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TITLE

SYNTHESIS AND CHARACTERIZATION OF VLS-DERIVED SILICON CARBIDE WHISKERS

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ABSTRACT

Silicon carbide (SiC) whiskers have great potential, some already realized, in reinforcing ceramic matrix composites to give significant improvements in toughness and strength. Los Alamos has been developing the vapor-liquid-solid (VLS) process to grow single crystal β-SiC fibers having relatively few defects and diameters of from 3 to 5 μm and lengths up to 100 mm. These whiskers have superb mechanical properties- strengths up to 16 GPa (2.3 Msi) and elastic modulus of 580 GPa (84 Msi) - and should have excellent stability at high temperatures. Two basic synthesis routes were investigated: 1) in situ SiO generation and 2) external gaseous Si source. Process 1) had a much more extensive prior developmental history and has been developed at Los Alamos to the point where significant and reproducible yields of prime whiskers can be obtained and scaleup could be considered. What we have learned about this process and its product will be the subject of this paper.

SILICON CARBIDE WHISKERS PRESENTLY AVAILABLE COMMERCIALLY are those which appear to be produced directly from the reaction of the constituents in the vapor phase. They are conventionally said to be grown by a vapor-solid (VS) mechanism. An example of such SiC whiskers are those grown by the "rice hull" process (1). Most VS SiC whiskers have diameters in the range of from 0.1 to 1 μm and relatively short lengths. While such whiskers have been used successfully in commercial application (e.g., in Al_2O_3 matrices for cutting tools), it is extremely difficult to use them in oriented configurations to realize maximum strengthening and toughening such as reported for Nicalon SiC fibers in glass or glass-ceramic matrices (2-4).

Los Alamos has for several years been developing the VLS process to grow larger diameter (~5 μm) single crystal β-SiC whiskers of up to 16mm (0.6") in length for chopping and subsequent use as short fiber reinforcement in ceramic matrices. Substantial improvements in mechanical properties have been shown to result from the use of these chopped whiskers in glass, ceramic and intermetallic composites (5-8). Recent work has extended this process to the routine growth of staple whiskers of up to 64mm (2.5") in length. Such whiskers were found to possess ultrahigh strengths over long lengths (9), suggesting that they might be used in fabricating staple yarns. Work is now in progress on this application. The exceptional strength, along with good high temperature stability, stem from the high degree of chemical and crystallographic purity found in whiskers grown by the VLS process. Other attributes of VLS SiC whiskers that make them of much interest for composite reinforcement are the larger diameter, which is theoretically favorable for toughening and allows improved packing with fine powders with minimum health hazard in handling, and the growth mode, which allows for in situ coating.

It therefore appears that there would be a commercial market for VLS SiC whiskers if they could be produced economically. Although a number of investigators have done extensive research on growing SiC whiskers using

the VLS process (10-12), there has to date been no published reports of successful scale-up. The object of this work was to develop an in-depth understanding and control of the VLS process, which could lead to the production of large quantities of high quality VLS SiC whiskers.

WHISKER GROWTH

MECHANISM OF THE VLS PROCESS - An idealized sequence for the growth of a VLS SiC whisker is shown in Fig. 1. Initially, metal catalyst particles are distributed over a suitable substrate (Fig. 1a). The catalyst must be a material that forms a eutectic system in which SiC has a primary phase crystallization field, as illustrated in Fig. 2. In this case, the substrate is carbon, one of the system components. The coated substrate is placed within a reactor, and, as it is being heated to the growth temperature (about 1400°C), the catalyst particle melts, spreading out to form a lenticular cap while taking some of the carbon substrate into solution (Fig. 1b). As the temperature continues to rise, the cap absorbs carbon and silicon from the process gases, and contracts into a droplet at the center of the crater (Fig. 1c). When sufficient carbon and silicon are absorbed into the droplet, it becomes supersaturated to the point where solid SiC is nucleated at the liquid-solid interface, causing the droplet to rise from a whisker base (Fig. 1d). This reaction sequence can be followed in Fig. 2 by moving from left to right at temperature T_1 to the composition where nucleation occurs (C_N). Here, ΔT represents the degree of undercooling (or supersaturation) required for nucleation. Another way to approach nucleation is to heat at a higher temperature (T_2) until reaching the liquidus at T_L and undercool to reach C_N. In certain instances, this has proved effective in reducing the induction time for nucleation.

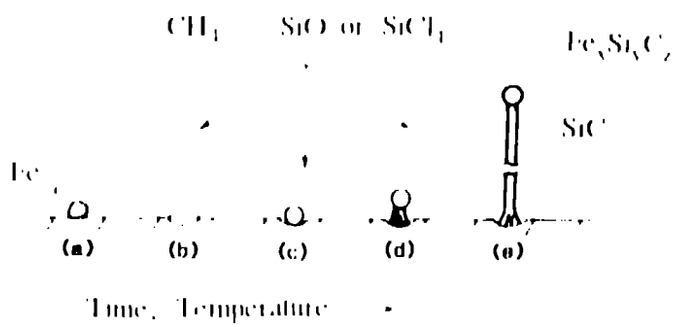

Fig. 1 - VLS whisker growth sequence (schematic).

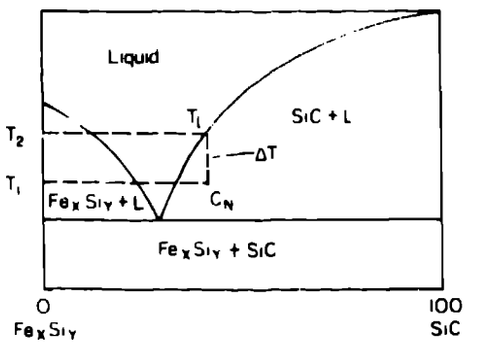

Fig. 2 - Pseudobinary phase relations for growth of VLS SiC whiskers (schematic).

The whisker will continue to grow away from the substrate (Fig. 1e), theoretically without limit as long as the droplet is fed from the vapor phase. Whiskers of up to four inches in length have been grown at Los Alamos at a diameter of about 5 μm. It is also possible to exert some control over the whisker diameter because a fixed relationship exists between it and the droplet, which is determined by the balance of interfacial surface energies illustrated in Fig. 3.

The process most extensively developed at Los Alamos used gaseous SiO and CH_4 as reactants and either iron- or manganese-based alloy particles as the catalyst. The term "catalyst" is used because the relative deposition rate of silicon and carbon from vapor through the liquid droplet onto the solid whisker (VLS) is much faster than that for depositing directly from the vapor onto the solid (VS). The SiO was generated within the reactor (in situ) at high temperature

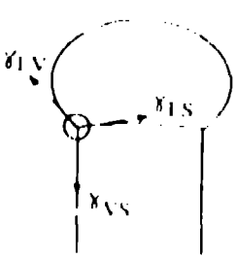

Fig. 3 - Balance of interfacial energies for the VLS whisker growth process.

because it is only stable as a gas above about 1100°C. With the help of inlet and exit process gas analysis, the reactions for our process were deduced with reasonable certainty to be-

A) For SiO generation:

$$SiO_2 + C = SiO + CO \quad (1)$$
$$\underline{CH_4 = C + 2H_2} \quad (2)$$
$$SiO_2 + CH_4 = SiO + CO + 2H_2 \quad (3)$$

Reaction (3) is much more favorable thermodynamically than reaction (1). The CH_4 participating in the reaction is believed to be that produced via reverse reaction (2) rather than that introduced in the process gas mixture (H_2, N_2, CO, CH_4.

B) For SiC formation:

$$SiO + H_2 = Si(\text{in liq}) + H_2O \quad (4)$$
$$CH_4 + H_2O = CO + 3H_2 \quad (5)$$
$$CH_4 = C(\text{in liq}) + 2H_2 \quad (6)$$
$$\underline{Si(\text{in liq}) + C(\text{in liq}) = SiC} \quad (7)$$
$$SiO + 2CH_4 = SiC + 2CO + 4H_2 \quad (8)$$

Calculations show that the reaction of SiO with CH_4 to form SiC is thermodynamically much more favorable than reaction with either carbon (solid) or CO. In this case, the participating CH_4 is believed to be that introduced in the process gas mixture.

IMPLEMENTATION OF THE VLS PROCESS - The type of reactor used in this work for growing whiskers of up to 3/4 inch long using the above reactions is shown in Fig. 4. All of the reactor parts except for the generators were machined from a fairly coarse-grained graphite.* The generators were made from a porous aluminosilicate insulating brick** infiltrated with a mixture of silicon and carbon to produce SiO according to overall reaction (3). The process gases (H_2, N_2, CO and CH_4) were brought into an open plenum running under the reactor chamber where they were directed upward through a row of small holes (jets) into the vertical growth compartments to mix with the heavier SiO being generated there. The reactor was heated up to the growth temperature inside of a sealed fused quartz muffle tube under an argon atmosphere. This particular type of process was

*HLM Grade, Great Lakes Carbon Co., New York, NY

**K30 Grade, Babcock and Wilcox Co., Pittsburgh, PA.

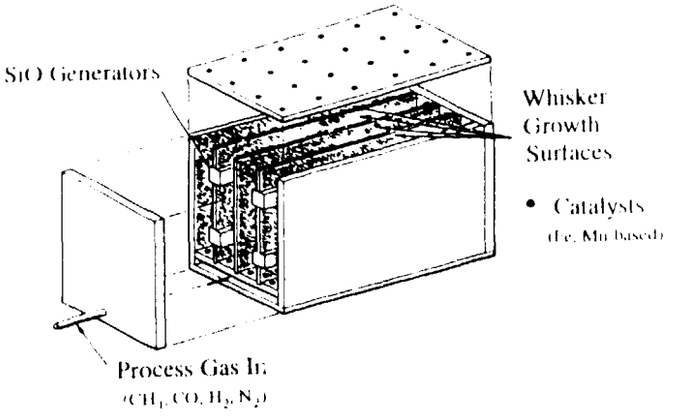

Fig. 4 - Whisker growth reactor for the in situ generator process.

extensively investigated many years ago by Shyne, et al, (13) but they were never able to understand and control the process sufficiently to obtain substantial and reproducible yields of prime VLS SiC whiskers. The object of our work was to build on this data base.

MOST CRITICAL PROCESS PARAMETERS - Although all process parameters had some effect on the product, a few stood out in their importance.

Reactant Mixing - This proved to be the single most important parameter affecting the in situ generator process. Uniform, reproducible yields of prime whiskers (5-10 μm) were not obtained until this parameter was understood and under control. Early experiments showed the mixing of the process gases entering the bottom of the reactor was strongly dependent on maximizing the inlet gas flow rate while minimizing the number and size of the inlet jets. This led to uniform yields of prime whisker growth, but only over short time periods. Long term reproducibility was found to depend on maintaining the optimum mixing conditions shown in Fig. 5, i.e., a secondary diffusion of the process gases through the open porosity of the plenum in concert with the jet action. A way was found to maintain this open porosity even though it tends to fill with SiC reaction product during a run, and it is now possible to reproduce prime whisker growth, such as shown in Fig. 6, over the long term. Currently we can obtain about 15 grams of prime whiskers in the reactor of Fig. 4 (12 inches in length) for a six hour run and proportionally more when this reactor is lengthened. To obtain

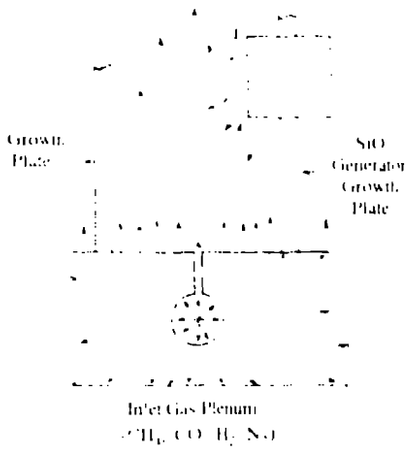

Fig. 5 - Most favorable gas mixing conditions for the in situ generator process.

the longer length whiskers, the three central growth plates are removed and replaced by three rows of staggered, vertical generator bricks.

Catalyst/Substrate Interactions - The interaction of different catalysts with the carbon (graphite) substrate was found to significantly affect the relative amount and length of prime whiskers obtained. The iron-based (stainless steel) catalyst gave only about 2/3 the weight yield of the manganese-based (brazing alloy) catalyst but the whiskers grown were much longer. We therefore use the Mn-based catalyst to grow whiskers intended for chopped fiber reinforcement and the Fe-based one to grow whiskers intended for staple yarn. A separate study on catalyst/substrate interactions showed that this difference in catalyst behavior was due to a phenomenon we called "catalyst breakup", which can be explained with reference to Fig. 1. Both the catalysts follow the general growth sequence shown in that figure. However, as the Fe-based catalyst melts and adsorbs carbon and silicon, it spreads out to form a much larger and thinner lens (Fig. 1b) than does the Mn-based one. When later the thinner lens receeds into a central catalyst droplet (Fig. 1c), some of the lens is left as a thin remanent film, which later breaks up into a multitude of small droplets to nucleate fine whiskers surrounding the larger whisker grown from the central droplet, as shown in Fig. 7. Thus, much of the Fe-based catalyst is wasted in fine whisker growth, whereas the Mn-based catalyst does not wet the substrate very well and little of it is wasted by "catalyst breakup".

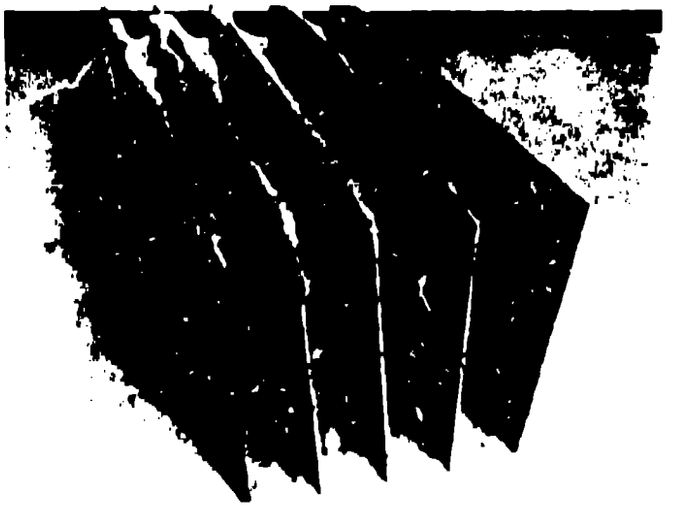

Fig. 6 - Prime VLS SiC whiskers on growth plates.

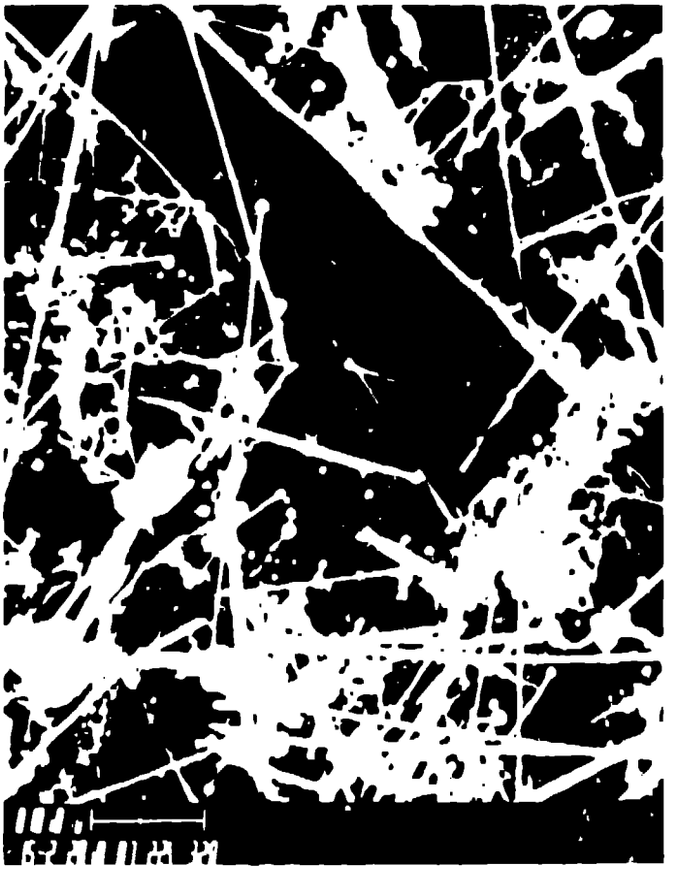

Fig. 7 - Example of catalyst breakup during growth of whiskers from an iron-based catalyst.

Nucleation and Growth Conditions - Throughout the development work, it was observed that both the C/Si ratio and the Si supersaturation of the reactant gases had a very important effect on both the morphology and amount of whisker growth. Fig. 8 summarizes these observations as an empirical phase diagram where the composition (C/Si ratio) of the reactant gases is shown on the horizontal axis, the pressure (supersaturation) of the gaseous Si on the vertical axis and the "phases" are the different types of whiskers that are nucleated and grow under the different conditions. No absolute values are given on the axes because the SiO produced by the in situ generators starts off at a high level, then decreases steadily as the run progresses. We have had no good way to quantify this until just recently when we installed and put into operation a gas chromatograph to monitor the inlet and exit process gases, as shown in Fig. 9. The exit gases are sampled inside and towards the top of the reactor.

The type of information we have obtained is illustrated in Fig. 10. In conjunction with thermodynamic calculations and some other tests, it has enabled us to arrive at the process reactions given in a previous section with a reasonable degree of certainty. The CH_4 is seen to begin reacting at a little over 1200°C and to become completely consumed at about 1300°C. Since it is unrealistic to expect all

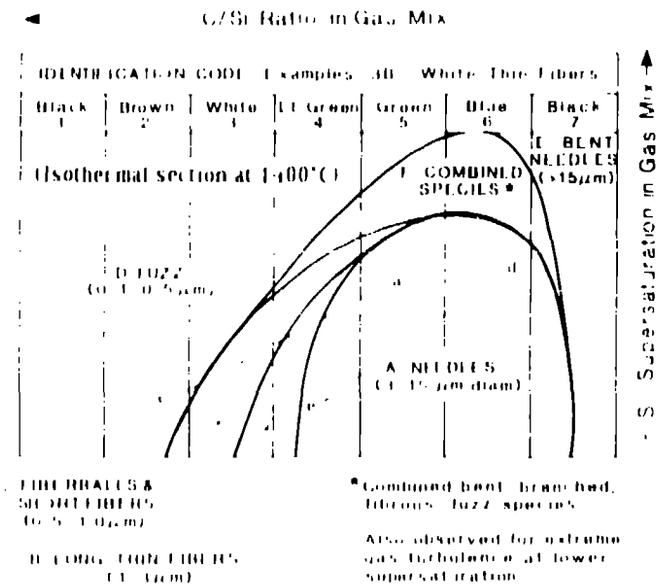

Fig. 8 - Empirical phase diagram for the growth of VLS SiC whiskers.

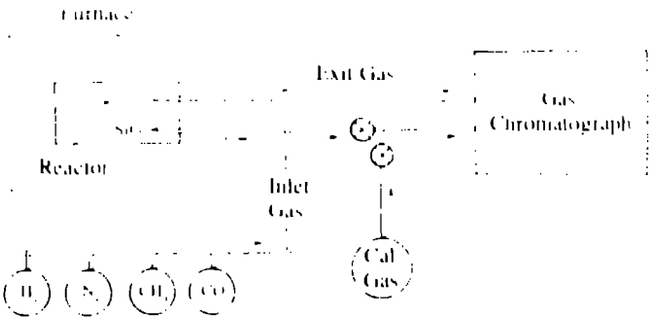

Fig. 9 - Setup for alternate inlet/exit sampling of process gases (standard analysis: H_2, CO_2, Ar/O_2, N_2, CH_4, CO).

of it to be absorbed into the finite number of liquid droplets according to equation (6), it is logical that the portion that isn't absorbed reacts to completion with the H_2O formed when the SiO goes into the liquid (equations (4) and (5)). The CH_4 can also be expected to react with any O_2 introduced in an air leak, which can be

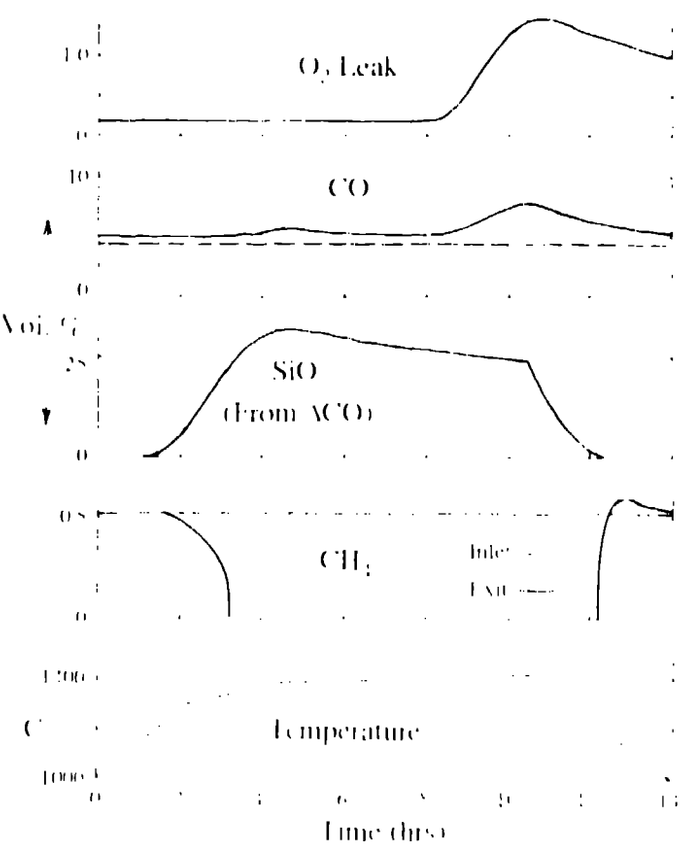

Fig. 10 - Gas chromatograph data for a whisker growth run.

identified by excess N_2 in the exit gas stream. Similarly, the amount of SiO generated can be equated to the amount of excess CO in the exit gases after that formed by reduction of SiO_2 to SiO and that caused by an air leak is subtracted.

The resulting curve for SiO concentration vs. time, shown in Fig. 10, indicates that a reasonably constant level of generation was obtained by using a heating cycle that increased slowly to the maximum growth temperature instead of an isothermal hold. Perhaps fortuitously, the ratio of SiO to CH_4 used in this run, as indicated on the figure, turns out to be in good agreement with the 1:2 ratio suggested by equation (8). As we continue to verify the reactions taking place, we will also be working toward eventual AI control of the process chemistry.

An identification code overlay is included in Fig. 8. In terms of this overlay, whiskers with designations 4A, 5A and 6A, having diameters ranging from 4 to 9 μm and colors ranging from light green to blue, are considered prime growth for composite reinforcement purposes. Within this region of A-type growth, there is usually only one whisker nucleated per catalyst droplet and the weight yield of whiskers seems to increase in direct relation to the Si supersaturation. If the C/Si ratio becomes too high, multiple nucleation and/or catalyst breakup occurs and many smaller diameter whiskers are grown from each catalyst droplet, the growth becoming progressively smaller in diameter, shorter and denser (phase areas B, C and D) as the C/Si ratio increases. Conversely, as the reactant gases become progressively more Si-rich, the whisker diameters progressively increase and, at the upper boundary of phase area A, the whiskers begin to bend in a random crystallographic direction, then become progressively more distorted. At all C/Si ratios, too high a Si-saturation level was seen to increase the tendency toward multiple nucleation and/or cause the appearance of distorted species (Phase areas E and F).

WHISKER CHARACTERIZATION

Macrophotos showing whiskers grown under carbon-rich (high C/Si), assumed stoichiometric, and silicon-rich (low C/Si) atmospheric conditions are given in Fig. 11. The white overlay growth shown at the bottom of Fig. 11a resulted from C-rich conditions that

Fig. 11 - Macrophotos of growth plates showing typical whisker species grown in (a) a carbon-rich atmosphere (high C/Si), (b) an assumed stoichiometric atmosphere (C/Si ~ 1:1), and (c) a silica-rich atmosphere (low C/Si).

prevailed at the end of a run when the SiO generation had dropped to a very low level and mixing was poor at the bottom of the reactor because of the dense growth there. In this case, the rapidly increasing C/Si ratio caused multiple nucleation within the catalyst

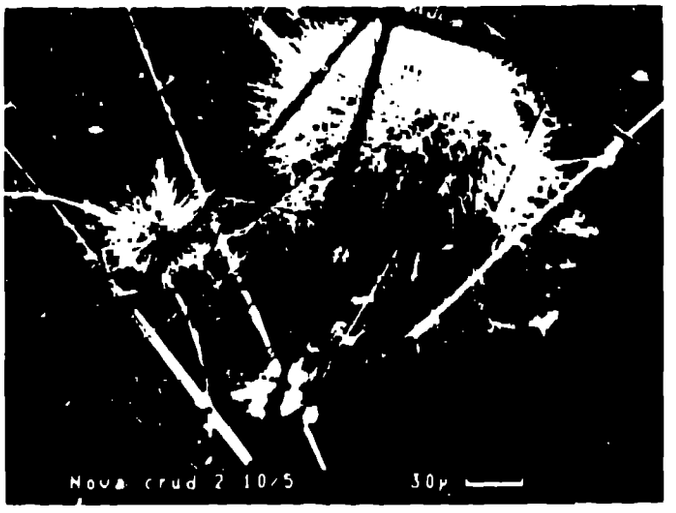

Fig. 12 - Secondary nucleation of fine whiskers in catalyst droplets caused by increase in C/Si ratio of growth atmosphere toward end of run.

as evidenced by "starbursts" of fine VLS whiskers (Fig. 12). In general, smaller diameter whiskers, i.e., those with diameters under 1-2 μm, have some tendency towards the knotted mode of growth illustrated in Fig. 13. In that photo, there are shown periodic transitions between α-SiC (defined by the transverse stacking faults) and β-SiC. The variations in diameter which accompany this are believed due to periodic changes in the composition of the catalyst droplet which affect its surface tension and thus the diameter of the whisker growing from it, according to the relationships shown in Fig. 3. Also evident in Fig. 13 is a fairly thick surface layer which has been identified by XPS as SiO_2 (14).

When the C/Si ratio during growth in the reactor is at an optimum (which is believed to be near stoichiometric), longer, larger "prime" whiskers with smooth surfaces and constant diameters are generally obtained (Figs. 11b and 14). These whiskers have diameters in the range of 4 to 12 μm and are the type that can be grown to lengths of several inches or more. They have a much higher degree of structural perfection than the smaller ones, showing only a moderate dislocation density and little evidence of stacking faults (see Fig. 15), especially as compared to VS SiC whiskers, which generally show a much higher density of such faults. There is little evidence

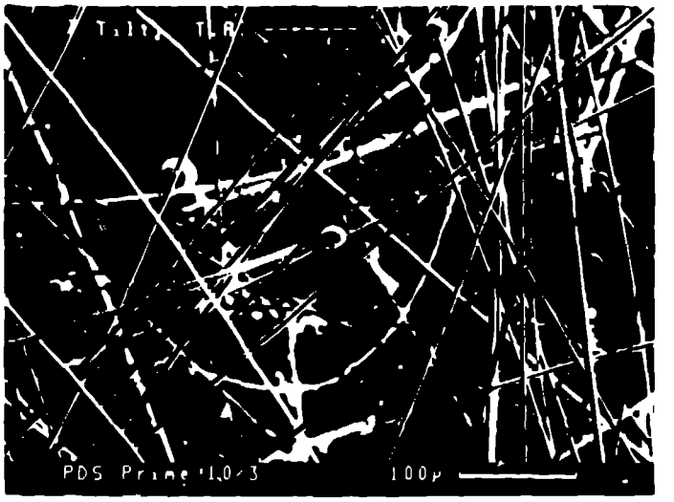

Fig. 14 - SEM of prime VLS SiC whisker growth illustrating the smooth surface and uniform cross section most typical of these larger diameter species (average here about 9 μm).

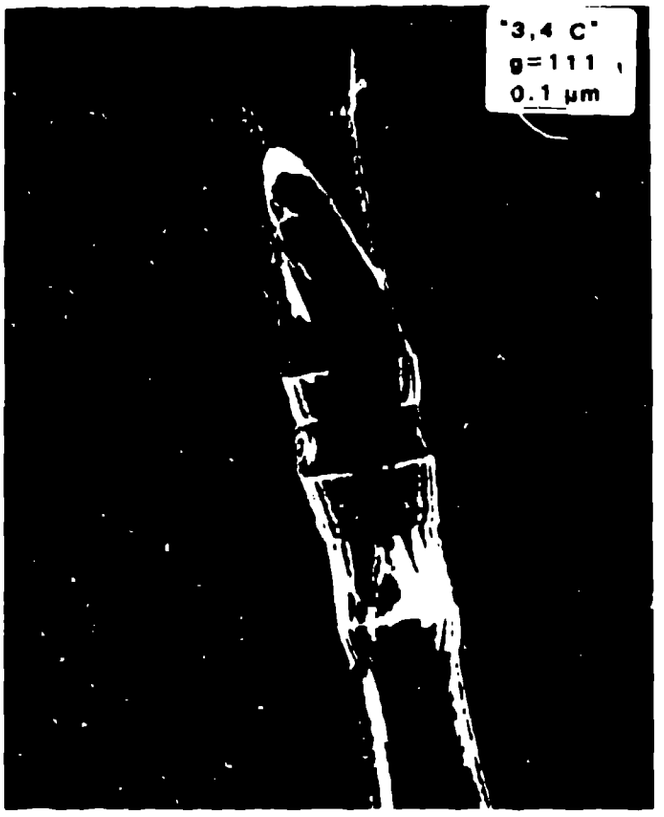

Fig. 13 - TEM of knotted growth sometimes observed for small diameter whiskers.

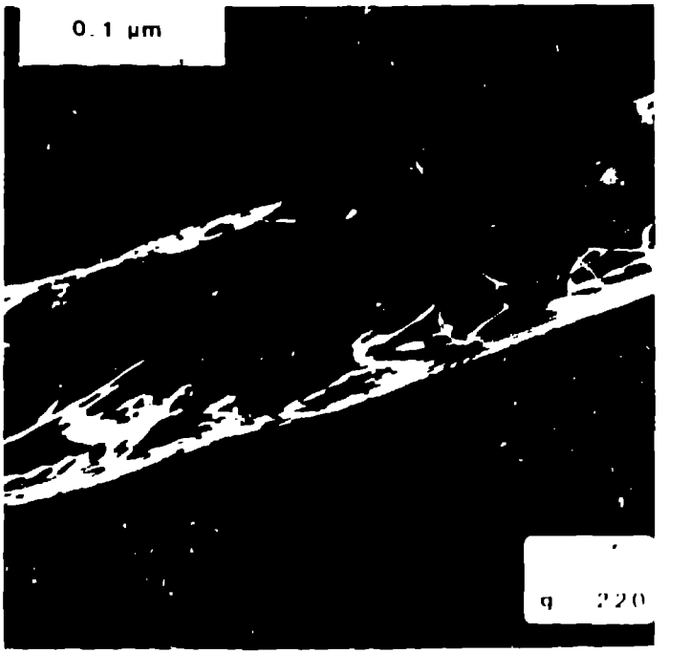

Fig. 15 - TEM illustrating the surface and dislocation density typical for prime VLS SiC whiskers.

of a surface layer here. It is this structural integrity that gives the VLS whiskers their exceptional mechanical properties.

Finally, as the growth atmosphere moves to the Si-rich side (low C/Si) of stoichiometry, the whisker morphology becomes progressively irregular. With only small deviations from stoichiometry, the whiskers retain their "prime" surface morphology but show occasional changes in growth direction to alternate <111> vectors. The extreme of this is shown in Figs. 11c and 16, which is growth obtained under a very Si-rich atmosphere. In this case, the growth has a black color and there are possibly small variations in diameter. The main manifestation of process instability, however, is the very irregular growth direction, which still gives indications of being crystallographically related.

Some detailed work has been done at Los Alamos to analyze the surface compositions of various whisker species.(14) The results of this and other efforts are summarized in Table 1. The surface layer on prime whiskers is seen to be minimal. The association of the darkening of the whisker surface at low C/Si with surface carbon suggests a potential for in situ coating at lower temperature at the end of a growth run.

Our desired product is prime whiskers such as shown in Fig. 14. These whiskers have been evaluated with a micro tensile tester developed at Los Alamos over lengths ranging up to three inches.(9) The results obtained in multiple fracture tests over lengths

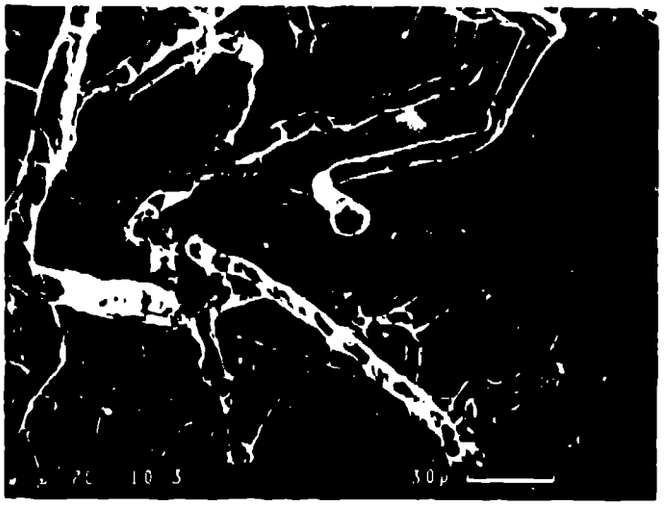

Fig. 16 - SEM of degenerate whisker growth obtained in a very Si-rich growth atmosphere.

Table 1 -

As Grown Surfaces of VLS SiC Whiskers

	White	(Prime) Green	Black
Diameter	0.1-1 mm	5-15 mm	15-90 mm
Atmosphere	High C/Si	Stoich.	Low C/Si
Surface	SiO_x Irreg. 1-3 nm XPS, HAI	SiO ~1 nm XPS, HAI	C Oxid. soon

starting at 25 mm are summarized in Fig. 17. In this sort of testing, a longer whisker is first tested and the successively shorter pieces resulting from fracture are then tested in turn. The steady increase in strength for the shorter pieces is interpreted as showing fracture at and the progressive elimination of the worst structural defects. The extremes of strength shown here, 15.9 GPa (2.3 Msi) at about

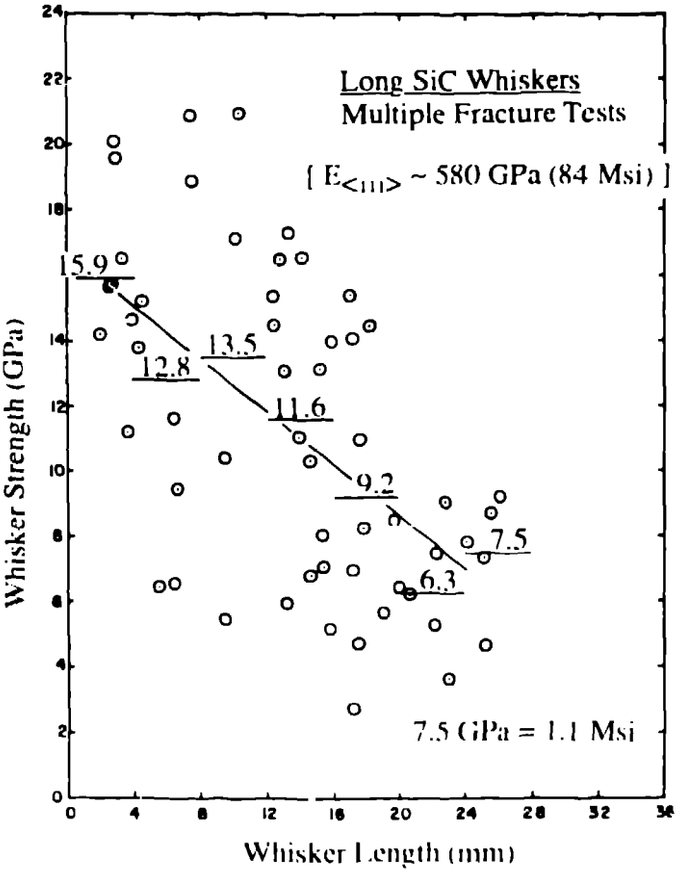

Fig. 17 - Multiple fracture data for 25 mm long VLS SiC whiskers.

3 mm length and 7 GPa (1.0 Msi) at 25 mm, are very pertinent to some projected uses for the whiskers. Exceptional strengths (>16 GPa) can be expected for the whiskers when used as short fiber (much less than 3 mm) composite reinforcement. The 25 mm length currently appears to be a good one for the staple yarn process now under development. The 7 GPa average tensile strength obtained at this length is much higher than that for any of the commercial SiC continuous fibers now available, not to mention an expected superior thermal stability. The high strength coupled with the very high elastic modulus derived in these tests seems very favorable for strengthening by load transfer.

SUMMARY

Prime silicon carbide whiskers grown by the vapor-liquid-solid (VLS) process have exceptional tensile strength and other properties which make them of much interest as reinforcement for ceramics and other materials. We have developed an in-depth understanding of the mechanisms and process variables involved in growing these whiskers by a process in which SiO reactant is generated inside of the process reactor. This knowledge has enabled us to grow moderate quantities of such whiskers in a controlled manner.

ACKNOWLEDGMENTS

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