings could result from waste heat recovery efforts (i.e., recuperators) in the glass, steel, and aluminum industries. For some applications, SiC is the material of choice. However, in some applications, notably aluminum remelt and glass furnaces, SiC is rapidly attacked by vapors in the atmosphere. In these situations, alumina would be the better candidate material of choice. However, alumina possesses poor thermal shock properties and is unacceptable. Tiegs and Becher[3] have demonstrated that alumina-silicon carbide whisker composites (Al_2O_3-SiCw) possess both excellent strength at up to 1000°C and excellent thermal shock resistance, which makes Al_2O_3-SiCw an excellent candidate for use in recuperators. The purposes of this study were to develop a process for extruding Al_2O_3-SiCw and to determine the mechanical properties of these extruded products.

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*Research sponsored by the Industrial Energy Efficiency Division, Office of Industrial Technologies, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

PROCESSING SiC WHISKER-REINFORCED Al_2O_3

This section considers raw material selection, whisker processing, batch preparation, extrusion, and firing.

RAW MATERIAL SELECTION

Perhaps the largest problem confronted during this investigation was the selection and procurement of suitable silicon carbide whiskers (SiCw). Silicon carbide whisker manufacture is a relatively new technology which operates at an essentially pilot plant scale. Most of the manufacturers of SiCw were (many still are) on a steep learning curve so that whisker quality changed with each lot of whiskers that was received from each manufacturer. Sometimes the quality improved; sometimes it declined. The principal manufacturers were ARCO Chemical Company, Tateho Chemical Company, and Tokai Carbon Company, Ltd. Based on various evaluations, the ARCO whiskers were judged to be the best, followed by Tateho, and finally Tokai Carbon. However, because of corporate-level decisions on the part of ARCO Chemical Company, the ARCO whiskers were not available in large lots [more than 1135 g (2.5 lb)] at the beginning of this investigation and were not available at all after August 1985. Therefore, the Tateho SCW1S whiskers, which were available in >10 kg lots, were chosen for this study.

WHISKER CLEANUP

As received, the Tateho whiskers contained high levels of metallic impurities. Presumably, these impurities were introduced during manufacture in the form of the catalyst used in making the whiskers.

The whiskers were cleaned by slurrying 250 g of whiskers in 3000 cm^3 of 50% concentrated HCl and mixing for >72 h. Dissolution of the metallic impurities was indicated by the appearance of a dark green color in the supernatant solution. The concentrated acid was filtered from the whiskers, after which the whiskers were washed about seven times until the pH of the wash water approached that of the starting deionized water (typically pH 6).

After washing, the whiskers were pan dried. To avoid affecting the physical properties of the whiskers, no settling, sizing, milling, or other mechanical processing steps were employed. The trace element concentrations present before and after acid treatment are given in Table 1. The acid treatment was effective in removing most of the transition metals (i.e., Fe, Cr, Ni, and Mn as well as P, Na, and K). Neither the Al nor the Ca concentrations were affected by the leaching treatment, which suggests that they may be present as bulk rather than surface contaminants.

BATCH PREPARATION

Tiegs[4] has shown that the best properties of SiCw-Al_2O_3 composites were obtained when the whiskers were well dispersed in the Al_2O_3 matrix. To achieve good dispersion, Tiegs typically slurried the starting powders and whiskers in water or hexane suspension, then dried the resulting mixture.

We chose to follow Tiegs' lead and concentrated much of our attention on producing a well-mixed slurry, then making our extrusion batches from the slurry or from the dried, mixed powders and whiskers. We describe these investigations in some detail. However, we discovered late in this investigation that the best extrusion batches could be made using a traditional ceramics approach of blending the dry powders with a binder solution in a high shear mixer. At the present time we are still not sure why the "traditional" processing route produces a superior extrusion mix to the "advanced" processing route.

Four different processing techniques were examined during the course of this study. These techniques are designated as:

- method 1 – slurry → thicken → partially dry,
- method 2 – disperse → thicken,
- method 3 – traditional, and
- method 4 – modified traditional.

These techniques are described below.

Table 1. Chemical composition of as-received and HCl-leached Tateho SCW1S SiC whiskers

Element	Concentration[a] (ppm)[b]	
	As received	Leached
Al	400	500
Ca	500	400
Co	<1	0.5
Cr	1000	25
Cu	20	1
Fe	600	150
K	50	25
Mn	100	20
Na	30	3
Ni	75	10
P	10	2
C	30.3 wt %	31.5 wt %
O	0.75 wt %	0.69 wt %

[a]Determined by semiquantitative (+100, -50% accuracy) spark source mass spectroscopy except carbon by LECO combustion and oxygen by neutron activation analysis.

[b]Except carbon and oxygen, which are wt %.

A typical batch composition for method 1 (slurry-thicken-dry) is given in Table 2. Method 1 had been used successfully in an earlier study[5] to extrude and pelletize SiO_2-carbon black mixes which were precursors to SiC powder. We were surprised to find that the Al_2O_3-SiCw batches we made using method 1 were unextrudable. The material was dilatant in every batch we made. If we left enough water in the mix to allow it to be extruded, it was too weak to support its own weight after extrusion, and the parts would slump. If on the other hand we dried it sufficiently to give it good wet strength, then it was too stiff to be extruded.

Two variations of method 1 were examined. The first variation was to produce an extremely well deflocculated initial mix. This was accomplished by adding 0.25 wt % Darvan C* (a polyelectrolyte dispersing agent) to the initial slurry of water and powders (step 1 in Table 2) prior to adding the Methocel. The second variation was to produce a highly flocculated slurry. This was accomplished by adjusting the pH of the initial slurry to pH 6 prior to adding the Methocel. The consistency of the final extrusion batches was unaffected by either of these variations of method 1 processing. The mixes were still dilatant and unextrudable.

The second method that was investigated was the "fully dispersed" technique (method 2). The composition and processing for method 2 are given in Table 3. The mix as made was soft and somewhat sticky. We could extrude the mix at 50 vol % solids; however, we encountered numerous problems. First, the as-extruded material was extremely soft and tended to slump and deform. Because the as-extruded material was weak, it would not support a column of material more than about 0.3 m (1 ft) long during vertical extrusion. Second, excessive shrinkage occurred during drying, which resulted in cracking along the length of most of the extruded tubes. Third, the as-extruded tubes were sticky and tended to adhere to our hands and other surfaces during handling and setting. This further contributed to cracking during drying.

---

*RT Vanderbilt Company, Norwalk, Conn.

Table 2. Batch composition and processing for method 1

Composition		Processing
Component	Amount (g)	
A16SG alumina	1000	1. Slurry powders, whiskers, and water.
Molycorp Y_2O_3	20	
ARCO SiCw	92.5	2. Mix on homogenizer for 5 min.
Water	1000	3. Add Methocel solution to slurry, agitate with a propeller mixer.
Methocel A4M	15	
		4. Heat mix in a 70°C oven to gel the Methocel and to dry the mix to an appropriate solids loading (~50 to 55 vol %).
		5. Cool to room temperature.
		6. Extrude.

Table 3. Batch composition and processing for method 2

Composition		Processing
Component	Amount (g)	
RCHPDBM alumina	1000	1. Dissolve Darvan C and citric acid in water.
Tateho SCW-1S	100	2. Add alumina, SiCw, and Y_2O_3 to water to form a slurry (~50 vol % solids); mix with an ultrasonic probe to aid in powder and whisker dispersion.
Molycorp Y_2O_3	20	
Water	275[a]	
Darvan C	13.6[a]	
Citric Acid	0.80	3. Place slurry in Σ-mixer.
Methocel E50 (8 wt % in water)	22	4. Slowly add binder to mixer.
		5. Mix until binder is fully dissolved.

[a]Volume in mL.

To alleviate some of these problems, we modified the batch composition to increase the solids loading of the initial slurry to ~55 vol % solids (step 2 in Table 3). After adding the binder powder and mixing to dissolve it, the extrusion batch became dilatant. Its wet strength was better but it could no longer be extruded. Other variations of method 2 in which polyvinyl alcohol was substituted for methyl cellulose produced essentially the same type of extrusion mix behavior.

Method 3 was the "traditional" technique which is described in Table 4. Batch preparation using method 3 produced the best mixes to date. The mix felt like wet clay. The mix had a relatively long working range as determined by observation of its consistency during mixing. The consistency changed slowly with polyethylene oxide addition from crumbly to plastic (too sticky, if too much binder solution was added). It could be extruded easily and had good wet strength; tubes >0.6 m (>2 ft) long could be formed in the vertical extruder.

One drawback to method 3 was that the whiskers were not always well dispersed in the alumina matrix. Also, we sometimes found large alumina agglomerates in the extruded material. To address these problems, we developed method 4.

Method 4 is a modification of method 3, but the results were so different as to warrant a separate classification. The batch composition and processing details of method 4 are given in Table 5. The only difference between method 3 and method 4 was in the premixing of the powders by milling in water followed by drying. Much to our surprise, the final extrusion mix made using method 4 was highly dilatant and had very low wet strength. Hand-molded specimens tended to slump quite badly. Also, the material was extremely sensitive to vibration. Simply working the material back and forth in one's hands caused it to flow. In many respects, the extrusion mix resembled "silly putty."

Why there is such a major difference in the behavior of extrusion mixes made using method 3 and method 4 is not at all clear to us. The physical mechanics associated with each system should be quite similar because the milling operation was quite mild; it was sufficient to provide mixing, but, based on the Tiegs et al. work,[4] it should not have

Table 4. Batch composition and processing for method 3

Composition		Processing
Component	Amount (g)	
RCHPDBM alumina	1000	1. Load dry powders in Σ-blade or muller mixer.
Tateho SCW1S	100	
Molycorp Y_2O_3	20	2. Add binder solution slowly to mixer.
Polyox WSR-N-60K 4% in water	258	3. Mix until a homogeneous batch is produced.

Table 5. Batch composition and processing for method 4

Composition		Processing
Component	Amount (g)	
RCHPDBM alumina	1000	1. Slurry alumina, SiCw, and Y_2O_3 in water.
Tateho SCW1S	100	
Molycorp Y_2O_3	20	2. Mix for 1 h in an 8 L (2 gal) polypropylene jar with 1000 g of alumina rods measuring 0.6 × 10 cm (0.25 × 4 in.) long.
Polyox WSR-N-60K 4% in water	258	
		3. Pan dry slurry.
		4. Place 435 g mixed dry powder in Σ-mixer.
		5. Slowly add 258 g Polyox solution.
		6. Mix until a homogeneous batch is produced.

caused significant breakage of the whiskers. Therefore, we are left with chemical considerations. Y_2O_3 is somewhat soluble in water. During mixing, there may have been dissolution of the Y_2O_3 and subsequent adsorption of Y^{+3} onto the alumina and/or the SiC surfaces. Such a process would likely affect the amount and type of particle-particle interactions in the system, creating a corresponding change in the flow behavior of the system. At present, this approach is mere speculation; however, it represents a fertile area for continued research.

RHEOLOGICAL STUDIES*

In an effort to understand the nature of flow in whisker-particle systems, we conducted a set of experiments to define their limits of processability. Fully dispersed systems were investigated.

Total solids contents from 25 to 55 vol % and whisker contents up to 60% were investigated. Rheological measurements have demonstrated that both the total solids loading and the whisker content of the solid affect the processability of the slurries.

Aqueous slurries were prepared from A16SG alumina,† and SCW1S SiC whiskers,‡ with Darvan 7** and citric acid†† as dispersants. Dispersant levels were held constant at 0.25 wt % Darvan 7 and 0.07 wt % citric acid, based on the weight of solid in the slurry. The pH was adjusted to 9.2 ± 0.1 for all slurries. The dry Al_2O_3 and SiC were added to an aqueous solution of the dispersants, mixed by hand to incorporate the powders in the liquid, and then sonicated using a 300-W ultrasonic probe.‡‡ Some difficulty was encountered in preparing the high-solids

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*Research partially sponsored by the Ceramic Technology for Advanced Heat Engines Project.

†Alcoa, Pittsburgh, Pa.

‡Tateho Chemical Company, Japan.

**R. T. Vanderbilt Company, Norwalk, Conn.

††Fisher Scientific Company, Pittsburgh, Pa.

‡‡Model 300, Fisher Scientific Company, Pittsburgh, Pa.

and high-whisker-content slurries; they tended to be dilatant in the hand-mixed condition and became fluid only after intensive ultrasonic mixing. After mixing, the slurries were aged, with continuous agitation, for 4 d prior to testing. Flow behavior was determined with a Model RFS-8400 fluids spectrometer* using a parallel plate geometry.

Flow curves for slurries with 25, 40, and 55 vol % solids are shown in Figs. 1-4. For each solids loading, there was a distinctive change in flow behavior from Newtonian or shear rate thinning (pseudoplastic) flow to dilatant flow at a characteristic whisker content. For the slurries studied here, the changes to dilatant flow occurred as follows: (1) at 25 vol % solids, between 40 and 60% whiskers; (2) at 40% solids, between 30 and 40% whiskers; and (3) at 55 vol % solids, between 15 and 20% whiskers. The occurrence of dilatancy at relatively low loadings, such as at 25 vol % solids (60% whiskers) and 40 vol % solids (40% whiskers), indicates that the "effective" solids loading is higher than the actual solids loading. For whisker-containing slurries, such an effect is not surprising; the "volume of influence" of a whisker is greater than its actual volume because of its large aspect ratio.

Figures 2 and 4 show the presence of a small, yet real, anomaly in the flow of the slurries with 40 and 55 vol % solids. In both cases, the flow curves for the slurries containing 5% whiskers fall <u>below</u> the flow curves for the slurries containing no whiskers. We believe that the packing of particles in the slurries containing 5% whiskers is somewhat more efficient than in the straight alumina slurries.

Summaries of the viscosity behavior for these Al_2O_3-SiC whisker slurries are shown in Fig. 5. Figure 5 shows the viscosity at 50 s^{-1} plotted against the whisker content in the solid phase at 25, 40, and 55 vol % total solids. As the total solids loading increases, the viscosity of the slurries also increases, and the amount of whiskers that can be incorporated into a flowable composition decreases. We observe that the slopes of the curves for viscosity vs volume fraction

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*Rheometrics, Inc., Piscataway, N.J.

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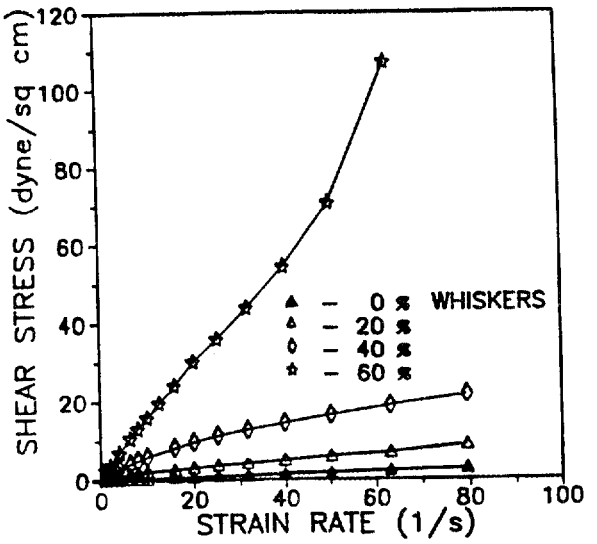

Fig. 1. Flow curves for 25 vol % A16SG-SCW1S slurries with 0, 20, 40, and 60% SCW1S whiskers.

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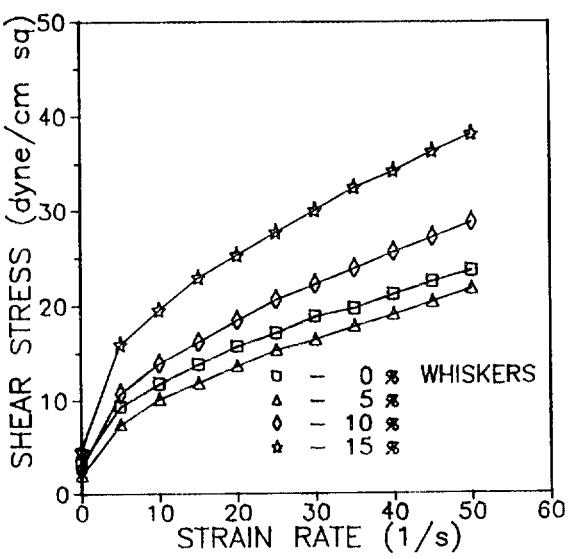

Fig. 2. Flow curves for 40 vol % A16SG-SCW1S slurries containing 0, 5, 10, and 15% SCW1S whiskers.

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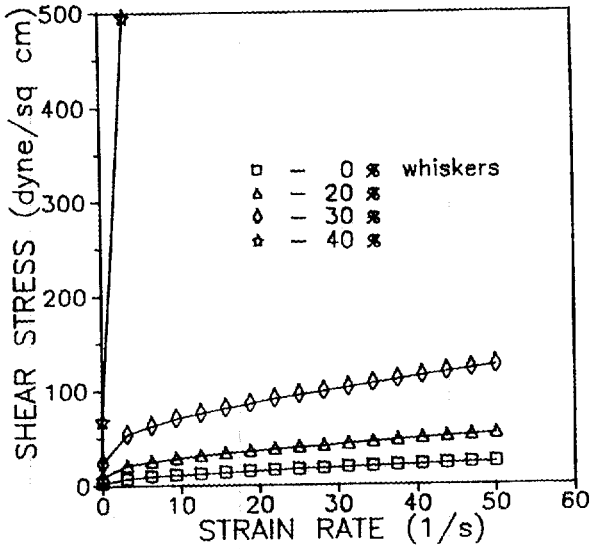

Fig. 3. Flow curves for 40 vol % A16SG-SCW1S slurries containing 0, 20, 30, and 40% SCW1S whiskers.

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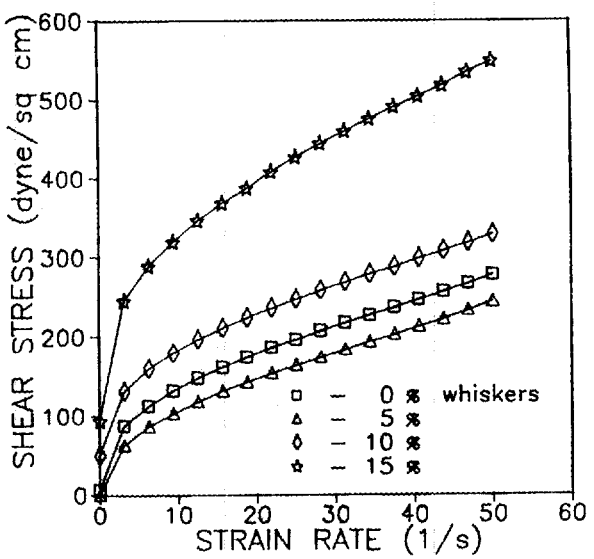

Fig. 4. Flow curves for 55 vol % A16SG-SCW1S slurries containing 0, 5, 10 and 15% SCW1S whiskers.

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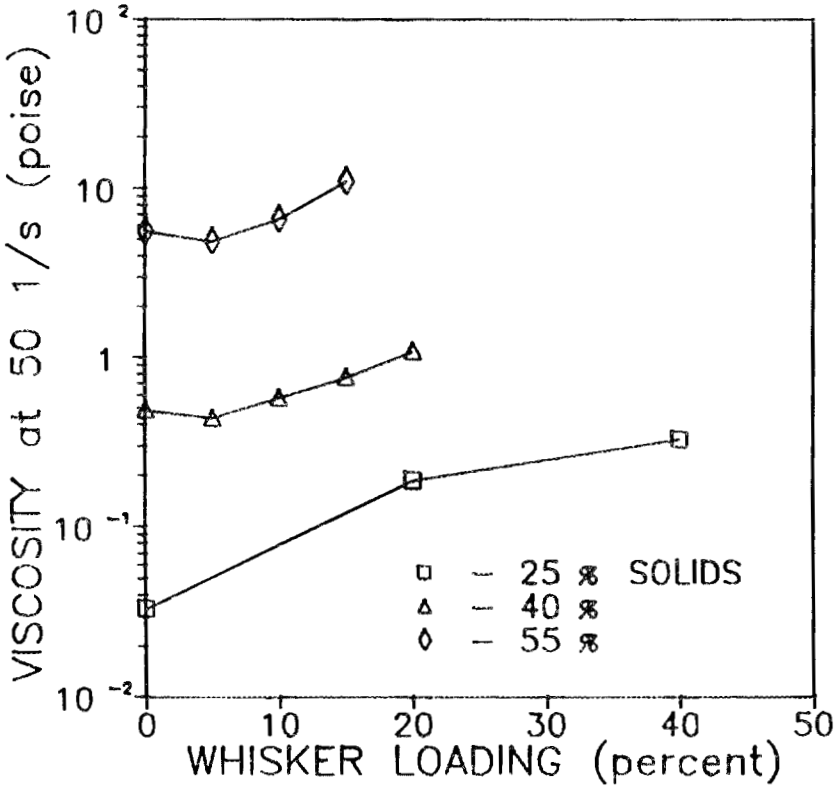

Fig. 5. Summary plot for A16SG-SCW1S slurries showing variation of viscosity (at 50 s^{-1}) with whisker content.

solids are relatively insensitive to the presence or absence of whiskers, at least up to 15% whiskers.

Flowable slurries containing a maximum of (1) 60% whiskers at 25 vol % solids, (2) 30% whiskers at 40 vol % solids, and (3) 15% whiskers at 55 vol % solids were produced in the A16SG-SCW1S-Darvan 7-citric acid-water system. Rheological characterization was used to define limits of processability for the slurries based on a transition from Newtonian or pseudoplastic flow to dilatant flow.

EXTRUSION

Extrusion was accomplished using a standard laboratory vertical piston extruder* having a 5-cm-diam (2-in.) barrel and a 20-ton capacity. After filling, vacuum was applied to the barrel to reduce the occurrence of laminations and voids. Both 0.64-cm-diam (0.225-in.) rods and 3.18-cm-diam (1.25-in.) OD by 0.33-cm-diam (0.130-in.) wall tubes could be extruded with the equipment. The tube geometry was chosen as appropriate for demonstration of a capability to produce heat exchanger tubes. The rod geometry was chosen because standard size bend bars [0.254 × 0.305 cm (0.100 × 0.120 in.)] could be machined easily.

FIRING

Extruded and dried tubes were fired in air to ~400°C to burn out the binder. High firing was accomplished in a carbon resistance tube furnace in argon. Parts were packed in a bed of Tateho SCW-1S whiskers in closed graphite boats to prevent dissociation of the whiskers in the body. The firing schedule was 10°C/min up to 1800°C with a 20-min hold at 1800°C, followed by natural furnace cooling to room temperature.

One intriguing aspect of the firing of these parts was the large differential shrinkage that we encountered. Table 6 gives a summary of the dimensions of as-extruded, dried, and fired parts. One observes

---

*Loomis Products Company, Levittown, Pa.

Table 6. Typical dimensions for extruded whisker-reinforced parts

	Dimensions			
	Rod		Tube	
	mm	(in.)	mm	(in.)
As extruded				
Outside diameter	5.72	(0.225)	31.8	(1.25)
Length	--		--	
Dried				
Outside diameter	5.61	(0.221)	31.52	(1.241)
Length	127.5	(5.02)	144.20	(5.677)
Fired				
Outside diameter	4.57	(0.180)	26.39	(1.039)
Length	118.92	(4.682)	128.59	(5.0625)
Dried:fired ratios				
Outside diameter	1.23		1.19	
Length	1.07		1.12	

that there is much greater shrinkage along the diameter of the parts than along their length. Furthermore, the differential shrinkage is much greater for the rods (1.23 shrinkage factor on the diameter vs 1.07 on the length) than for the tubes (1.19 diam vs 1.12 length).

The differential shrinkage can be directly related to the alignment of the whiskers in the body. As can be seen in Fig. 6, the whiskers in the rods are aligned very closely to the extrusion direction, but the whiskers in the tubes are aligned at ~45° to the extrusion direction. The differences in alignment are related to the differences in flow in each of the dies. In the rod die, there is a continuous reduction in area from the barrel down to the final 0.64-cm (0.25-in.) diameter that forms the rod. The whiskers are subjected to a single shear field, which forces them to align in a single orientation (i.e., along the rod axis). In the tube die, the presence of the spider and central mandrel (which form the hole in the tube) creates a more complicated flow pattern for the whiskers. First the material is split into three parts as it flows around the spider, then it is forced to rejoin to form a solid tube below the spider. Because the act of rejoining requires both circumferential and axial flow, the whiskers align at an angle to the axis rather than directly along the axis as was the case with the rod die.

Additional views of the microstructures of both rods and tubes are given in Figs. 7-10. The most obvious feature in these micrographs is the large (~50 μm) porosity. These features are not pores, however. A typical fracture surface is shown in Fig. 8. We observe from the fracture surface that what appear to be pores in the polished microstructures (Figs. 6 and 7) are actually clumps of silicon carbide whiskers (Fig. 9). These SiCw clumps were the fracture origins for most of the bars that were examined fractographically.

The presence of the SiCw clumps is a direct result of the mixing procedure that we used. All of these micrographs are for samples made using method 3, the "traditional" approach. Apparently the shear forces generated during mixing in the Σ-mixer were not high enough to break down all of the SiCw agglomerates. Milling the whiskers and powders in water prior to making the extrusion batch would normally be the solution

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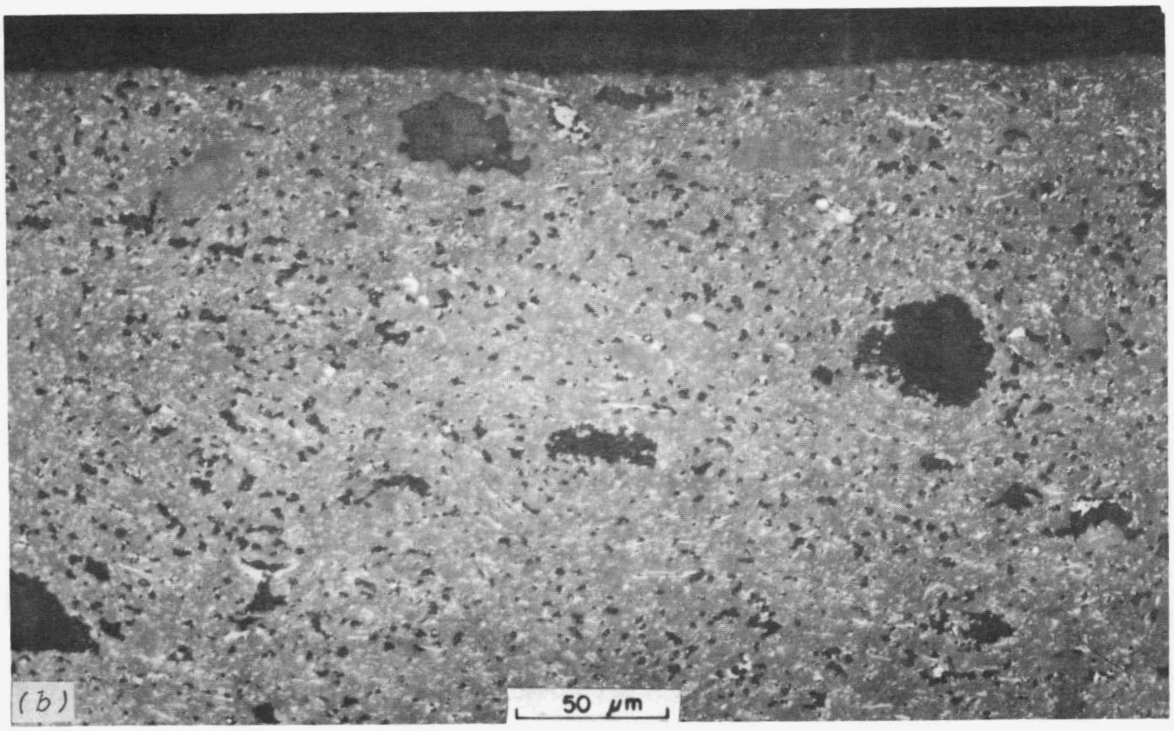

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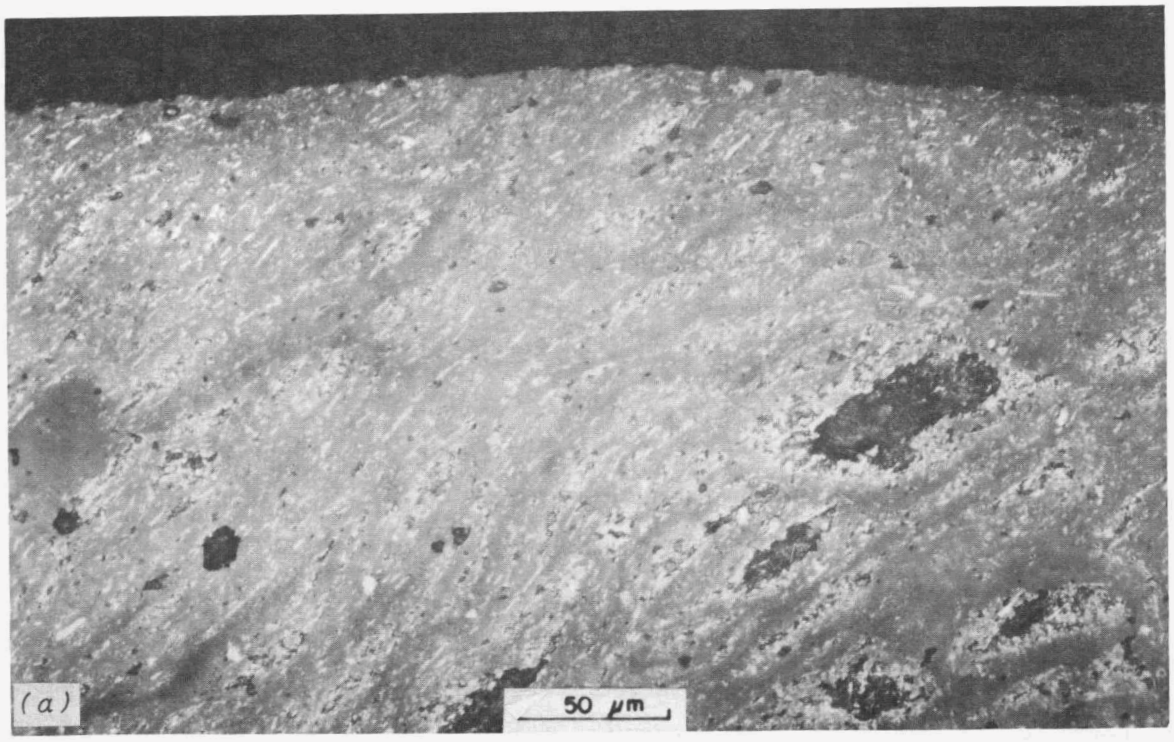

Fig. 6. Microstructures of (*a*) extruded tube and (*b*) extruded rod.

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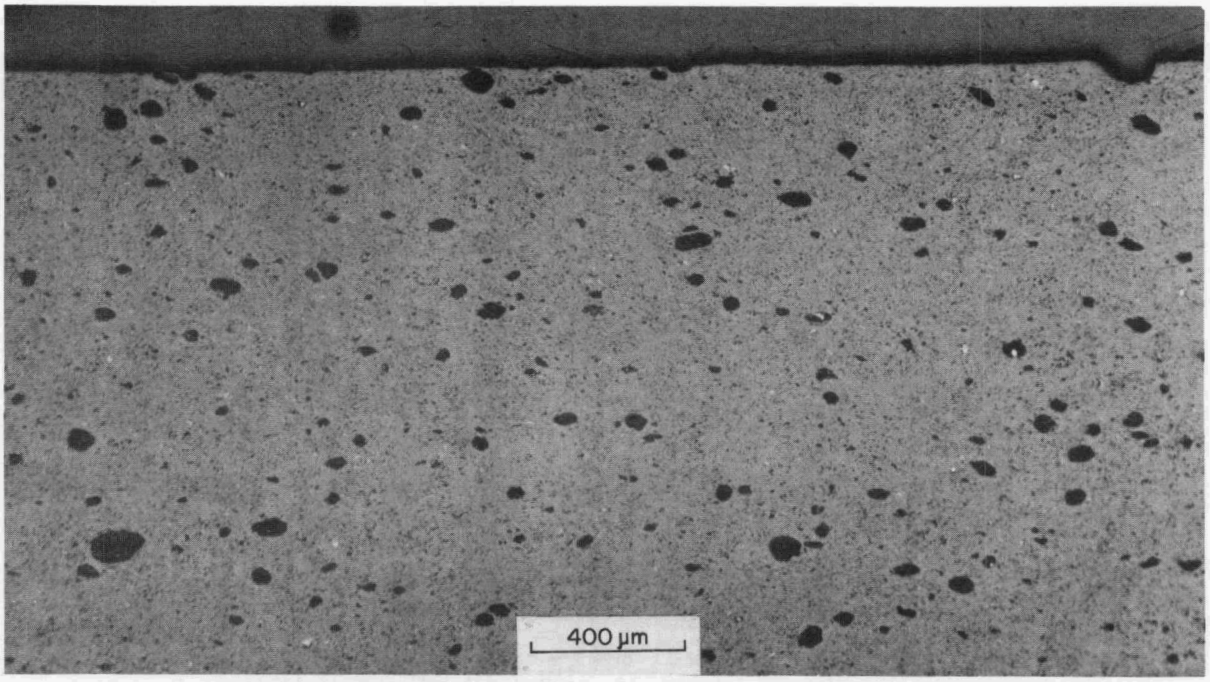

Fig. 7. Cross section of extruded rod.

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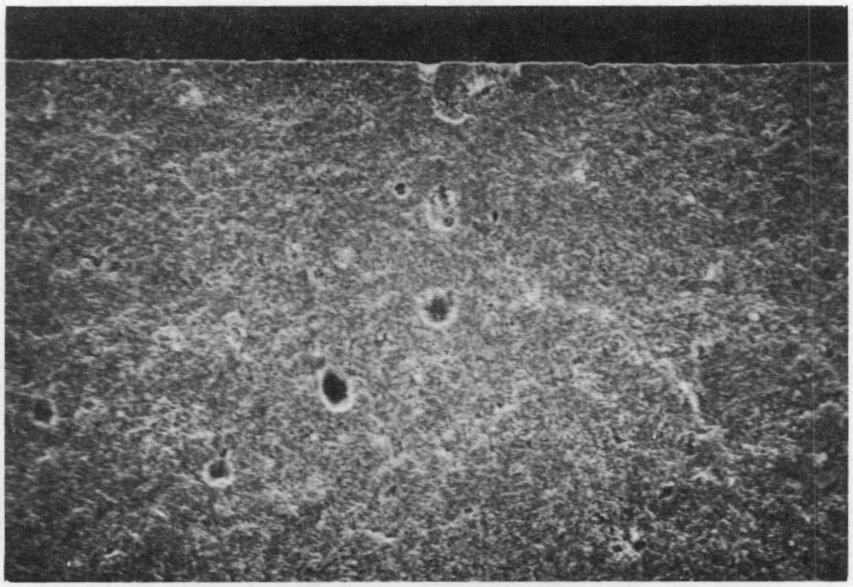

Fig. 8. Typical fracture surface for extruded rod.

L1328

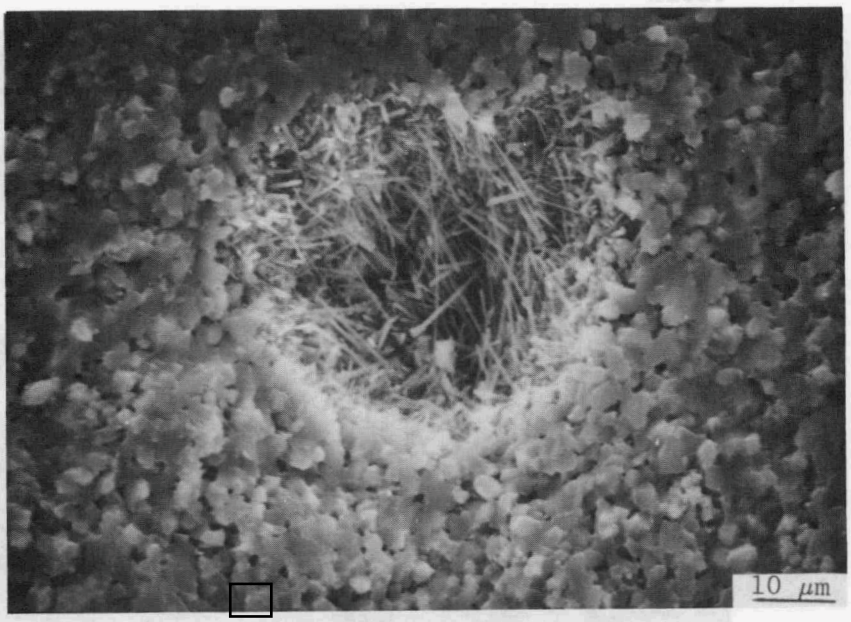

Fig. 9. Whisker clump in extruded rod.

L1329

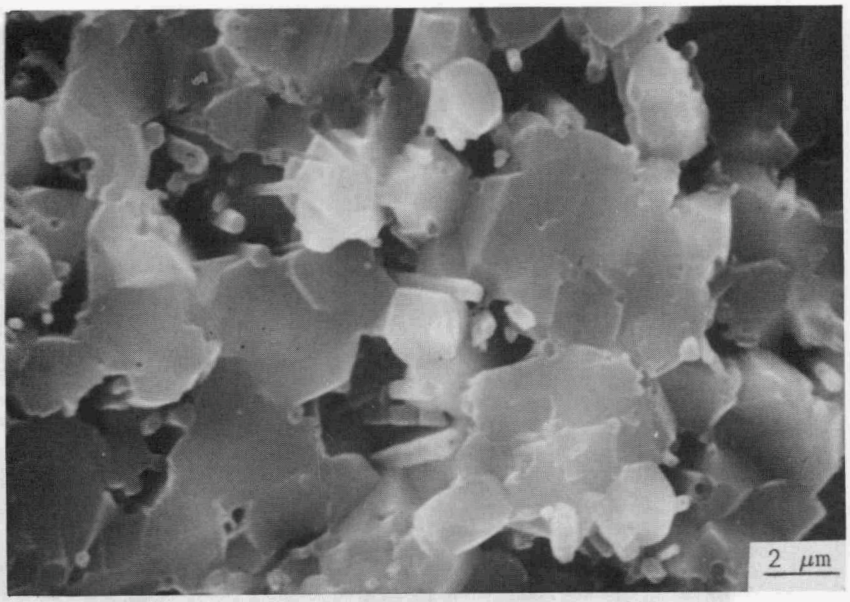

Fig. 10. Fracture surface of extruded rod showing transgranular fracture of the Al_2O_3, pullout of and crack deflection around SiCw, and SiCw alignment.

to such a problem as this. However, such a procedure produced dilatant mixes. It is suggested that milling the powders and whiskers in an organic medium such as methyl ethyl ketone prior to making the extrusion batch may permit good mixing and may eliminate the whisker balls without the complications of Y_2O_3 dissolution.

A high magnification detail view of the fracture surface is shown in Fig. 10. Fracture occurred predominantly as transgranular fracture. There is evidence of both whisker pullout and crack deflection around the whiskers. Also, one observes that the whiskers are generally aligned perpendicular to the plane of the fracture (i.e., in the extrusion direction).

MECHANICAL PROPERTY EVALUATION

Mechanical properties were determined using bars machined from extruded rods. We determined flexural strength at ambient temperature, 800°C, and 1000°C. We also evaluated the thermal shock resistance of the bars.

PROCEDURES

A four-point flexure test was used to measure fracture strength. Samples were ground parallel to the long axis with a 140/170-grit resin-bonded diamond wheel to 3.0 × 2.5 × 25 mm dimension. The tensile edges were beveled to eliminate edge flaws. The bars were tested at a crosshead speed of 0.51 mm/min. The outer and inner test spans were 1.9 cm (0.75 in.) and 0.64 cm (0.25 in.), respectively.

A qualitative measure of susceptibility to thermal shock can be obtained by measuring the reduction in flexure strength of a ceramic following single or multiple exposures to thermal shock. The method of choice is a technique suggested and evaluated by Becher.[6] Thermal shock is accomplished by dropping preheated bend-bar samples into boiling distilled water. Becher observed that this test was much more reproducible than other quench tests.

Sample holders were made from 0.5-mm (0.020-in.) platinum wire. One end of the wire was coiled into a small cage. The holder was positioned at the vertical center of the furnace. Convective flow of air through the tube was minimized by plugging the top end of the furnace tube.

Each sample was preheated for 10 min, then dropped into the water bath. Sample sets of five bars each were quenched from 700, 800, 900, and 1000°C. In addition, one set of five bars was quenched ten times from 1000°C.

FLEXURE STRENGTH

Mechanical property evaluations were performed on two separate extrusion batches. Method 3 (dry powders and whiskers mixed with 4 wt % PEO solution in a Σ-mixer) was used in both cases. Bar set #1 received a relatively short mixing time (~10 min after all the binder solution was added) and bar set #2 received a longer mixing time (~25 min). Physically, these different mixing times resulted in different degrees of homogeneity of the extrusion batches. After extrusion, rods that were used to make bar set #1 exhibited a number of "white spots" which were alumina agglomerates that did not break up during mixing. Rods that were made into bar set #2 did not exhibit these alumina agglomerates and were more homogeneous.

The mechanical properties for both bar sets are given in Tables 7 and 8. The mean flexure strengths at 25°C did not vary appreciably from set #1 to set #2 and were similar to strengths reported by Tiegs and Becher[3] for press-and-sinter 10% SiCw composites, ~380 MPa. The standard deviation of flexure strengths at 25°C was somewhat smaller for bar set #2, which probably reflects the more uniform microstructure produced by longer mixing. Neither bar set exhibited a degradation of strength at 800°C or at 1000°C, again in agreement with the results of Tiegs and Becher.

While there were no differences in fast fracture behavior between set #1 and set #2, there were differences in thermal shock resistance. Set #1 retained an average of only about 60 to 80% of its strength at

Table 7. Summary of mechanical properties for "short mixing time" - bar set #1

Test condition (°C)	Number of bars	Mean flexure strength (MPa)	Percent of 25°C strength (thermal shock only)	Confidence limits (95%) on mean (MPa)	Standard deviation (MPa) [% of mean]	Flexure strength (MPa)	
						Highest	Lowest
25	20	288	--	259/316	60 [21]	401	173
800	10	297	--	263/330	48 [16]	359	230
1000	10	282	--	253/312	41 [15]	360	226
Thermal shock from							
700	5	233	81	--	97 [42]	387	117
800	5	180	63	--	80 [44]	293	71
900	5	207	72	--	125 [60]	381	99
1000	5	211	73	--	96 [45]	350	160
1000/10 quenches	5	110	38	--	31 [28]	150	73

Table 8. Summary of mechanical properties for "long mixing time" - bar set #2

Test condition (°C)	Number of bars	Mean flexure strength (MPa)	Percent of 25°C strength (thermal shock only)	Confidence limits (95%) on mean (MPa)	Standard deviation (MPa) [% of mean]	Flexure strength (MPa)	
						Highest	Lowest
25[a]	20	281	--	260/301	40 [14]	343	181
25[b]	20	309	--	291/328	40 [13]	359	230
800	10	312	--	331/293	26 [8.3]	356	287
1000	10	274	--	298/251	33 [12]	342	232
Thermal shock from							
700	5	326	116	--	25 [7.7]	352	288
800	5	277	99	--	18 [6.5]	302	259
900	5	254	90	--	91 [36]	328	108
1000	5	318	113	--	18 [5.6]	341	301
1000/10 quenches	5	85	30	--	19 [22]	116	70

[a]First firing.

[b]Second firing.

25°C after one quench from 700 to 1000°C. Set #2, however, retained at least 90% of its 25°C strength, and in two cases the average retained strength was higher. (Note: these higher mean strengths are probably just statistical sampling variations. In actuality, the strength probably did not change.) Upon closer examination of the data, we discovered the reasons for the difference in thermal shock behavior. When we compared the bars with the highest strengths at each condition, we observed that they were similar for both set #1 and set #2. However, when we examined the bars with the lowest strengths, we found that for set #1 the lowest strength bars had strengths <160 MPa. However, for set #2, only one bar had a strength below 250 MPa. Bars from set #1 contained regions that were less resistant to thermal shock (i.e., the large alumina agglomerates that were devoid of whiskers). Bars that contained such regions exhibited a lower strength after quenching. Bars that did not contain these alumina agglomerates retained their strength. Thus, we observed a broadened strength distribution (the standard deviation increased from 60 MPa for the bars at 25°C to ~100 MPa after quenching) and a lower average strength.

The good thermal shock resistance of bar set #2 is similar to thermal shock data presented by Tiegs and Becher.[7] There was no change in strength on quenching small bars [2.5 × 3.0 mm (0.100 × 0.120 in.)] from as high as 1000°C. Tiegs and Becher also tested samples with 10 successive quenches and observed only a small (~10%) reduction in strength for 20 vol % whisker samples. In contrast, our samples lost ~70% of their strength after being quenched 10 times. The differences are probably related to the large whisker clumps in our samples, to the unidirectional alignment of whiskers in our samples, and to the lower whisker content of our samples (10% vs 20%).

SUMMARY AND CONCLUSIONS

1. We have identified a process for producing an extrudable, clay-like mix for the Al_2O_3-10 wt % SiCw system.

2. The preferred process consisted of blending dry alumina, yttria, and SiCw with a 4 wt % poly(ethylene oxide) aqueous solution in a Σ-mixer, then mixing for ~25 min after all of the binder had been added. [The batch size for our experiments was ~700 g dry powders in a 1L (1 qt) mixer at ~52.5 vol % solids.]

3. Other batch preparation methods which involved slurrying the components together in water produced dilatant, unextrudable mixes or soft mixes that slumped after extrusion.

4. Whisker alignment was observed in extruded rods and tubes. In the rods, alignment was along the extrusion axis. In the tubes, alignment was ~45° to the extrusion axis.

5. Whisker alignment produced large differences in axial and radial shrinkage during firing. For rods, shrinkage factors (green/fired dimension) were 1.07 axial and 1.23 radial. For tubes, factors were 1.12 axial and 1.19 radial.

6. Large whisker clumps (~50 μm) were observed in the as-fired tubes and rods. These clumps were present because the whiskers were added dry, without being premilled with the alumina and yttria.

7. The mean strength of bars machined from extruded rods was ~300 MPa. The bars retained this strength at both 800°C and 1000°C.

8. Good thermal shock resistance was observed in bars made from extruded rods. For our best material, $\Delta T_{crit} > 900°C$.

9. Mechanical properties were similar to those observed by Tiegs and Becher[3] for press-and-sinter parts.

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