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TITLE: FABRICATION OF SiC WHISKERS AND COMPOSITES

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FABRICATION OF SiC WHISKERS AND COMPOSITES

by

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For

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SUMMARY

The Los Alamos Structural Ceramics Program is a multi-faceted program with an overall objective of producing superior strength and fracture toughness in ceramic bodies for load bearing applications. One phase of the program is pursuing the development of silicon carbide whiskers which are used to prepare ceramic matrix composites. The purpose of this work is to investigate strengthening and toughening mechanisms in ceramic composites. In the following we describe some elements of the whisker development program in which we are endeavoring better to characterize the whisker growth process in order to scale up its production potential. We have used these whiskers in the preparation of four types of ceramic matrix representative of a range of materials. The nature and reasons for choosing these materials are described in Section II. Composites have been prepared by dry-blending followed by hot pressing which yields high density bodies. In addition we are beginning an investigation of wet processing (slip casting) to produce a silicon-silicon carbide body which will be reaction sintered in nitrogen.

Composites of glass -, hot pressed silicon nitride -, and molybdenum disilicide - silicon carbide whiskers have been tested in flexure to determine strength and fracture toughness. Results, as presented in Section IV, have been promising, with substantial toughening exhibited in all systems, and strengthening in the glass and $MoSi_2$ composites. The reaction bonded silicon nitride is not yet to the testing stage.

I. INTRODUCTION

The need for materials having elevated temperature properties surpassing those of the best modern superalloys is an important driving force for the development of structural ceramic materials. Current materials and processing conditions lead to bodies having attractive strengths but low fracture toughness. In the specific case of Si_3N_4 and SiC, impurities are typically used to aid the consolidation by hot pressing. Such impurities may in some cases affect the elevated temperature stability and are therefore undesirable.

The Los Alamos Structural Ceramics Program addresses both problems in different ways. We are investigating the preparation, properties, and consolidation of ultrafine ceramic powders such as SiC and Si_3N_4. Use of such powders has the potential for enabling the fabrication of dense bodies without densification additives. If these powders can be prepared with uniform particle size, the combination of purity and uniform packing may lead to stronger and more reliable bodies at both low and high temperatures.

Our approach to the problem of improving fracture toughness is to investigate the use of high strength, high modulus ceramic whiskers incorporated into a matrix of ceramic such as $MoSi_2$, Si_3N_4, or borosilicate glass. The ceramic whiskers are β-SiC, grown by the Vapor-Liquid-Solid (VLS) process.[1-3] These whiskers can be grown with diameters of a few microns and lengths of several centimeters. In this form, the whiskers can be characterized, and have been shown to exhibit high average strength, and high modulus. VLS whiskers offer the advantages of diametral size which can be blended with commercially available powders, and high, known strength properties which can be used in modeling of composite behavior.

The end goal of all of this work is to combine the technologies of ultrafine powder production and consolidation, with that of the use of whiskers to increase fracture toughness. At present, the work on handling of ultrafine powder focuses on its dispersion and consolidation to form high quality green bodies. This report describes our current work on the scaleup of the VLS whisker process, and on our work to use these SiC whiskers to toughen the four types of ceramic matrices described above.

II. MATERIALS SELECTION

Four materials were selected to serve as matrices for evaluation of the Los Alamos SiC whiskers as a reinforcement and/or toughening additive. These materials were a borosilicate glass (Corning code 7740*), reaction bonded silicon nitride (Si_3N_4), hot pressed Si_3N_4, and molybdenum disilicide ($MoSi_2$). The reasons behind the selection of these materials can be explained by examining Table I. First, these materials represent a range of elastic moduli varying from 63 to 407 GPa (9-59 Mpsi), compared to 581 GPa (84.3 Mpsi) for the SiC whiskers. This provides the opportunity to investigate strengthening based upon the concept of modulus, or load, transfer. Second, the glass and Si_3N_4 display a coefficient of thermal expansion (CTE) which is lower than the SiC, while the $MoSi_2$ exhibits a higher CTE. Thus, the influence of CTE mismatch in both directions can be evaluated. Third, the four matrices represent four different chemical systems, i.e., an oxide, a metal,** a nitride, and a silicide, which are processed over the temperature range of 800 to 1750°C. This allows study of the thermodynamic compatibility between the whiskers and matrices.

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*Product of Corning Glass Works, Corning, NY 14830.

**Reaction bonded Si_3N_4 is produced by reacting silicon metal with nitrogen.

All of the above reasons stem from scientific logic. There also exists practical engineering interest behind selection of the four matrices. The glass provides the avenue for identifying some of the salient features of whisker composite fabrication, because it is basically an uncomplicated matrix, in that it is unaffected by grain size and grain boundary effects. In addition, it offers the opportunity for direct comparison to the chopped Nicalon[+] reinforced 7740 glass developed by Brennan and Prewo at the United Technologies Research Center.[4] Silicon nitride offers promise for heat engine and fossil energy applications, but hot pressed Si_3N_4 displays an undesirable reduction in strength above 1200°C, and reaction bonded Si_3N_4 is simply not very strong, unless it is subjected to a post sintering or hot isostatic pressing treatment. In addition, neither material is very tough. Composite technology, however, offers potential for improving these problems. Finally, $MoSi_2$, though satisfactory as heating element material, offers promise for use as a structural material at temperatures as high as 1700°C, if its mechanical properties could be improved. Thermodynamic calculations indicate that SiC and $MoSi_2$ should not react at the 1600-1750°C processing temperature. In fact, at such high temperatures, SiC whiskers appear to be the only fiber reinforcement material suitable for composite synthesis. In summary, then, the four matrix materials serve as discriminative stepping stones for the investigation of SiC whisker reinforced composites.

[+] A polycrystalline SiC fiber manufactured in Japan by Nippon Carbon and distributed in the U.S. by Dow Corning, Midland, MI 48640.

III. FABRICATION PROCEDURES

A. Whiskers

The VLS process is used for SiC whisker growth following the procedures described in Reference 3. Schematically, as shown in Figure 1, a metal catalyst ball is melted on a graphite substrate in a flowing gas stream. This catalyst ball extracts the reactants Si and C from the gas, and when supersaturated, nucleates a SiC crystal on the substrate. At steady state, this crystal then grows away from the substrate carrying the ball with it.

In practice the whisker growth is substantially complicated by the interaction of the catalyst and substrate, by variations in the feed-gas mixture, and by other factors such as fluid flow characteristics. Scaleup of the process depends on controlling the catalyst - substrate interaction to yield a dense growth of uniformly - sized whiskers. This control also requires engineering of the other process variables to provide appropriately uniform growth conditions.

It is evident from Figure 1 that the whisker size must be related to the size of the ball, at least under instantaneous conditions. Most of our growth runs are conducted using a catalyst material having the composition shown in Table II. This material is used as an atomized powder which is screened to give a fairly narrow particle size distribution. Cuts made using the Alpin screen classifier were analyzed using the Elzone Model 80XY Particle Size Analyzer. Results in Table III show that a reasonably narrow particle size distribution is obtained, with few particles below ∿3 μm. Direct observation of this catalyst, Fig. 2, confirms that few very fine particles are found.

Consideration of the mechanism by which the catalyst accretes reactants shows that changing the gaseous supersaturation can change the minimum diameter of ball which can become supersaturated. However Fig. 2 shows that few, if any balls are found with diameters less than or equal to 3μm to account for the very small (sub micron) whiskers which are observed in some runs. To account for these observations we are now examining the details of the catalyst substrate interaction. A preliminary result appears to show that upon melting, the catalyst described in Table II is redistributed to leave large globules and small droplets, with a size distribution unrelated to the starting distribution. If verified, these observations could indeed help account for the presence of small whiskers growing from the substrate.

Harvesting and post-harvesting processing of the VLS whiskers is a further developmental issue in the use of whiskers for composites. Whiskers are grown in lengths of from a few mm to several cm, resembling grass, on the graphite substrate. These are then removed by scraping off with a razor. Since current thought is that finite length-to-diameter (L/D) is required for efficacious ceramic composite toughening, harvested whiskers are subsequently chopped in a blender and then screened to remove fines. Our empirical observation is that this screening appears to remove much of the catalyst impurity.

It is, of course, pertinent to examine the question of how these harvesting and processing procedures may affect the strength of the whiskers. As-harvested whiskers tested with 5 mm gauge length exhibit average strength of 814 GPa (1.2 Mpsi) with considerable scatter.[6] Conceivably, strength after processing may be reduced if the chopping process introduces surface damage. We are currently investigating this possibility by carrying out tests on whiskers which have been handled in a manner simulating the processing operation.

B. Blending of Whiskers with ceramic/glass powders

In developing techniques for fabricating composites of Los Alamos SiC whiskers in different matrices, consideration was given to packing relationships based on work of Milewski.[7] This is summarized in Fig. 3 for 25% fiber loading, very close to the 20% loading that was common to the three composite systems discussed in this paper. A general conclusion to be drawn from Fig. 3 is that for fiber length to diameter (L/D) ratios of greater than 12, it becomes increasingly advantageous to mix smaller diameter spheres into larger diameter fibers (R<1).

Pertinent data for the three systems is summarized in Table IV. Using these data, Fig. 3 predicts a maximum packing of about 60% solids for the glass system, 35% for the $MoSi_2$ and 50% for the Si_3N_4. The lower hot pressed density for the $MoSi_2$ composite may well be a reflection of its poorer packing efficiency. In retrospect, it might have been advantageous to use somewhat shorter fibers, as there was only one size of $MoSi_2$ powder available.

A dry blending technique was used for these initial compositing trials as it was by far the easiest method and gave satisfactory results for all three systems. For the glass and $MoSi_2$ composites, the whiskers were roll-blended with the matrix powder for one hour, then final-blended in a Waring blender at high speed (23,000 rpm) for 30 seconds. This product was used as the feed to the hot pressing die. The Si_3N_4 composites were prepared somewhat differently, as 5 weight percent MgO was used as sintering aid. The Si_3N_4 and MgO powders were initially wet milled in t- butanol for 4 hours, dried and screened to -20 mesh. This material and the whiskers were fed directly into a smaller Waring-type blender (20,000 rpm) and final-blended in two 15 second increments with breaking up of caking in between. Using either procedure, the whiskers were mixed evenly throughout the matrix with no clumping apparent in the feed or final product. The fibers did, however, show some tendency to align in a direction perpendicular to that of hot pressing.

C. Hot Pressing

Hot pressing of the composite blends was done in graphite dies with Grafoil disks and DAG graphite spray lubricating the die surface to assist in compact release. The 7740 Pyrex glass and the $MoSi_2$ composite pressing were done in air with the die insulated by a packing of carbon black powder. The Si_3N_4 composites were pressed under nitrogen to suppress volatilization. In all cases, the powder charge was precompacted to 1000 psi. For the glass and $MoSi_2$ composite pressings, the pressure was not increased until an intermediate temperature to allow escape of volatiles, whereas for the Si_3N_4 composites the pressure was increased steadily from room temperature. Hot pressing conditions and results are summarized in Table V. Matrix control samples were pressed under similar conditions to densities comparable to those of the corresponding composites.

Whereas the glass and the $MoSi_2$ composites were pressed only until punch movement had stopped, the Si_3N_4 composites were pressed at finite time and temperature to establish either α- or β-Si_3N_4 as the predominate matrix phase, β being favored at the higher temperature and reportedly giving enhanced mechanical properties.[8] A typical hot pressing compaction plot for the nitride composite work is shown in Fig. 4. It is apparent that the higher (1750°C) pressing temperature is not needed for densification but only to promote phase transformation.

D. Wet Techniques

Although the dry blending technique described previously provided satisfactory results, uniform dispersion of any multicomponent system is generally best accomplished in a liquid medium. To that end, development of the SiC whisker reinforced reaction bonded Si_3N_4 composite is being pursued via slip casting. The immediate research plan is as follows:

1. Verify the compatibility of the SiC whiskers with the silicon matrix during the nitriding (reaction bonding) cycle, in which the silicon is converted to Si_3N_4.
2. Optimize a silicon slip for casting compacts with green densities of >>60% of theoretical, preferably 70-75%.
3. Modify the silicon slip by the addition of Nextel AS-2 Microfibers,* which simulate the size and density of Los Alamos type

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*Product of the 3M Co., St. Paul, MN 55144.

5A/6A SiC whiskers; the green density target is again 70-75% of theoretical.

4. Using the information gained from step 3, optimize a silicon slip containing various loadings of Los Alamos SiC whiskers.

Based upon preliminary investigations by the Garrett Turbine Engine and AirResearch Casting Companies, in which Los Alamos SiC whiskers were added to a silicon slip and then the silicon was nitrided, it appears that there was little or no reaction between the whiskers and matrix.[9] Thus, step 1 has been partially completed. Research to yield a silicon slip with cast densities of >>60% has commenced. The keys to success appear to be, 1) adjustment of the pH of the slip to ≥ 9, 2) optimization of the silicon particle size distribution to achieve maximum packing, and 3) elimination of agglomerates by ultrasonication.[10]

IV. COMPOSITE PROPERTIES

Samples of each of the composite systems were sawn from hot-pressed disks for mechanical testing. Fracture toughness was determined using a chevron notch sample,[11] 2.54 cm long, and strength was measured in 4 - point flexure with 1.9 cm between outer supports. Table VI compares these properties for the three systems at 20 vol% loading of SiC whiskers. It can be seen that fracture toughness was enhanced in all three systems, and strength, in the glass and $MoSi_2$ composites. Preliminary examination of fracture surfaces in the glass and Si_3N_4 systems has shown evidence of fiber pullout, a mechanism which is thought to contribute to the work of fracture. The reduced strength in the Si_3N_4 sample reinforced with SiC probably results from flaws introduced during processing. It should be noted that no attempt has as yet been made to optimize the processing. Work continues to characterize the structure and fracture surfaces of these composite materials.

V. ACKNOWLEDGMENT

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Table I. Property Comparison for Matrix Materials vs. Los Alamos SiC Whiskers

	SiC Whisker (ref. 3,6)	Corning Code 7740 Glass (ref. 13)	Reaction Bonded Si_3N_4 (ref. 14)	Hot Pressed Si_3N_4 (ref. 14)	Hot Pressed $MoSi_2$(ref. 15)
Processing Temp. (°C)	≡1400	800-1200	1400	1600-1750	1600-1700
Coeff. of Thermal Expan. ($x10^{-6}$/°C)	(4.3-5.4)[a]	3.25	1.9-3.3	1.9-3.3	8.1-8.8
Modulus of Elasticity (GPa)	581	63	97-221	290-303	338-407
Tensile Strength (MPa)	8.4	-	69-207	359-343	124-193
Flexure Strength (MPa)	-	74	117-241	683-910	317-379
Fracture Toughness ($MPa\text{-}m^{1/2}$)	3.2 (ref. 12)	≤ 1	2.1-3.0	4.3	5.3[b]

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[a] Value reported for various types of polycrystalline SiC (ref. 16)

[b] Measured at Los Alamos.

Table II. Alloy 62 - Chemical analysis of atomized powder catalyst.

Element	Weight %
Mn	65
Ni	20
Co	14
B	0.25
Si	0.25
Fe	0.1
Cr	0.2
Zn	0.25

Table III. Particle Size Distribution, Microns
Screening to a given nominal size range is indicated in the first column. The other 2 columns show the measured size distribution.

Nominal Size	Mode	Peak Width
-20 + 15 (Dry)	8.6	-11 + 6.6
-25 + 20 (Dry)	11.7	-14.4 + 8.5
-30 + 25 (Dry)	19.5	-23 + 14.2

Table IV. Data related to packing of composite systems (20% fiber loading)

Matrix	Fiber	A Avg Part. Dia, Matrix (µm)	B Avg Part. Dia. (µm)	R (=A/B)	Theor. Packing (% Solids)	Hot Pressed Density (% T.D.)
7740 Pyrex Glass	Los Alamos 7A L/D: 20/1 → 19/1*	7.2	7.5	0.96	60	>99
$MoSi_2$	Los Alamos 3B/4B L/D: 55/1 → 35/1*	6.2	2	3.1	35	$\sim$95
Si_3N_4 (94% α)	Los Alamos 5A/6A L/D: 100/1 → 40/1*	0.3	5.5	0.05	50	$\sim$99

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*L/D was estimated to be reduced to this intent by the 30 second dry blending of components.

Table V: Hot Pressing Data for Composite Systems
(20 vol.% Los Alamos β SiC Whisker loadings)

System	Time to Temp. (min.)	Max. Temp. (°C)	Hold at Temp. (Min.)	Max. Press. (Psi)	Hot Pressed Density (% T.D.)
7740 Pyrex/ SiC Whiskers	30	780	End of Movement	3500	>99
MoSi$_2$/ SiC Whiskers	50	1640	End of Movement	6000	∿95
Si$_3$N$_4$/ SiC WHiskers	60 83	1600 1750	20 40	3500 3500	∿99

Table VI. Fracture toughness and strength for composites with 20 V/O loading of SiC whiskers

Sample	K_{IC} (MPam$^{\frac{1}{2}}$)	Flexure Strength (MPa)
Glass (7740)	1.24*	74
Glass - SiC	3.86	131
$MoSi_2$	5.32	150
$MoSi_2$-SiC	8.20	307
Si_3N_4	7.1	669
Si_3N_4-SiC	10	535

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*Upper limit; sample broke under weight of sub-press ram.

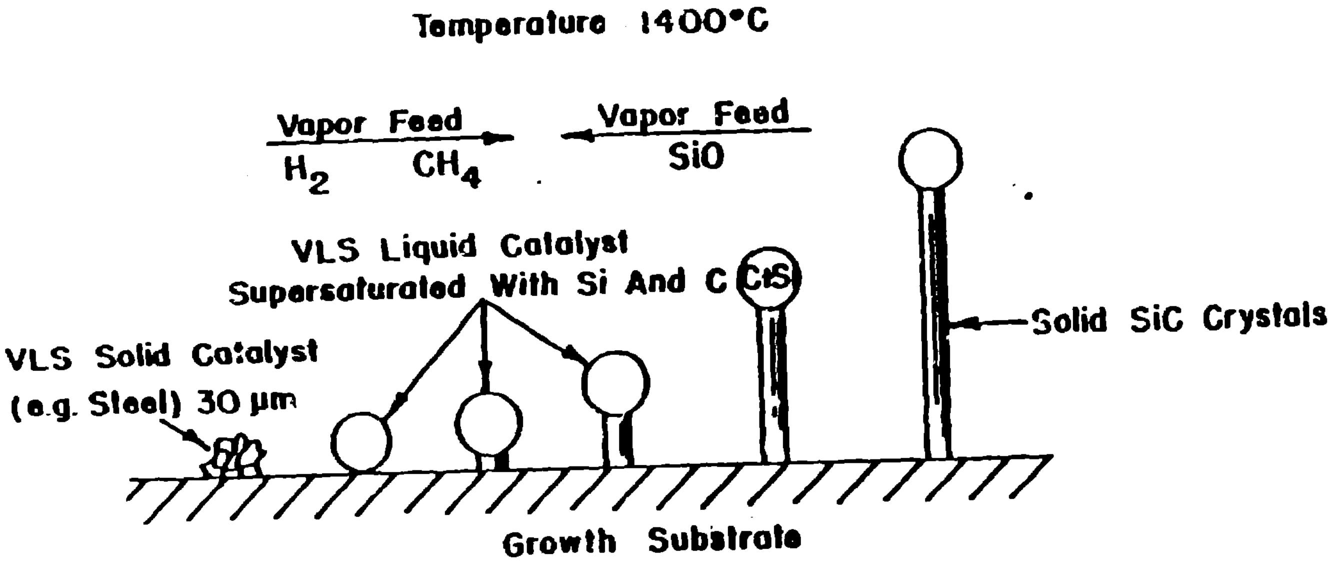

Figure 1. Schematic visualization of VLS crystal growth. (From Ref. 3).

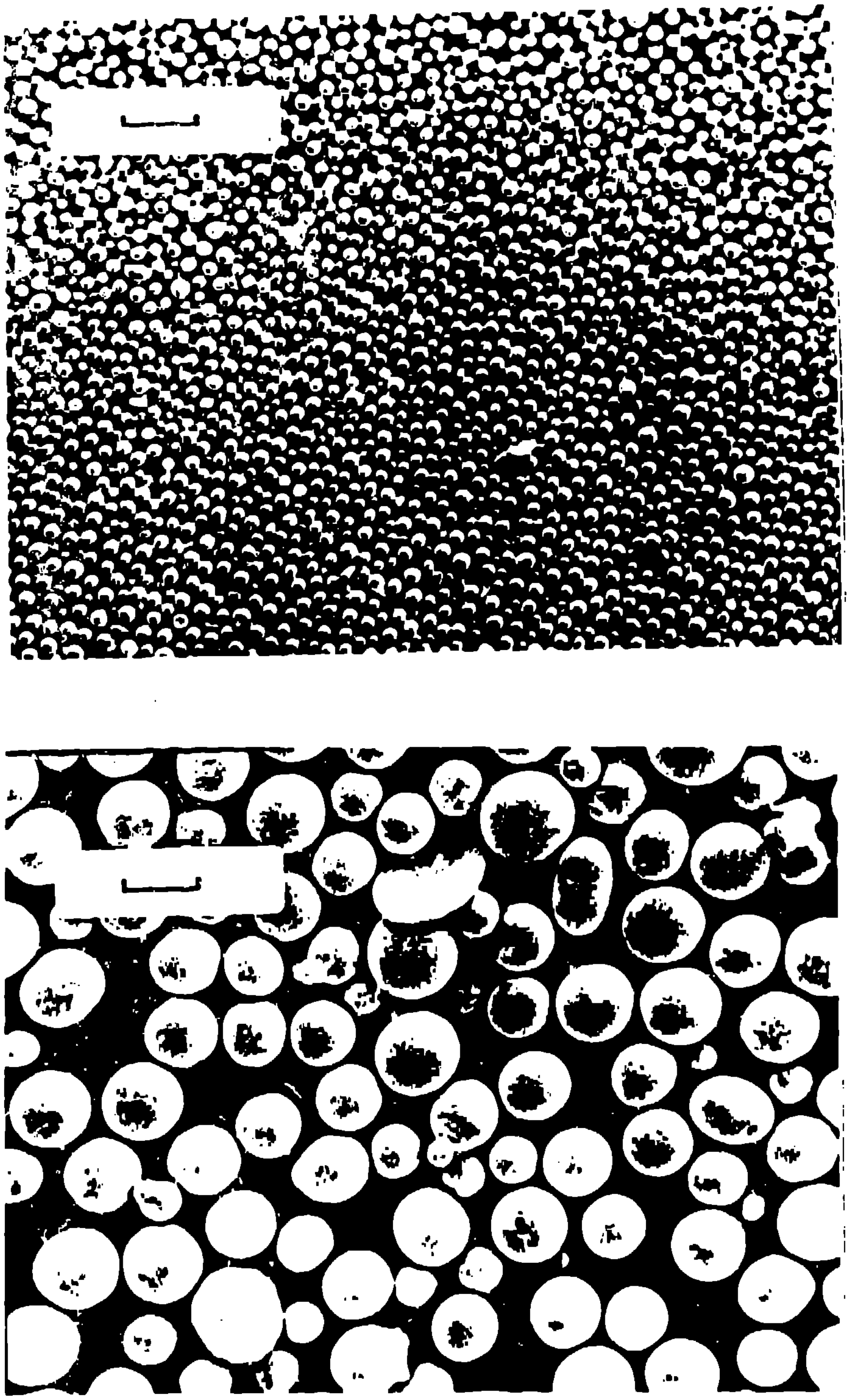

Figure 2. SEM photograph showing the distribution of particle sizes. Bar = 100 µm, upper photo; 20 µm lower photo.

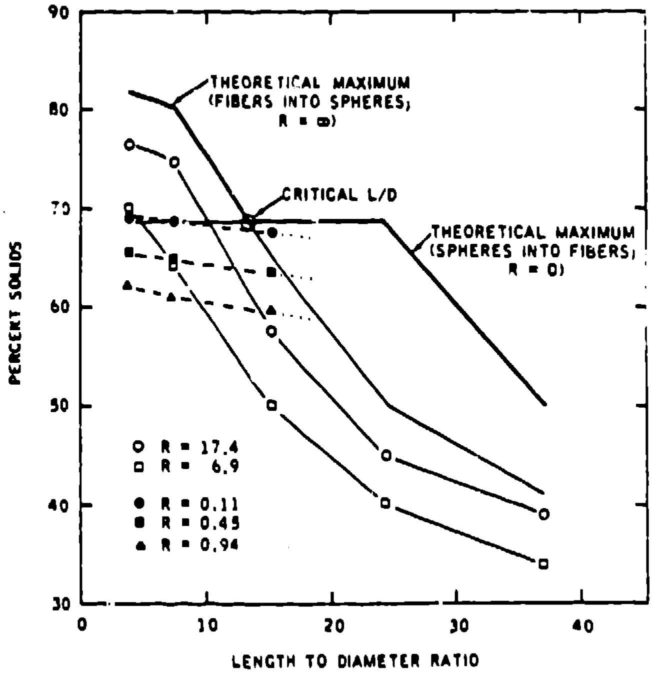

Figure 3. Theoretical maximums and experimental percent solids at 15% fiber bondings and various R values. From reference (7). (R = Ratio: sphere diameter/fiber diameter)

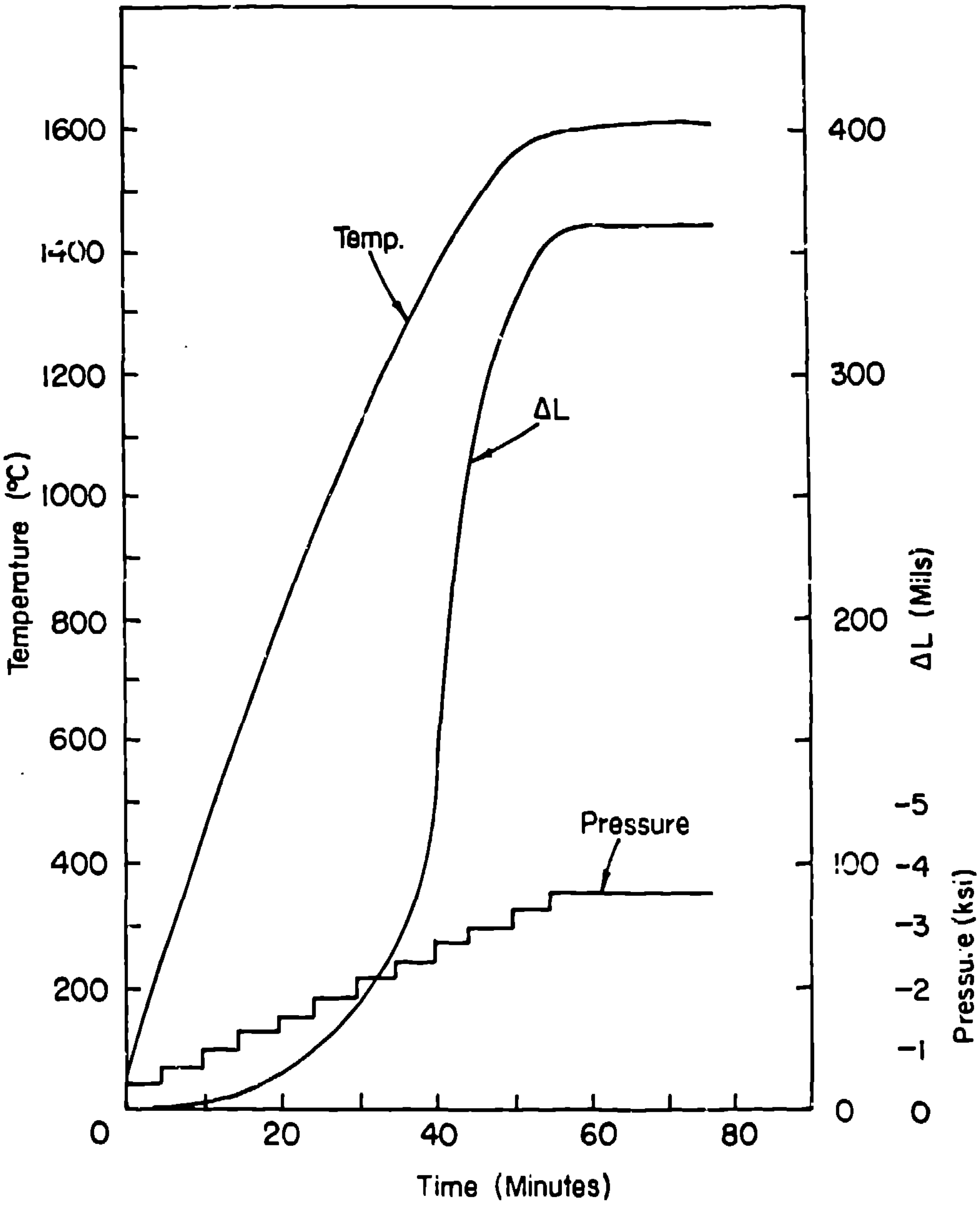

Figure 4. Typical hot pressing compaction curve for Si_3N_4 matrix/SiC whisker composites.