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STUDY OF THE GROWTH PARAMETERS INVOLVED IN SYNTHESIZING BORON CARBIDE FILAMENTS

by

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SUMMARY

The purpose of the present program has been the investigation of the following:

1. The growth of B_4C whiskers.
2. Characterization of the B_4C whiskers in terms of mechanical properties and crystalline perfection.
3. Incorporation of B_4C whiskers in composite specimens.

B_4C whiskers have been grown in a chimney-type graphite resistance furnace. The temperature gradient developed at the chimney top controls the supersaturation of B_4C vapor for subsequent nucleation and growth of the whiskers. The geometry of the whisker growth zone of this furnace causes the whiskers to grow curved instead of the more desirable straight variety.

Studies were continued on investigating the effects of the growth and deposition-zone geometry of the chimney type furnace on whisker production. The new furnace geometry continues to produce markedly more whiskers per run. Efforts are continuing to increase the length of the whiskers since they are presently shorter than the whiskers grown by the internal mandrel technique.

A renewed effort has been made to grow B_4C whiskers by the dynamic method. Kinetic and thermodynamic calculations have been re-examined and equipment accumulated.

Annealed whiskers have straightened after heat treatment above 1500°C. The (oko) plane of these whiskers have roughened increasing the probability of notches which in turn can influence the strength of the whiskers. Whiskers annealed at 1700°C and 1900°C were thus weakened; however, whiskers annealed at 1600°C straightened and still retained their as-grown strength.

$Al-B_4C$ composites were fabricated by infiltration and tensile tested at room temperature. The strongest composite tested at 13000 P.S.I. The composite contained low concentrations of whiskers in the 5% to 10% range.

I. INTRODUCTION

Boron Carbide (B_4C) whiskers exhibit attractive properties for utilization in composite materials. In terms of their high strength, low density and high elastic modulus, these whiskers when utilized as reinforcements, offer a great potential for high strength-to-weight or high stiffness-to-weight materials for future space applications. In addition, their refractory properties make them valuable also for high temperature applications.

Although more than one method of B_4C whisker growth has been studied, the most successful one to date has been the pure vapor method(1). This method consists of the vaporization of B_4C powder at high temperatures and subsequent condensation of B_4C whiskers on a graphite substrate at a lower temperature. It has been used to study the growth parameters and to obtain an adequate whisker supply for composite fabrication. Geometric changes in the whisker deposition area of the pure vapor method has led to increased whisker production and to reduction of the number of curved whiskers. However, it is apparent that this process will not be amenable to scale-up because of the slow rate of growth of the whiskers and also the severe temperature conditions necessary to initiate and sustain growth. Thus a renewed look at the dynamic vapor process(2) was initiated. This approach holds the greatest promise of success since B_4C whisker supply is a critical problem which must be solved.

It had been observed that long time annealing of B_4C whiskers at high temperatures resulted in the straightening of curved whiskers. Tensile tests showed that annealing had not up-graded the strength of B_4C whiskers. These studies were continued and included whiskers annealed for one hour at 1800°C, 1700°C, 1600°C, 1500°C, 1300°C and 1100°C. Whiskers annealed at 1500°C and lower no longer straightened. Room temperature tensile tests showed a weakening of the whiskers annealed above 1600°C. Optical and x-ray examination of the whiskers before and after annealing showed that at high temperatures a roughening of the (oko) plane occurred leading to the speculation that these added notches could account for the low strength values found. Tensile tests of whiskers annealed at 1600°C showed that their tensile strength was unaffected by the heat treatment and essentially duplicated the as-grown values.

Aluminum-B_4C whisker composites were produced by vacuum infiltration[3]. From a fabrication point of view, excellent appearing composites of high density (no voids, etc.) were cast. Tensile tests of the composites were performed at room temperature but no improvement in mechanical properties over those composites made previously[3] was noted.

II. EXPERIMENTAL PROCEDURES AND RESULTS

A. GROWTH STUDIES

A modification of the deposition zone discussed in a previous report[1] resulted in an increase of approximately an order of magnitude in the number of whiskers grown per run.

An added result of the geometric change has been the reduction of the number of curved whiskers grown. This occurs presumably because of the alteration of the symmetrically shaped temperature gradients which were present in the former deposition geometry. However, even these encouraging results have not solved the whisker supply problem or simplified the growth process so that scale-up of the process would be feasible. Thus, although as has been pointed out already, the evaporative method for preparation of boron carbide whiskers is a simple and convenient way of obtaining research quantities of materials, the yield per unit operating time and unit power input is low and total production is insufficient for fully investigating the important areas of coating and composite formation. Consequently there is a pressing need to investigate on a more detailed level, the chemical approach to whisker formation. This method had been subjected to preliminary study earlier in the program[2] but was set aside in favor of the evaporative method to acquire sufficient material for characterization. In the interim, work on other programs has added to the background of experience available for reopening the study of dynamic vapor processing (DVP) methods. Accordingly, apparatus was assembled to permit passage of reactive boron - and carbon - containing materials into a heated tube under controlled conditions.

Several factors contribute to the yield and type of whiskers which may be grown from a particular chemical system. These include the thermodynamic and kinetics of production of reduced species in the vapor phase, concentration and gas velocity, temperature and total pressure which influence diffusion rates, and the nature of the substrate. As a point of departure, initial depositions will be made in the region of 1400^{o}C, using boron trichloride and carbon tetrachloride as gas species, with hydrogen as a carrier and reducing agent. At this temperature, the thermodynamics of reduction of boron trichloride and carbon tetra-chloride, at low concentrations in the gas phase, indicate that the equilibrium vapor pressures of both carbon and boron will be far exceeded, and that therefore deposition will occur. However, the kinetics of these reductions are unknown and must be determined experimentally. Previous experience on other programs indicates that boron is rapidly reduced and carbon less so. However, the stoichiometry of depositing species at any given point on the deposition surface is also unknown. Since whisker growth is a slow process and influenced by the concentration gradients and stoichiometry of depositing species, experimental approaches must be used to determine at what gas velocity and feed ratios deposition may be expected in whisker form.

Several experimental runs have been carried out to date in which temperatures in the vicinity of 1250-1300°C were reached with the available power supplies. In one case in which a mullite tube was used as the substrate container (a graphite tube was used as the deposition surface), only aluminum oxide, and beta silicon carbide from the mullite tube were formed on the graphite surface. Using a quartz containing tube, no deposit was observed at this temperature. Since the deposition system was limited in power and versatility, it has been abandoned in favor of more the versatile graphite resistance heated furnaces. Construction and arrangement of this system is now in progress.

B. WHISKER ANNEALING STUDIES

Many of the B_4C whiskers grown by the pure vapor method are curved and also have growth steps on their surface. Curved whiskers have been shown to contain significant residual stresses(1) which could lead to weakened material while whiskers which contain severe growth steps can be weakened significantly because these growth steps could act as stress raisers with notch efficiences of 5 to 10.

Previous results(3) had shown that such areas undergo a change in geometry after extensive annealing and therefore, experiments were perfromed to determine whether annealing improves the properties of B_4C whiskers. Results after anneals at 1900°C were not encouraging. These studies were extended during this reporting period to include one hour anneals at 1800°C, 1700°C, 1500°C, 1300°C and 1100°C. Further studies on the morphology and crystal structure of annealed whiskers were also made and are presented in another section of this report.

The tensile data on all annealed samples (including previous work[1]) are presented in Table I. It is apparent that specimens annealed at temperatures above 1600^{o}C are weakened by the annealing treatment. It is noted that the heat treatments which do not have a straigthening effect on the curved whiskers leave the whiskers as strong as the as-grown whiskers. This occurs at annealing temperatures below 1600^{o}C. Further, it is observed that at 1600^{o}C appreciable straightening of curved whiskers has occurred without the weakening effect observed at higher temperatures.

TABLE I

STRENGTH OF ANNEALED AND AS-GROWN B_4C WHISKERS

Spec. No.	Heat Treat	LT(mm)	LO(mm)	Area(μ^2)	σ m(PSI)
1*	1900°C 1 hr	1.50	0.60	92.6	100,000
2*	1900°C 1 hr	1.84	0.55	43.5	336,000
3*	1900°C 1 hr	2.90	0.77	43.6	147,000
4*	1900°C 1 hr	4.24	0.57	71.5	169,000
5	1700°C 1 hr	--	1.71	38.8	184,000
6	1700°C 1 hr	4.53	0.86	163.0	272,000
7	1700°C 1 hr	5.57	1.98	31.5	326,000
8	1600°C 1 hr	3.32	0.54	5.95	1,200,000
9	1600°C 1 hr	2.60	0.44	68.0	370,000
10	1500°C 1 hr	3.89	0.49	21.8	490,000
11	1500°C 1 hr	3.59	0.58	264.0	324,000
12	1500°C 1 hr	3.77	0.55	9.4	295,000
13	1300°C 1 hr	3.38	0.66	11.5	566,000
14	1300°C 1 hr	2.87	0.60	24.1	710,000
15	1100°C 1 hr	2.28	0.50	30.5	410,000
16	1100°C 1 hr	4.95	0.46	42.5	735,000
17*	as-grown	--	0.87	141.3	873,000
18*	as-grown	4.51	0.35	22.4	760,000

* Previous work

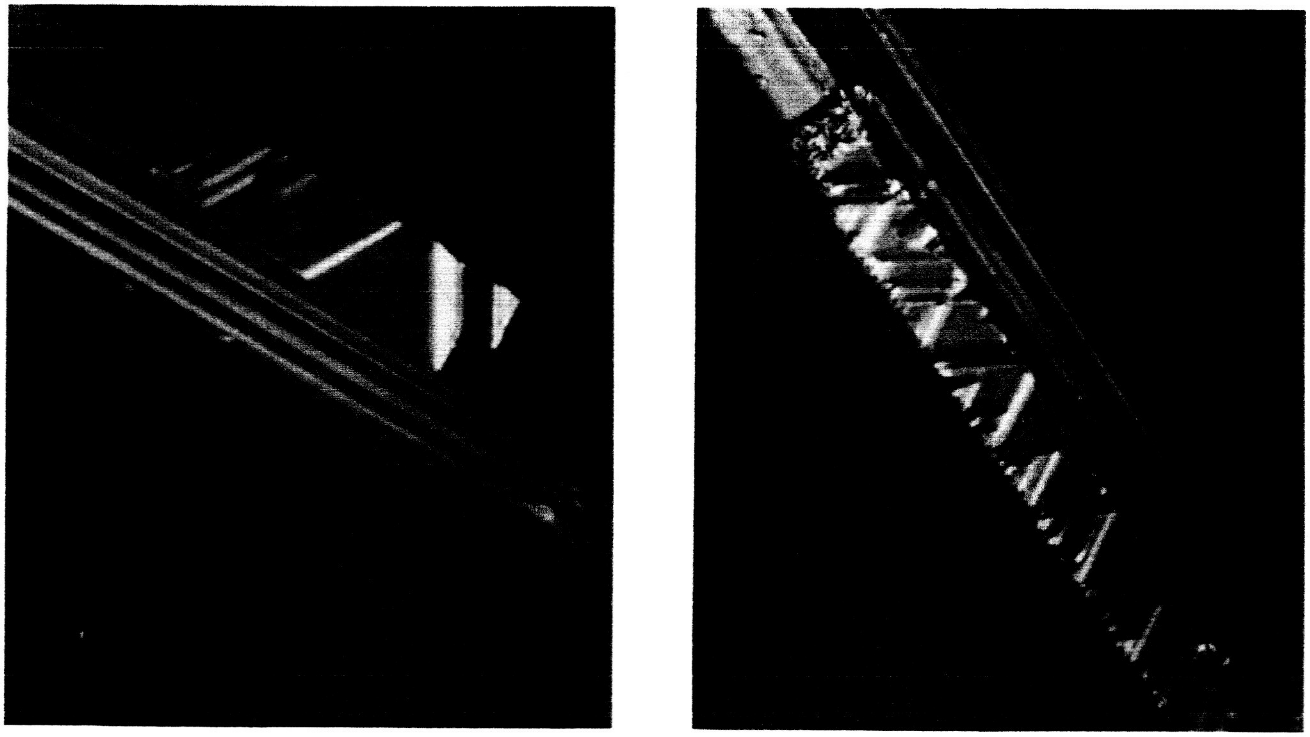
C. WHISKER CHARACTERIZATION

Because of the particular furnace geometry employed in the growth of B_4C whiskers in this program, isotherm shapes exist in the reactor chamber which cause the resulting whiskers to be curved[3]. It was previously determined[1] that the magnitude of the internal compressive stresses in the curved regions of the whiskers are in the order of E/600 where E is the elastic modulus. During the present report period attempts were made to relieve internal whisker strains through thermal treatments in order to strengthen the whiskers. The remainder of this portion of the report describes the character of thermally treated whiskers, and explains why thermal treatment, although found to straighten the curved whiskers, tends to weaken them at temperatures above $1600^{o}C$.

The effects to be described resulted when B_4C whiskers were thermally treated using the following schedule: $1800^{o}C$, in vacuum (85×10^{-3} torr) for one hour. Figures 1A and 1B are photomicrographs of B_4C whiskers before and after thermal treatment respectively. X-ray diffraction analyses of the "before" and "after" specimens showed that they were B_4C single crystals. The major whisker axis was parallel to the $\vec{a}_1$ hexagonal unit cell edge, i.e. (h, o, o). There was no indication in the diffraction photographs of individual "after" whiskers that any new phases, e.g. oxides, nitrides, etc., had formed as a result of thermal treatment. (Note that the diffraction method used in these studies would not, under normal conditions, be sensitive enough to detect "new" phases if their concentrations were below about one percent by volume.) Although most of the recently grown B_4C whiskers contain extensive smooth regions, the fields in Figure 1 show whisker regions in which typical steps[2] are contained. These regions were chosen in order to illustrate the points which will now be discussed.

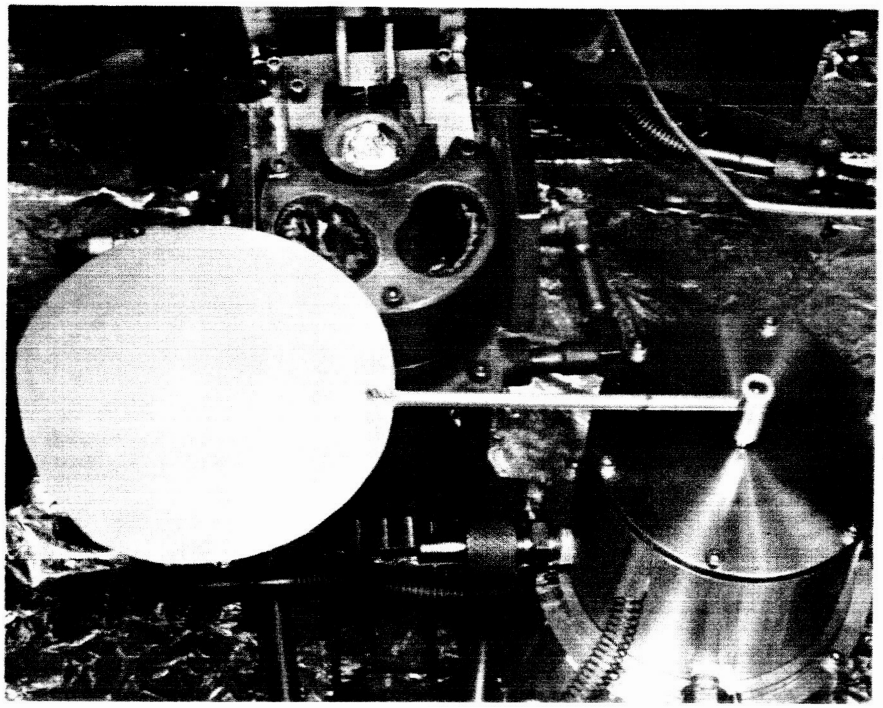
The major differences found between "before" and "after" whiskers, other than the fact that heat treatment straightens curved whiskers, are that the height of whisker steps seem to be reduced and importantly, certain whisker planes tend to become roughened.

Typical roughening is illustrated in the left whisker edge shown in



A. BEFORE HEAT TREATMENT — 10μ — B. AFTER HEAT TREATMENT

Figure 1. B_4C Whiskers Before and After Heat Treatment, 1800°C, 1 Hour, 85×10^{-3} Torr, Magnification = 1300X. Note the Irregularities Produced on the (oko) Surfaces Through Heat Treatment.



Photograph of the solenoid shutter as it is installed in the vacuum chamber. The shutter blade is at the left and the electron-beam evaporation source is at the upper center

F I G U R E 2

Figure 1B (compare with the "before" whisker shown in 1A). Close examination of Figure 1B reveals that only those crystal edges parallel to the left edge experience roughening. The planes which intercept to form the edges in question are the (ool) and (oko) planes. The (ool) family of planes is parallel to the surface containing the triangular steps (e.g., parallel to the plane of the photograph) in Figure 1B. The (oko) planes are perpendicular to the photograph. A schematic representation of a portion of a typical heat treated whisker showing the resulting roughening is presented in Figure 2.

Roughening probably results from one or both of the following reasons:

(a) The rate of evaporation of B_4C from the (oko) planes is markedly greater than from other planes. However, this does not seem to be likely since the overall appearance of the (ool) planes are somewhat smoother after thermal treatment.

(b) The (ool) plane edges are very reactive to the ambient atmosphere (air at 85×10^{-3} torr) under the conditions of annealing time (1 hour) and temperature ($1800^{\circ}C$). This appears to be the most logical explanation for the observed roughening.

As may be seen in Figure 1B, and is also shown in the sketch of Figure 2, the boundary or edge formed by a smooth (ool) plane and a roughened (oko) plane is extremely irregular.

Irregularities of this kind are in effect notches in the crystal. These notches then act as stress raisers which in turn serve to weaken the crystal. Hence any gain in strength resulting from internal stress relief through straightening the whisker by annealing is probably more than offset by the weakening due to notch formation during the annealing process.

Therefore, unless annealing is done at low temperatures (ca. $1600^{\circ}C$) or at low pressures (ca. 10^{-6} - 10^{-7} torr) or in an inert atmosphere (e.g. He), annealing will probably be deleterious to whisker strength.

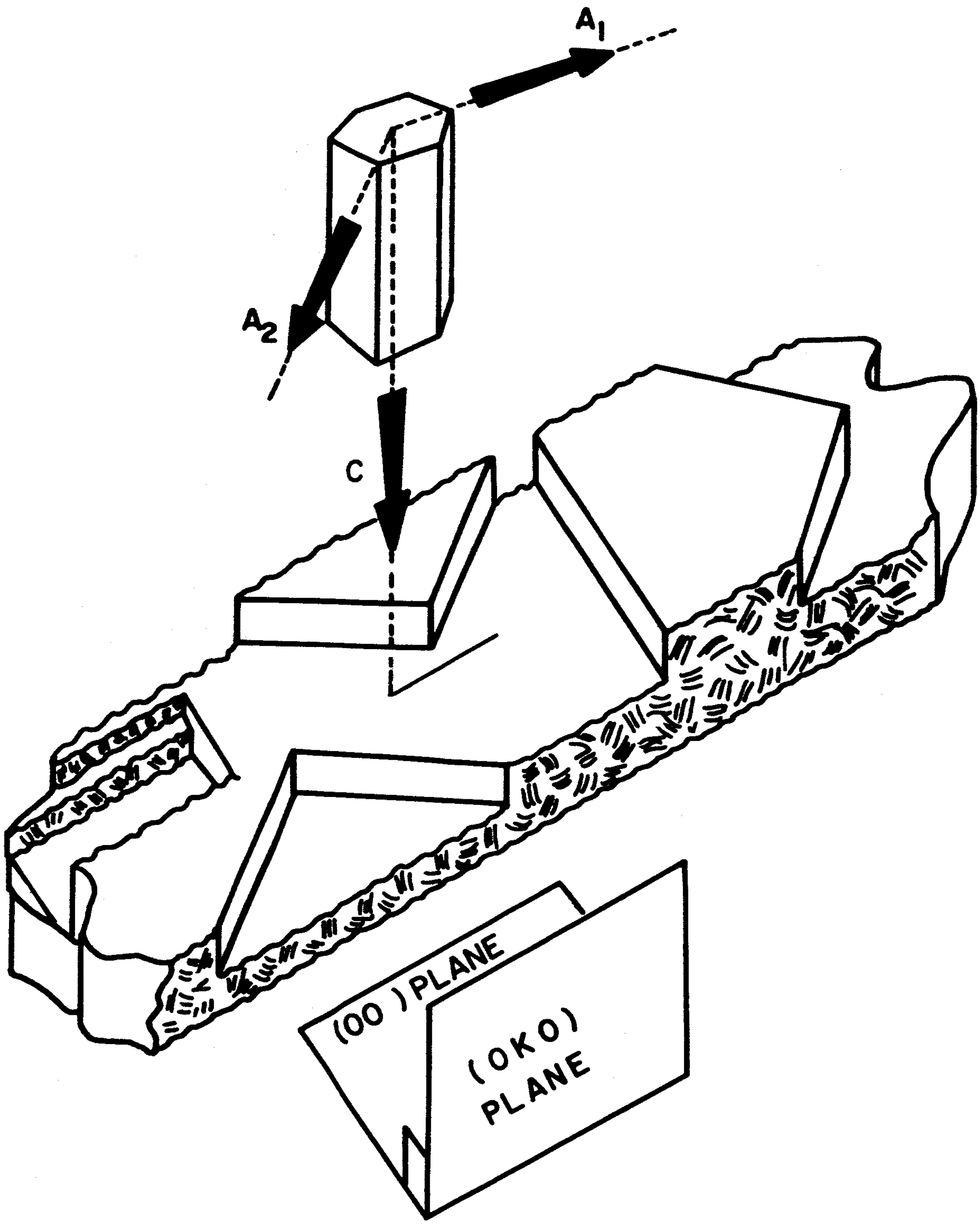


Figure 2. Schematic Representation of Thermally Treated B_4C Whisker Showing Roughened (oko) Planes and Resulting Edge Notches.

III. COMPOSITE FABRICATION AND TESTING

Aluminum - B_4C whisker composites were fabricated by a liquid infiltration method developed earlier[(3)]. All whiskers on hand were coated with Ni-Ti to promote wetting and separated by screening into four groups according to average length. The long group of whiskers were at least 1/4" long. The medium length group was in the 3/16" to 1/8" length range, the fine group was in the 1/8" to 1/16" range. A fourth group contained all the debris which was left.

The composites were of excellent quality, however, as has been the case in the past, high volume fraction loadings of the specimens could not be achieved. Thus the tensile values obtained on the specimens (Table II) are only indicative of composites containing volume fractions in the 5 to 10 percent range as confirmed by cross-section studies of the fractured areas of the tensile tested specimens. These low concentrations of whiskers in composites have been encountered before (1, 3) and are attributable to whisker curvature and whisker roughness.

Thus it is apparent that the growth and separation of strong, smooth straight, long B_4C whiskers still continues to be a critical problem area for study.

TABLE II

TENSILE DATA FOR B_4C-Al FORMED BY INFILTRATION TECHNIQUE

Sample #	Whisker length	Test Temp °C	UTS PSI
080201	(See text)		
Test #1	long	RT	8,900
Test #2	long	RT	9,400
080202			
Test #1	med.	RT	11,500
Test #2	med.	RT	13,200
080203	fine	RT	10,000

IV. CONCLUSIONS

1. Although considerable progress has been made in B_4C whisker growth technology using the pure vapor method, geometric conditions existing within the growth area restrict the perfection and ultimate length of whiskers which can be grown. Further, the vapor process is not amenable for scale-up because of low material transport rate and high operating temperatures. Thus, a more exhaustive study of the Dynamic Vapor Process has been started. It is hoped that B_4C whiskers can then be grown at higher rates and at lower temperatures.

2. Annealing studies have shown that extensive weakening of B_4C whiskers occurs when the whiskers are heated in vacuum for one hour above $1600^{\circ}C$. Although an apparent decrease in surface roughness and curvature of as-grown whiskers occurs, the excessive loss of material has a weakening effect on the whiskers. Whiskers annealed for 1 hour at $1600^{\circ}C$ lost their curvature but still retained their as-grown strength. A technique has thus been developed which can be used to reduce whisker curvature if this problem persists. Whiskers annealed for one hour at $1500^{\circ}C$ and below show no reduction in curvature, surface roughness, or strength.

3. No high strength composites of Al-B_4C whiskers have been made due to an insufficient volume fraction of whiskers in the composites. The packing of high density composites requires whiskers which are smooth, straight and long. Since the problems of surface roughness and curvature of B_4C whiskers grown by the pure vapor method have not as yet been solved, packing densities of over 5 to 10% by volume have not been reached.

V. FUTURE WORK

The ultimate goal of this program is the development of high strength composites reinforced with discontinuous whiskers of B_4C. The attainment of this goal depends first on a supply of long, high strength, structurally perfect B_4C whiskers. The potential strengthening qualities of B_4C whiskers has been shown; the production of large quantities of material for composite studies is lacking.

Further work then will be directed along two separate paths:

1. The attainment of a B_4C whisker growth process which is amenable to scale-up and capable of growing high quality material. It is felt that the Dynamic Vapor Process has the greatest potential of achieving success in this critical area.

2. A large supply of continuous filaments of B_4C vapor deposited on a tungsten substrate is available to serve as a substitute system to the B_4C whisker system while the growth area is being critically examined. Thus, composite technology can be advanced without a whisker supply with a minimum of transition envolved when and if B_4C whiskers become available.

Initially, chopped B_4C filaments will be substituted for whiskers and Al-B_4C composites containing chopped filaments fabricated. The strength of these composites will then be studied as a function of volume fraction, critical length to diameter ratio, spacing geometric, orientation, etc. as time and funds permit.

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