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TITLE: WHISKER REINFORCED STRUCTURAL CERAMICS
(PROGRESS IN THE VLS GROWTH AND USE OF SILICON CARBIDE WHISKERS)

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WHISKER REINFORCED STRUCTURAL CERAMICS
(PROGRESS IN THE VLS GROWTH AND USE OF LONG SILICON CARBIDE WHISKERS)

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ABSTRACT

A VLS whisker growth process, optimized for the production of short (~10 mm lengths) SiC whiskers, was modified to produce ≥ 25 mm long whiskers. In conjunction with this modification, a plan was developed for incorporating an AI system to enhance the whisker growth process. An oriented whisker ribbon was produced from the long whiskers, as a step toward the development of a staple whisker yarn.

INTRODUCTION

It has long been recognized that there is a need for a high strength fiber that is resistant to high temperature oxidizing environments. Hence, one reason why the Dow Corning Corporation was awarded a contract in 1983 by the Defense Research Projects Agency (DARPA) to develop a silicon-carbon based fiber whose properties surpassed the Nicalon fiber developed in Japan.[a,b] The need for such a fiber was again emphasized in January 1987 by two keynote

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[a]Air Force Contract F33615-83-C-5006; DARPA funding administered by Major Steven G. Wax through Dr. Allan P. Katz of the Air Force Wright Aeronautical Laboratories (AFWAL).
[b]Product of the Nippon Carbon Co., Tokyo, Japan; distributed in the U.S. by the Dow Corning Corp., Midland, MI 48686-00995.

speakers, Persh and Stein, at the 11th Annual Conference on Composites and Advanced Ceramic Materials.[1,2] Most recently, in March 1987, AFWAL published a Program Research and Development Announcement,[3] in which the requirements for a high temperature fiber were outlined.

Los Alamos has been involved in the synthesis[4-7] and use[8-10] of silicon carbide (SiC) whiskers, produced by a vapor-liquid-solid (VLS) crystal growth process, since 1982. These whiskers display an average tensile strength in the range of 8.4-14.6 GPa (1.2-2.1 Mpsi) and an elastic modulus of 578 GPa (83.8 Mpsi).[11,12] These tensile strengths are markedly higher than the 2 GPa (0.3 Mpsi) average reported for Nicalon.[13] The whiskers are normally grown in ∿10 mm lengths but experimentation revealed that the whiskers could be grown in 25-75 mm lengths. Consequently, it was concluded that the long VLS SiC whiskers might lend themselves to the fabrication of a staple yarn which could be evaluated as a candidate high temperature "fiber."

Review of staple yarn theory showed that, depending upon the length and twist of discontinuous fibers within a staple yarn, one can observe up to ∿90% of the modulus of a continuous fiber.[14] Therefore, the potential exists to achieve staple yarn strengths that represent a considerable fraction of the strength of the discontinuous fiber, or whisker, in this case. Assuming this translated to only 25% of the tensile strength of the whiskers, this would still represent a minimum average value of 2.1 GPa (0.3 Mpsi), which would be equivalent to the Nicalon. However, it should be noted that single crystal, highly stoichiometric nature of the whiskers lends itself to enhanced elevated temperature resistance, compared to that expected for the predominantly amorphous Si-C-O Nicalon fiber.

The remainder of this paper addresses the VLS growth of long SiC whiskers and initial attempts at producing a staple yarn from such whiskers. In addition, plans for incorporation of an artificial intelligence (AI) system in the whisker growth process are discussed. An AI system offers the potential for further improving the yield, quality and reproducibility of the whisker growth process at a fraction of the human resources. Such a payoff is especially attractive from the standpoint of technology transfer. The timing for incorporation of the AI system is ideal since a new, more meaningful database is being generated in conjunction with the shift from growing short whiskers to growing long whiskers.

PROGRESS DURING FISCAL YEAR 1987

LONG SiC WHISKER GROWTH

Growth of long VLS SiC whiskers required a modification of the well understood, controllable process for growing short whiskers. A brief review of the short whisker growth process is presenced as background information. The process makes use of the reactor shown in Fig. 1. The whiskers are grown from a metallic catalyst distributed

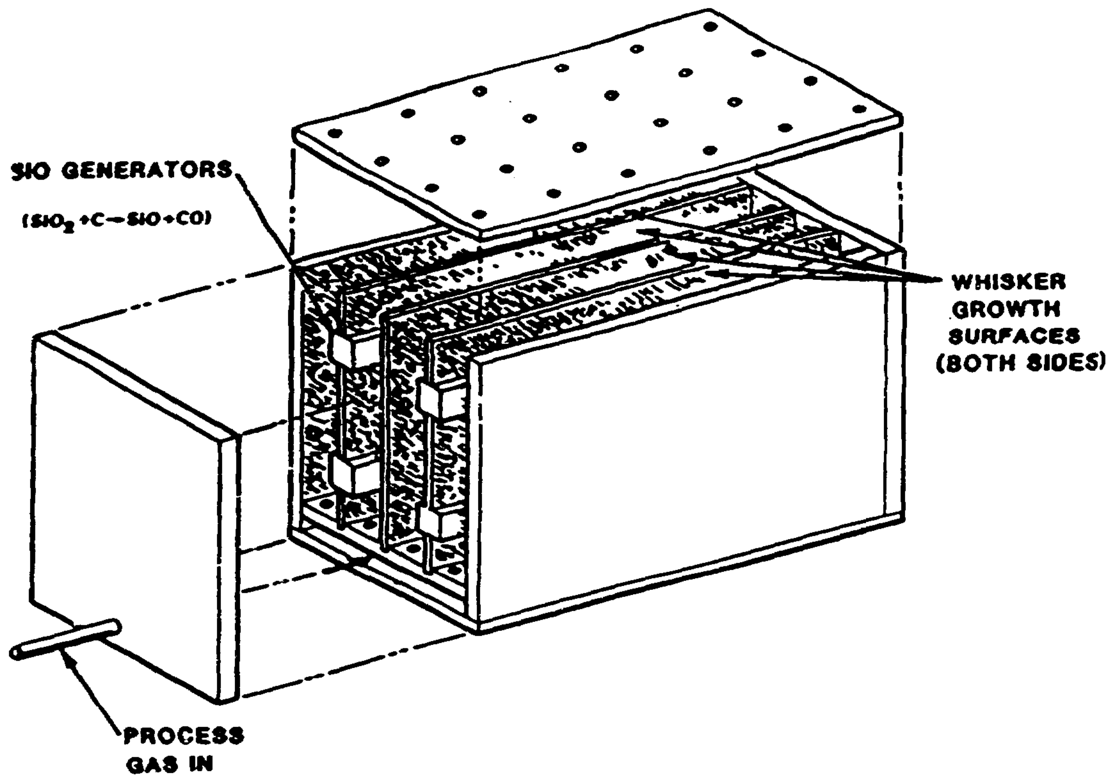

Fig. 1. Type of reactor used in growing short VLS SiC whiskers.

on vertical graphite plates. The methane (CH_4) reactant in the process gas stream mixes with the silicon monoxide (SiO) reactant being generated in situ to nucleate whisker growth. Figure 2 illustrates the uniform yield of prime whiskers (4-8 μm diameter) that could be obtained throughout the reactor when the process parameters were optimized. These whiskers were produced from the Alloy 62[c] (manganese-based) catalyst, which always gave the highest weight yield.

In order to obtain the prime whiskers, it was necessary to control the reactant gas composition so as to nucleate whiskers in the appropriate portion of phase area A of the phase diagram shown in Fig. 3. In this diagram, the reactant composition (carbon-to-silicon (C/Si) ratio) is on the horizontal axis, the reactant pressure (silicon (Si) supersaturation) is on the vertical axis, and the phase areas represent different morphologies of SiC whiskers that are nucleated and grow there.

One of the most important factors contributing to good whisker growth was the homogeniety of the reactant gas (SiO, CH_4) mixing. Flow visualization studies showed that vigorous jet action was needed to achieve optimum mixing. In actual practice, it was found that diffusion of the process gases through the plenum porosity was necessary, in concert with the jet action, for optimum mixing (Fig. 4). The plenum porosity, however, was not stable over a long period of time, as it progressively filled with SiC reaction product with an eventual deterioration in the quality and amount of whisker growth. A new plenum designed for long term stability is under evaluation, where the bulk porosity is purposely sealed and then simulated with a pattern of fine holes, as shown in Fig. 5.

Numerous modifications were made to the short whisker reactor configuration in an attempt to grow long whiskers. The modification shown in Fig. 6 has proven to be the best thus far; the center of the reactor has been opened up and the same generator weight is used but in a vertical rather than horizontal array. A stainless steel catalyst is used instead of Alloy 62 because it has proven to grow the longest whiskers. Other process conditions such as heating cycle, gas composition and flow rate remain essentially the same.

Some long whiskers grown in the modified reactor are shown in Fig. 7. At the end of the run, they were almost perpendicular to the plates with some of about 76 mm in length extending to the center of the reactor, having since settled. Yields of up to 6 grams per run have been obtained, compared to about 12 grams per run for the short whisker setup, in the same, small developmental reactor.

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[c]Product of Coast Metals Inc., Little Ferry, NJ (no longer a supplier).

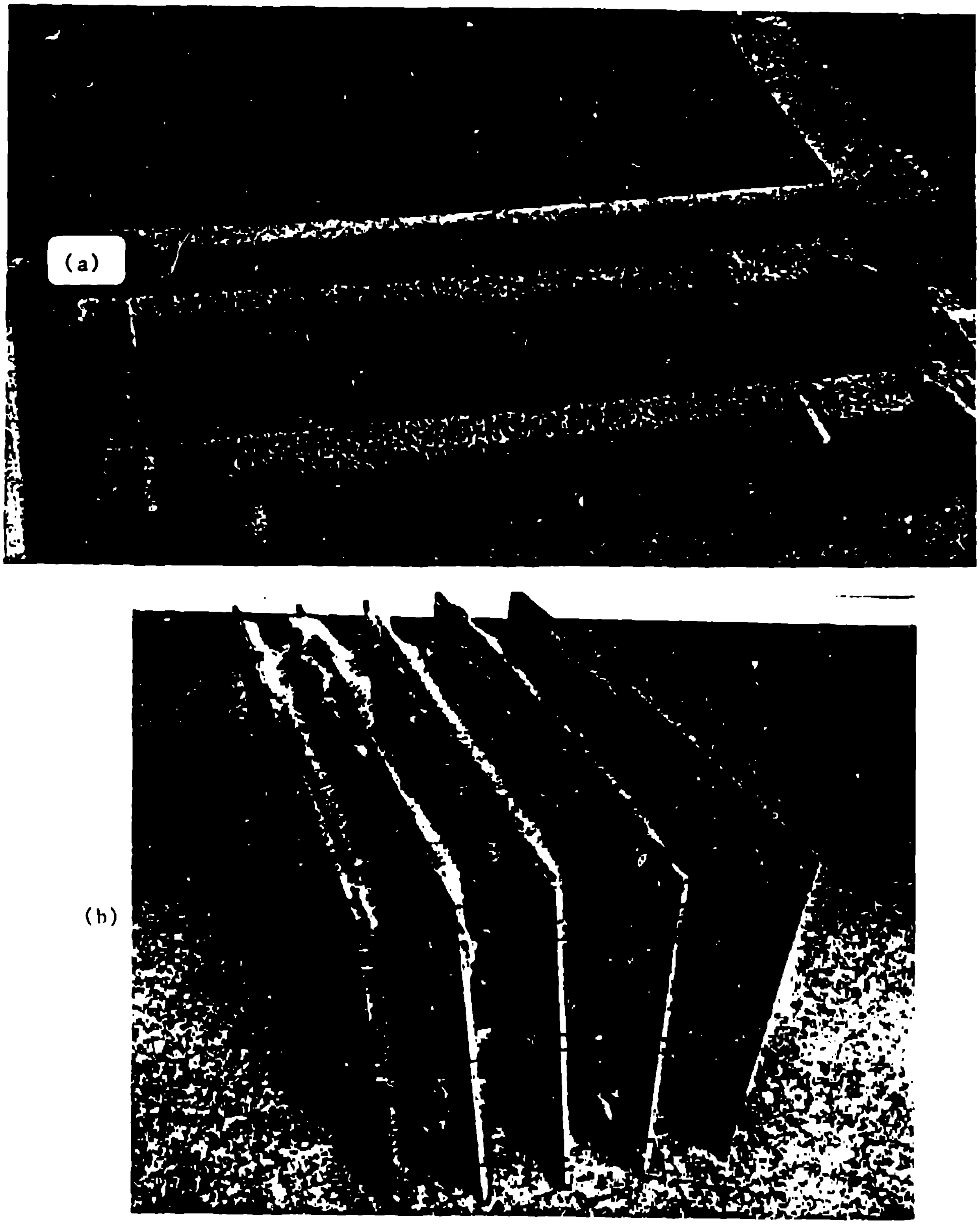


Fig. 2. Copious, uniform growth of prime VLS SiC whiskers resulting from optimized process, as seen (a) across plates and (b) across reactor.

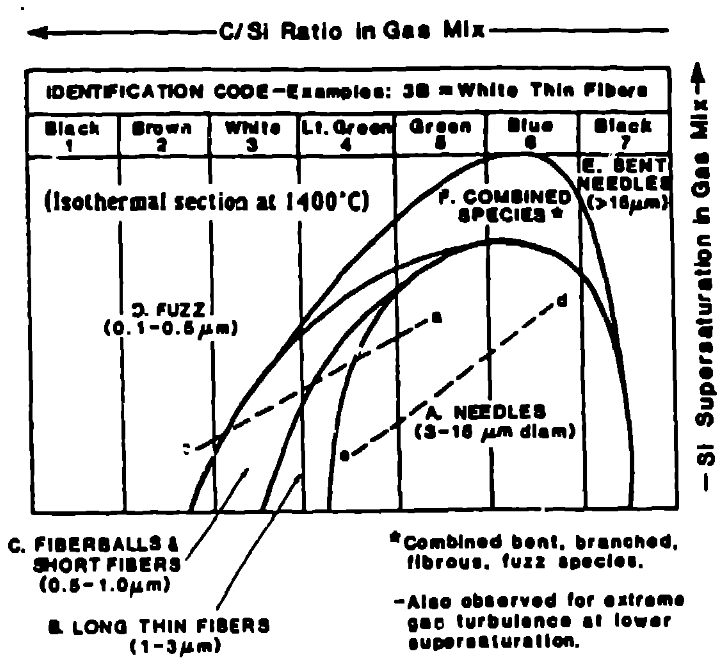
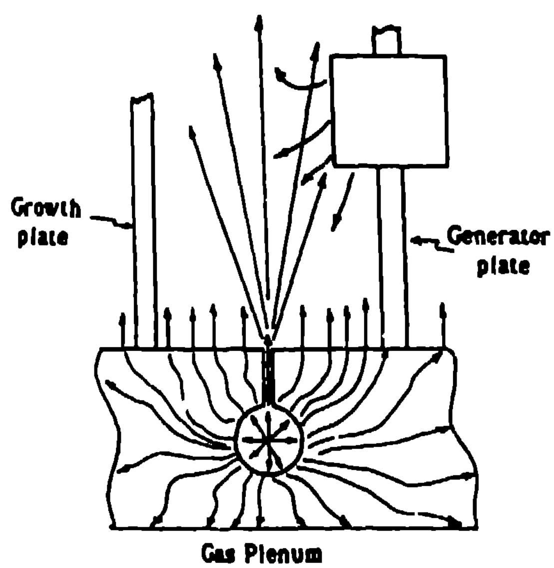


Fig. 3. Empirical phase diagram for VLS SiC whisker growth (1400°C, Alloy 62 catalyst).



Jet action coupled with diffusion thru a porous plenum has given the most favorable reactant gas mixing for whisker growth.

Fig. 4. Jet action coupled with diffusion through a porous plenum has given the most favorable reactant gas mixing for whisker growth.

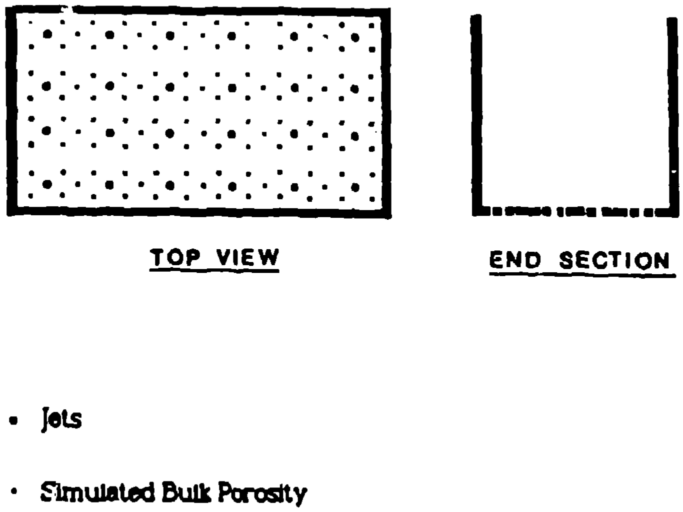


Fig. 5. Stable VLS SiC whisker growth reactor design (under evaluation) utilizing a bored plenum, jet mixing and simulated diffusion.

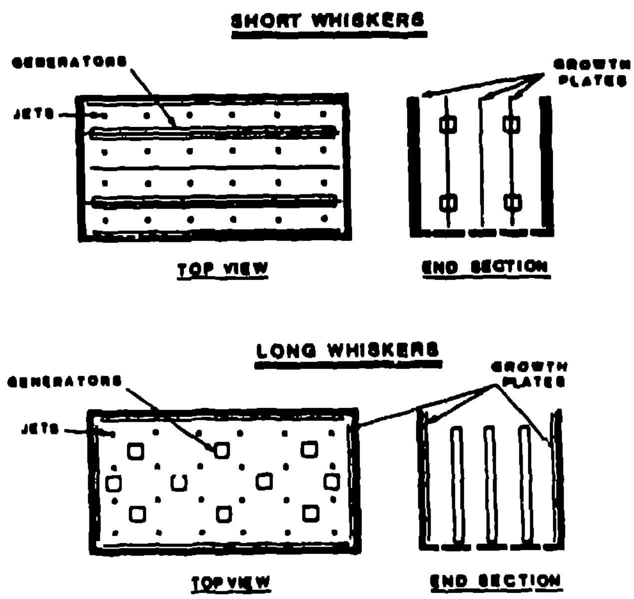


Fig. 6. Current reactor configurations (semi-stable) for VLS SiC whisker growth; both utilize a bored plenum, jet mixing and natural diffusion.

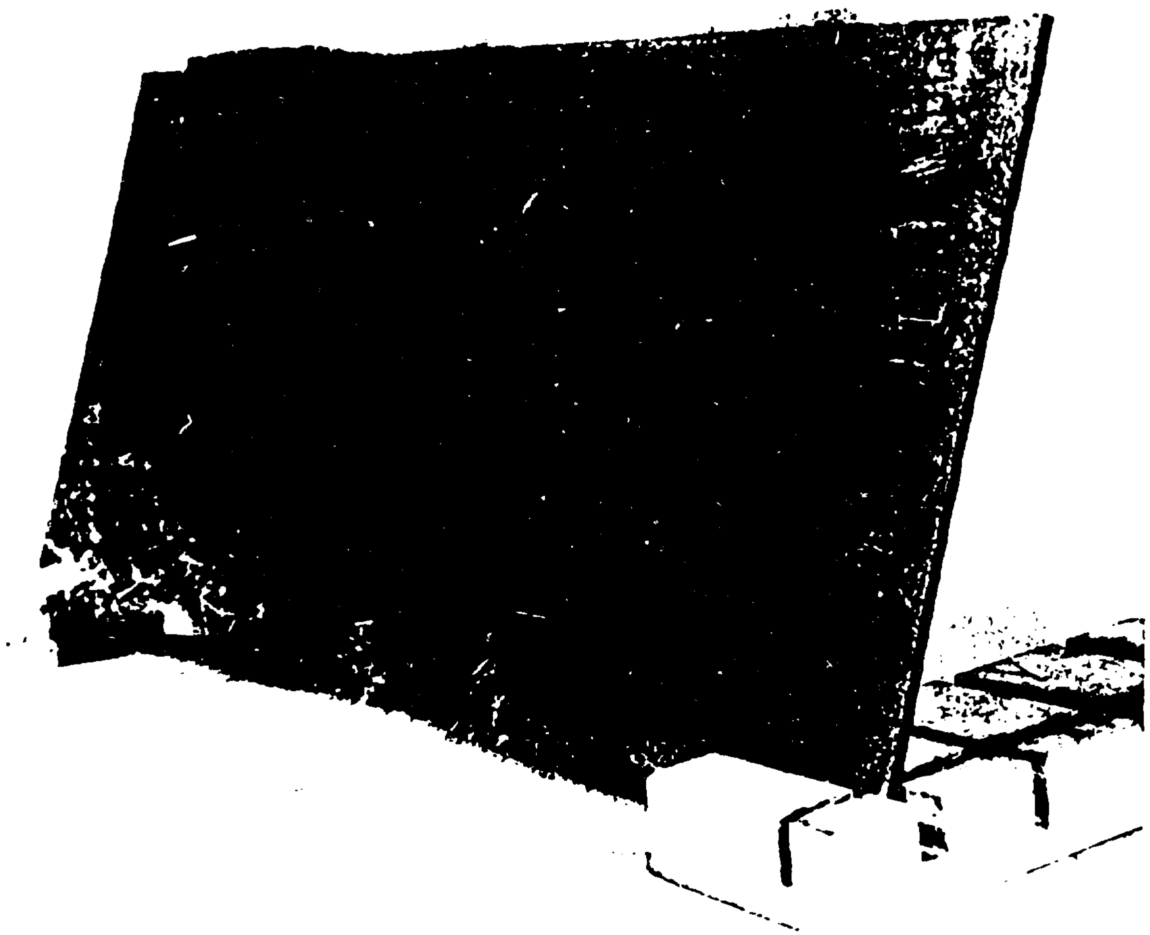


Fig. 7. Long whiskers grown in modified reactor of Fig. 6.

In order to increase the yield of long whiskers, a higher SiO concentration must be maintained in the reactor. The in situ generator process presents a problem in that the SiO generation starts at a very high level, then falls off rapidly with time, as shown in Fig. 8. The reactant composition thus follows the paths shown by dotted lines a-c and d-e in Fig. 3. Good growth, as shown in Fig. 2, is obtained when the reactant composition stays within phase area A for the entire run (path d-e). A path such as a-c, however, can result in the nucleation of secondary phases on the prime whisker growth, as shown in Fig. 9.

Two approaches are presently being investigated to increase long whisker yield and eliminate secondary growth. One involves tailoring the SiO concentration-time profile by programming the partial pressure of carbon monoxide (CO) to give constant SiO generation, and therefore a constant C/Si ratio. This will eliminate secondary growth and will allow an increase in generator weight for significantly increased yield. A numerical program is in place for determining the CO overpressure profile. The second approach entails programming the partial pressure of CH_4 to match the decline in the partial pressure of SiO. This will eliminate secondary growth but gives only a small increase in yield. This approach is the easier of the two to implement.

INCORPORATION OF ARTIFICIAL INTELLIGENCE

An AI scheme will be applied to the VLS SiC whisker growth process by developing two expert systems, or more precisely, one expert system in two stages that will do two distinct jobs. Work has commenced in laying the groundwork for a whisker growth consultant, the first expert system or the first stage of the final product. The whisker growth consultant will help the current user set up whisker growth experiments and future users set up production runs. The second expert system will be a control program for the whisker growth process that will be piggy-backed upon the knowledge base of the whisker growth consultant. This two phase plan is illustrated in Fig. 10.

Artificial intelligence programs, or in this case expert systems (which are a subset of AI programs), differ from conventional programs in several ways. The most significant difference is that expert systems use symbol manipulation to solve problems that require heuristic solutions, whereas conventional programs manipulate numbers to solve problems that can be solved algorithmically.

Some of the reasons why AI will be particularly useful for VLS whisker growth are as follows:

1. The process cannot be described adequately with a mathematical model. Therefore, one cannot develop a control algorithm for the whisker growth process. Control will have to be rule-based.

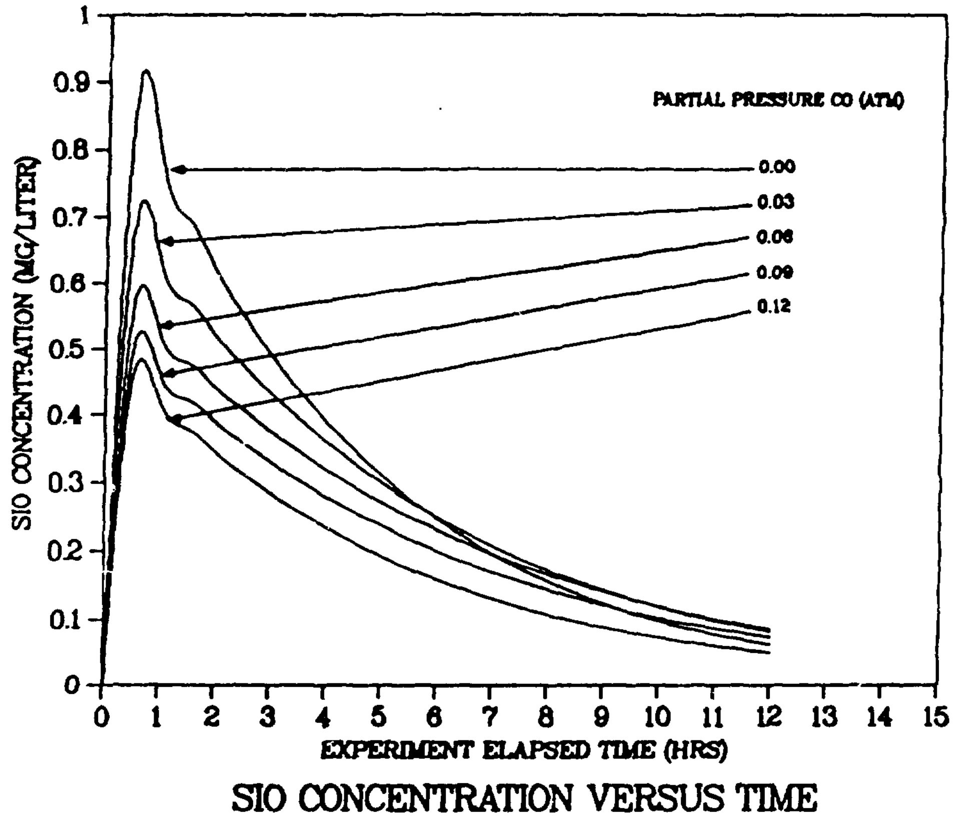
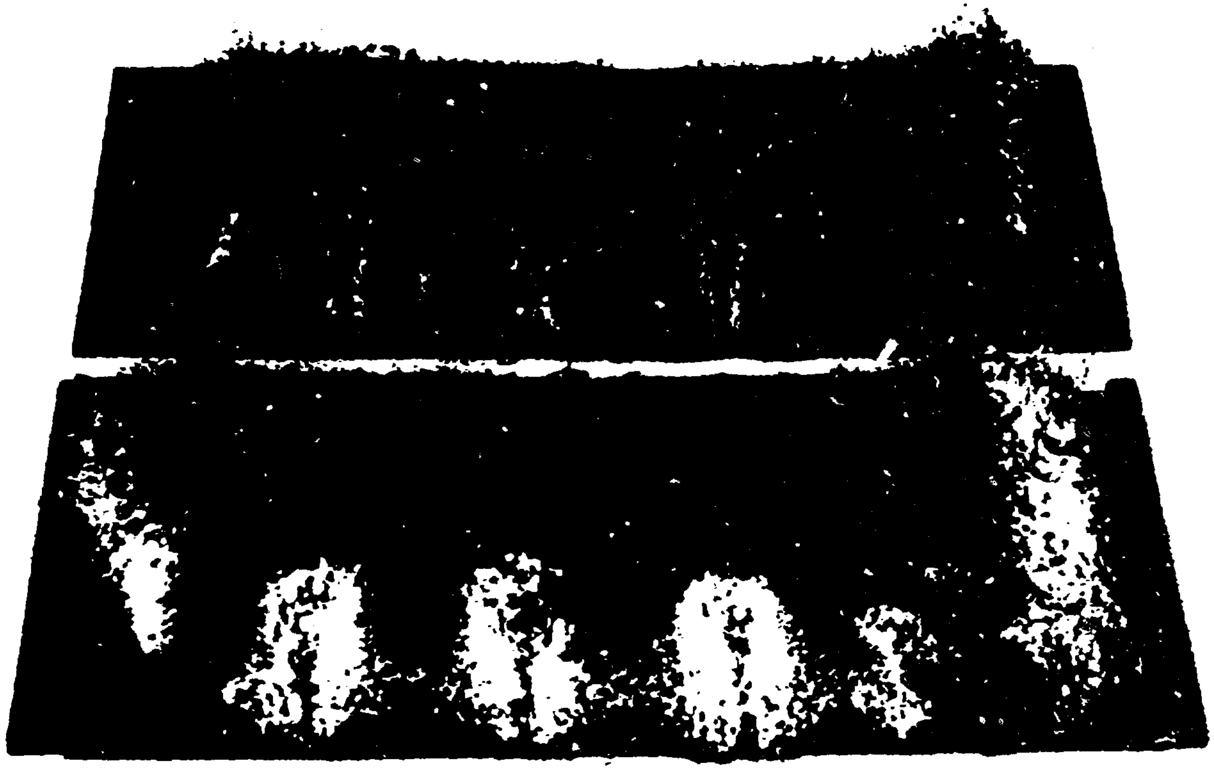


Fig. 8. Change in SiO concentration with time for reactor with in situ generators.

(a)



(b)

Fig. 9. Whisker growth along path a-c in Fig. 3 showing secondary phase overgrowth after (a) 5 hours and (b) 7.5 hours at 1400°C.

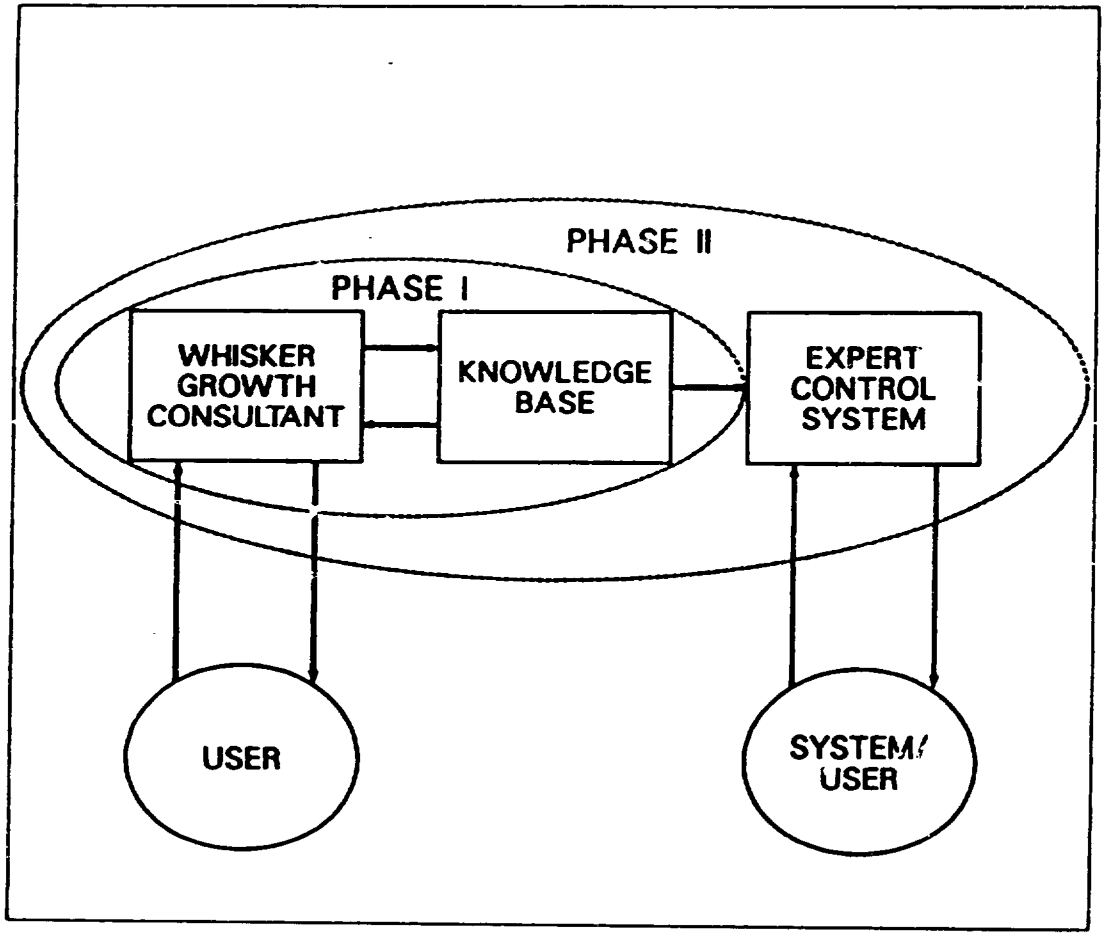


Fig. 10. Conceptual representation of expert systems envisioned for the VLS SiC whisker growth process.

2. We can make the process work because we have experienced experts who use hueristic rules in addition to understanding the physics and chemistry of the process. The AI system would function in the same way.

3. Technology transfer of a rule-based process will take place easier if the rule set and knowledge base are defined and computerized. In other words, we cannot readily transfer the actual experts.

The major challenge impeding the development of an expert system for the VLS whisker growth process is that all of the rules have yet to be identified and defined. The first step toward remedying this situation entailed building a relational database using the INGRES[d] database management system. Correlations, obtained by manipulation of the database, will be used to develop rules and confidence levels for those rules. A partial list of categories from that database that will be examined is as follows:

1) amount of SiO generation,
2) catalyst characteristics,
3) substrate characteristics,
4) inlet gas composition and flow rate,
5) reactor characteristics, and
6) exit gas composition as a function of time.

When the whisker growth consultant is completed, a dialogue between a user and the expert system may proceed like this:

USER:

"I have catalyst X and reactor Y, and I wish to produce Z grams of whiskers of type W. What should my initial conditions be?"

COMPUTER:

"The initial temperature should be A, the initial flow rate B, and the initial composition C, with an initial peak concentration of CO of D."

OR

"If I know more about the substrate I could answer that question with greater confidence."

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[d]Product of Relational Technology, Inc., Berkeley, CA 94705.

The control system will be a direct outgrowth from the consultant, and in fact, will use the same knowledge-base. The expert control system will sense the reactor temperature and exit gas composition, use the information provided to the whisker growth consultant, and adjust the inlet gas composition and possibly the reaction temperature to achieve the required results.

VLS SIC WHISKER STAPLE YARN DEVELOPMENT

Progress in developing a staple yarn from VLS SiC whiskers has proceeded along two paths. The first attempt entailed folding ∿25 wt% of as-grown (i.e., not beneficiated) VLS SiC whiskers, measuring $\leq$ 20 mm long, into the core of a rayon sliver. The purpose of the rayon was to serve as a carrier and lubricant during subsequent yarn processing. The handmade "composite" sliver is shown in Fig. 11; the dark gray material is the whiskers and the white fibers are the rayon. Scanning electron microscope (SEM) examination of this sliver, Fig. 12, revealed that the whiskers (the slender, straight rods) were quite disoriented while the rayon fibers (the thicker, curved fibers) displayed considerable orientation. This sliver was then rotor spun to produce the yarn shown in Fig. 13. This proved to be too aggressive a treatment for the whiskers in that the whisker length was reduced to $\leq$ 4 mm and ∿60% of the whiskers was lost as powder that accumulated in the rotor spinner. A high magnification view of the rotor spun yarn is presented in Fig. 14. Few whiskers could be easily identified amongst the rayon and those that were present, though displaying some orientation, were quite short.

In view of these results, it was concluded that a second, much less aggressive, non-conventional approach would have to be explored to develop an acceptable staple whisker yarn. To that end, three basic processing steps were identified. The first was to disrupt the as-grown whisker bundles in such a way so as to not reduce the whisker lengths. This was accomplished by air agitating the whiskers while immersed in glycerine. The second step was to orient and collect the whiskers in a form that would facilitate the production of a yarn. This was accomplished by vacuum casting onto a translating piece of filter paper to produce the oriented whisker ribbons shown in Fig. 15. Concurrent with the vacuum casting operation, the whiskers were washed with water to remove the glycerine. SEM examination of the ribbon revealed that the whiskers displayed a considerable degree of orientation and that not all of the glycerine was removed during washing, as shown in Fig. 16. The third step is envisioned to involve rolling up and rayon wrapping the ribbon to produce a yarn.

Fig. 11. Handmade "composite" sliver consisting of ~25 wt% VLS SiC whiskers folded into the core of a rayon sliver.

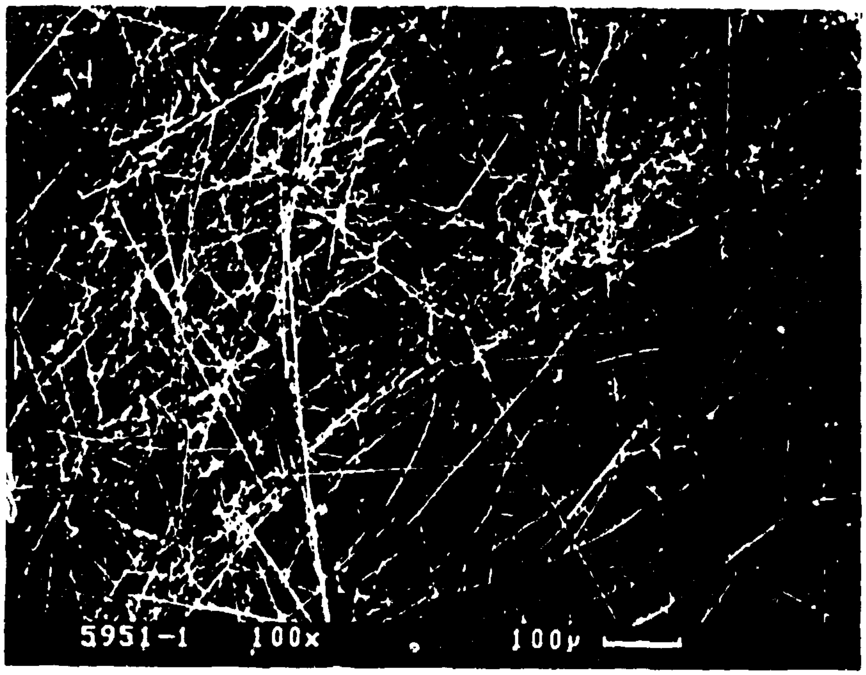

Fig. 12. SEM photomicrograph of handmade whisker-rayon sliver; whisker length is ≤ 20 mm.

SUMMARY

A VLS whisker growth process, optimized for the production of ∿10 mm long SiC whiskers, was modified to produce longer whiskers measuring ≥ 25 mm in length. Efforts are underway to tailor the partial pressure of CO and/or the partial pressure of CH_4 to 1) achieve more stable SiO generation, 2) increase the yield of long whiskers, and 3) eliminate undesirable secondary whisker growth. A plan was developed for incorporating an AI system to enhance the quality and reproducibility of whisker growth. Attempts at producing a staple whisker yarn by rotor spinning revealed that this technique was too aggressive. A non-conventional approach was developed in which an oriented whisker ribbon was produced as a predecessor to a staple yarn. Future work in this area will focus on twisting the ribbon and incorporating a fugitive rayon fiber around the ribbon to facilitate subsequent handling and actual yarn production.

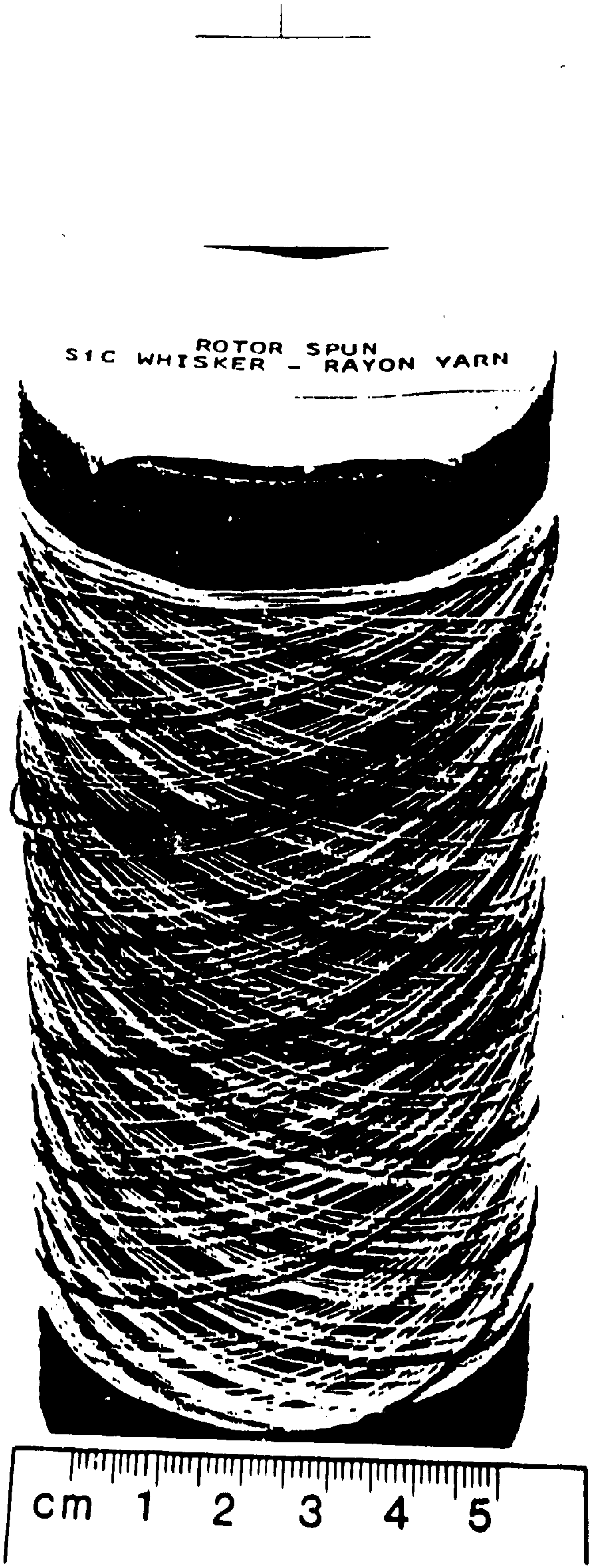

Fig. 13. First iteration staple whisker yarn with rayon carrier.

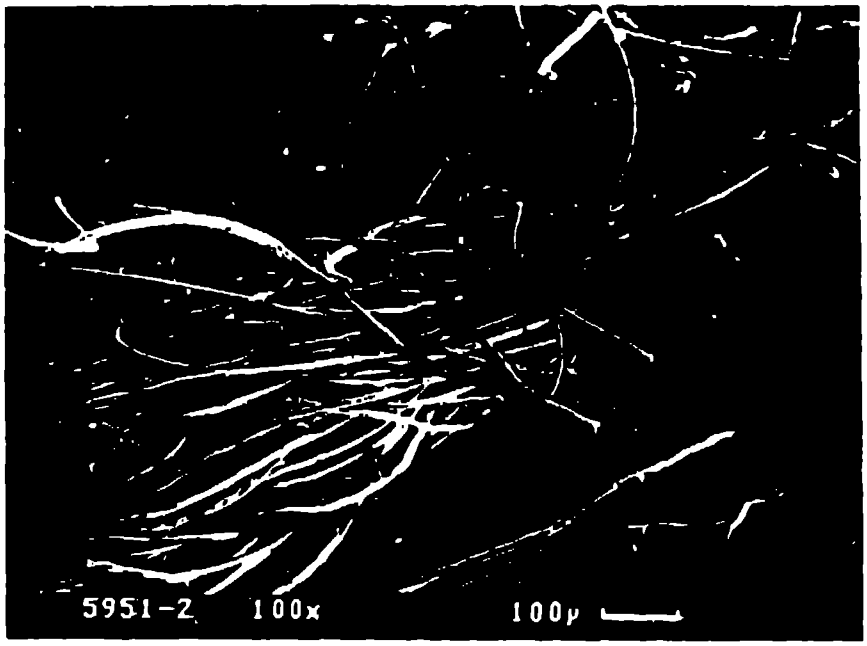

Fig. 14. SEM photomicrograph of whisker-rayon rotor spun yarn; whisker length is ≤ 4 mm.

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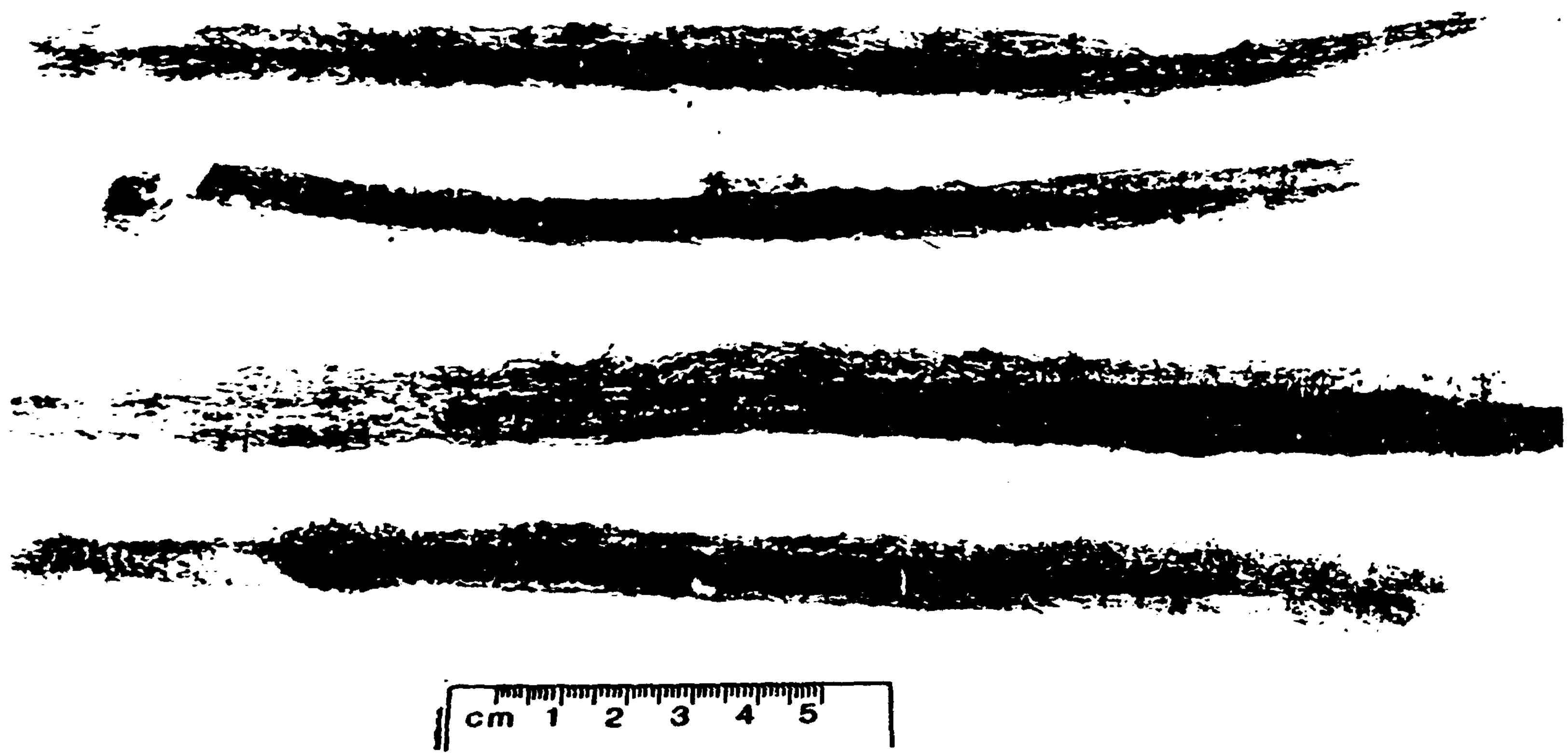

Fig. 15. VLS SiC whisker ribbons produced by glycerine dispersion and vacuum collection.

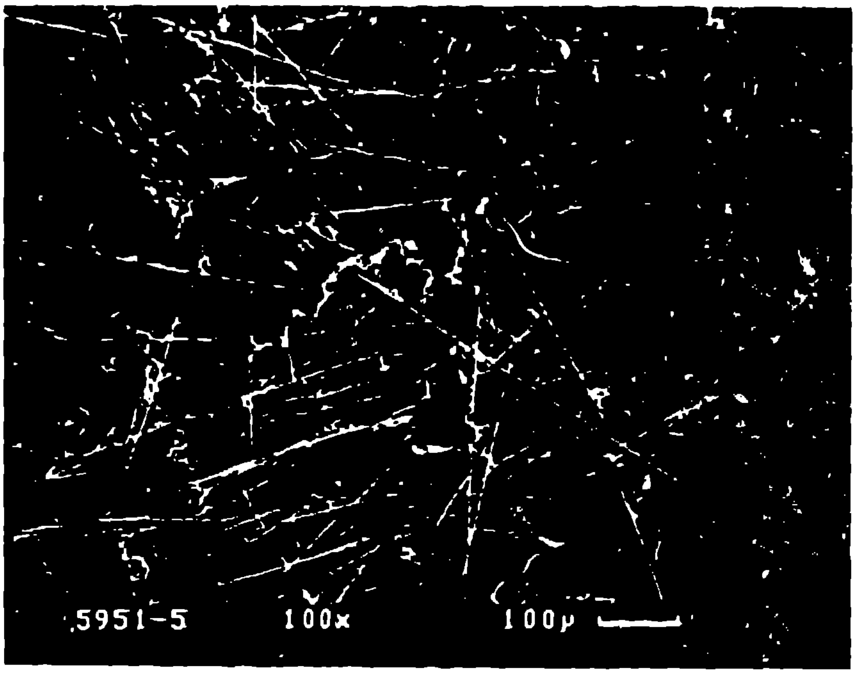

Fig. 16. SEM photomicrograph of VLS SiC whisker ribbon; the clumps are residual glycerine.

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