JOURNAL OF MATERIALS SCIENCE 21 (1986) 687–691

Interfacial void formation in boron filaments

F. E. WAWNER, JR
School of Engineering and Applied Science, University of Virginia, Charlottesville, Virginia 22903, USA

J. W. EASON
TRW Co., Rogers, Arkansas 72756, USA

Experiments have shown that when boron filaments are heated in an environment containing a reactive species such as oxygen, formation of boron oxide on the surface and subsequent vaporization causes removal of boron atoms from the surface. Removal of this material results in a contraction of the filament which is due to redistribution of internal stresses and anelastic recovery. The magnitude of the contraction observed is found to be dependent upon the concentration of oxygen in the annealing atmosphere. Examination of the interior of the filaments showed massive void formation around the core and hence separation of core and sheath. An empirical relationship was constructed to fit the contraction data based on an exponential relationship. Activation energies were determined and were reasonable when compared with similar studies. A possible mechanism for the observed phenomena is that there is a net outward diffusion of boron atoms to the surface, and an inward diffusion of vacancies which coalesce at the interface between sheath and core to form the voids. The disordered structure of the vapour-deposited boron (i.e. microcrystalline with crystallite size 2 to 4 nm and highly disordered) is such that it contains many vacancies.

1. Introduction

Boron filaments, because of their desirable mechanical properties, are a very interesting material for utilization as a reinforcement for structural composites. Several review articles [1–3] have been published which present the characteristics of the individual filaments as well as some properties when they are incorporated into composites. During the past few years several studies have been made which delineated very interesting and fundamental phenomena that are characteristic of the filament. For example, Behrendt [4] has clearly defined the residual stress distribution and magnitudes in the filaments. DiCarlo [5] has investigated the anelastic effect, stating that all nonelastic deformation in boron filaments can be explained by an anelastic model. Vega-Boggio and co-workers [6, 7] have reported on fracture phenomena in the filaments. And Eason *et al.* [8] have proposed a model for the elongation of boron during production by chemical vapour deposition.

During the course of this latter study a phenomenon was observed which is believed to be fundamental to boron filaments, and which is extremely important because of its deleterious influence on the mechanical properties of the filaments. It was seen during heat treatment of the filaments in an inert environment that large internal voids were formed which seriously impaired the strength of the filaments. It is the propose of this paper to describe this phenomenon and its cause.

2. Experimental procedure

Boron filaments were heat treated in the apparatus shown in Fig. 1. The filaments were suspended vertically in a glass tube sealed at the ends by mercury contacts. The mercury served as electrical contacts as well as gas seals. Using a d.c. power supply the filament was heated electrically to the desired temperature. A preselected atmosphere was passed through the chamber at positive pressure.

Monitoring of changes in the length of the filament during annealing was made by a change in the inductance of a coil located in a bridge circuit. Atmospheres of H_2, N_2, argon and air were used in the study. Boron filaments used in the experiments were obtained from Avco Speciality Materials, Lowell, Massachusetts, and had four different histories:

(a) standard production 102 μm boron on tungsten (B/W), recently made;

(b) standard production 102 μm B/W stored for 4 years;

(c) standard production 107 μm boron on carbon (B/C); and

(d) standard production 107 μm B/C that had been etched to 74 μm diameter.

3. Results and discussion

3.1. Contraction of boron filaments during annealing

The fact that boron filaments display anelastic behaviour [5] indicated that the material should exhibit axial recovery from elongation that occurs during production. Initial experiments were made to anneal the filaments in different inert atmopheres (N_2, argon and H_2). A contraction of 1.3 to 1.9% was observed for all gases used, following annealing at 900° C for 10 min. Annealing was also conducted in a vacuum

0022–2461/86 $03.00 + .12

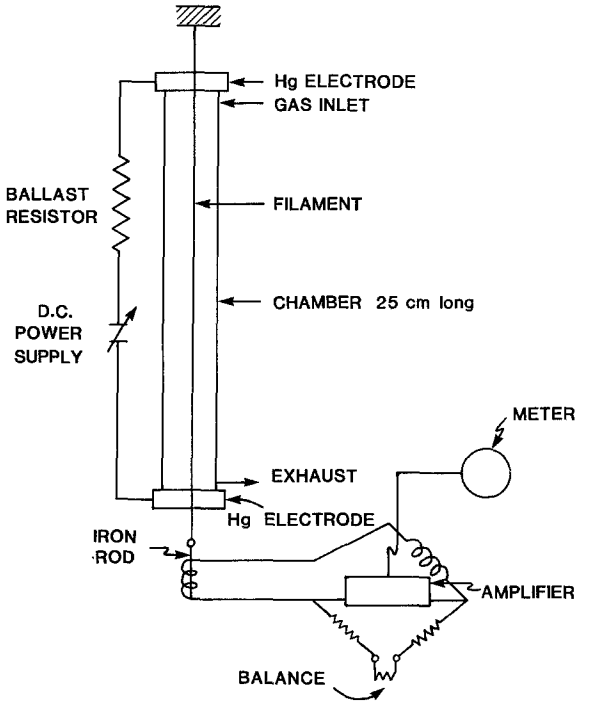

Figure 1 Schematic diagram of apparatus for static elongation measurements.

(10^{-7} torr), and when crystallization did not occur, no contraction was observed.

Examination of the data suggested a common mechanism involved with the gaseous environments. It is known that the presence of water vapour has undesirable effects on boron growth during the deposition process, and care was taken to ensure that all gases were dry before entering the system. The common factor believed to be involved was trace amounts of oxygen present in the annealing environments. Consequently, experiments were carried out in dry air to accelerate the mechanism. Boron filaments with the different histories were used, and the results are shown in Fig. 2. This shows that all the boron filaments contract upon annealing. The temperature was kept constant at 900° C. After 10 min, the standard production B/W filaments contracted by 1.7%; whereas the B/W filaments that had been stored for 4 years contracted somewhat less (1.4%), indicating some anelastic recovery even at room temperature.

Boron on carbon filaments contracted to a lesser extent, approximately 1%, but this should be expected because of the difference in magnitude and distribution of the residual stresses [4] and less original elongation as compared to B/W filaments. Similarly B/C filaments that had been reduced in diameter by etching, thereby redistributing residual stresses in the filaments, contracted by only 0.3%. Etching the filament removed the compressive layer on the outer surface of the filament, allowing the tensile stresses in the inner portion of the boron sheath to relax. This in itself permitted some contraction in the filament, which reduced the contraction resulting from annealing.

All annealing experiments resulted in coating the inside walls of the chamber with a white film that physically resembled boron oxide (B_2O_3), i.e. it was soluble in hot water and slightly soluble in ethyl alcohol, and hexagonal crystals were observed. Therefore, oxygen was considered to be the most likely gaseous species in the annealing environment responsible for the relatively large contractions observed. In a subsequent set of experiments, research-purity nitrogen (guaranteed to contain < 1 p.p.m. O_2) was used as a carrier gas, while small amounts of dry air were added to the flow to vary the oxygen content of the annealing atmosphere. Fig. 3 shows the results of these experiments. The solid circles shown on the graph represent individual experiments, except for the one corresponding to 0% O_2. Several runs were made in this pure nitrogen atmosphere for period of time exceeding 20 min (1200 sec) in order to accurately define the result. The solid line represents an exponential decay toward equilibrium, which will be discussed later.

The contractions observed were found to be the result of oxidation of boron at the surface of the filament. Boron oxide is volatile at the temperatures used when annealing the filament, as evidenced by the film of boron oxide on the chamber walls, so that this oxidation was an effective method of removing boron from the surface of the filament. Scanning electron microscopic examination showed that the surface was considerably smoother than that of an as-produced boron filament, but the original diameter did not change.

The surprising factor in these data is the magnitude of the contraction. The magnitude of contraction from etching is 0.17%. This places the tungsten

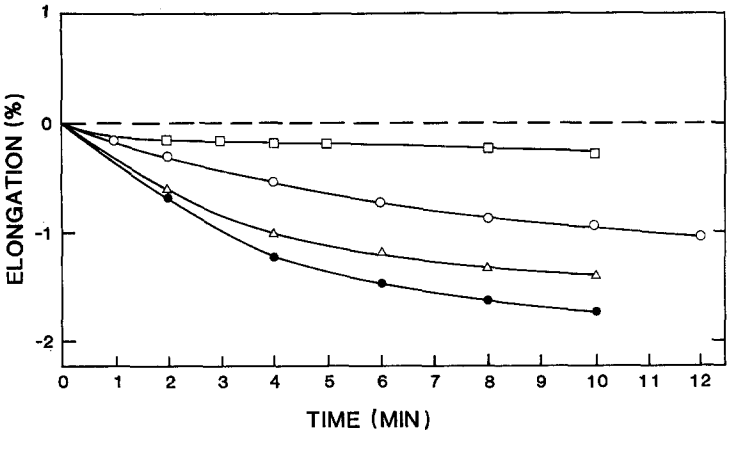

Figure 2 Effect of heat treating boron filaments at 900° C: (●) B/W, (△) B/W stored for 4 years, (○) B/C, (□) B/C etched with HNO_3 to diameter 2.95 mil (74 μm). Initial diameters 4 mil (102 μm); tension 5 g.

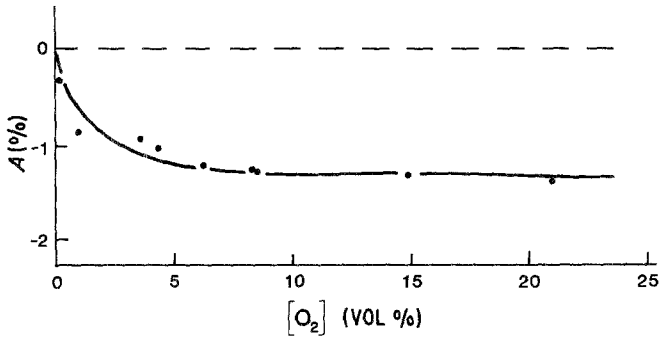

Figure 3 Elongation against concentration of oxygen in annealing atmosphere for B/W filament. Temperature 950° C, time 300 sec.

boride core, which is bonded to the boron sheath, in a very high compression; a value of $-163\,000$ psi (-1.12 GPa) has been calculated [4] for the change in core stress. Consequently with the core constraining the boron it is difficult to see how the filament can contract further without debonding from the core.

In addition, filaments that had been annealed in the various atmospheres exhibited slight curvature and were extremely brittle. There was no evidence of crystallization. To determine if, in fact, there was some internal factor leading to the large contractions measured, filaments that had been annealed were cleaved (i.e. scratched with diamond paste and then flexed to fracture the filament smoothly across the cross-section). This presents an undisturbed surface such as would not be obtained if the filament were polished.

3.2. Observation of voids

Cleaved filaments were placed in a scanning electron microscope (SEM) for observation. In every instance large voids were seen surrounding the core, allowing for separation of the core. Fig. 4 is a typical example of internal void formation in the filaments. It can be seen that the core is displaced to one side of the void and is probably buckling along the length of the filament. The presence of the voids around the core allows the boron sheath to be released from the constraining core, which permits the large contraction observed. By this separation, the large residual tensile stresses in the boron sheath are allowed to relax and any anelastic effect is allowed to recover, thus leading to the large contraction.

The immediate question that is suggested by the above observations is where did the boron go which formed the voids. One possible explanation is further diffusion and reaction in the tungsten boride core. Measurements show, however, that there is no increase in diameter of the core as would be expected if further boride formation occurred, nor were there any changes in core structure. To determine if the core had any influence on the void formation, boron on carbon filaments were annealed and subjected to SEM examination. In this type of filament there is no reaction in the core to form boride phases. Fig. 5 shows the cross-section of an annealed B/C filament. Extensive void formation around the core region is obvious and is similar in magnitude to that observed in B/W filaments. The ring of material around the carbon monofilament substrate is not a reaction zone but is a graphite layer deposited prior to deposition of boron, and is considered part of the core. Hence it can be concluded that the interfacial void formation is not related to further core development or to core material.

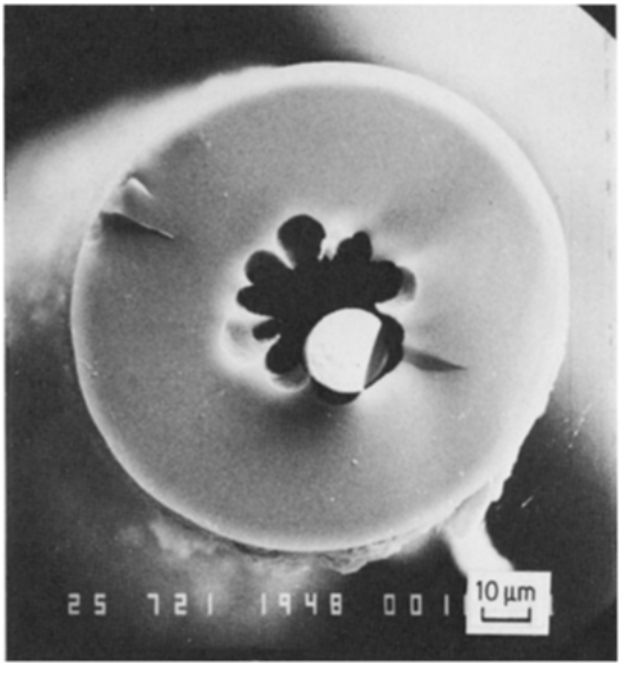

Figure 4 Interfacial void formation in B/W filament heated to 1200° C for 5 min.

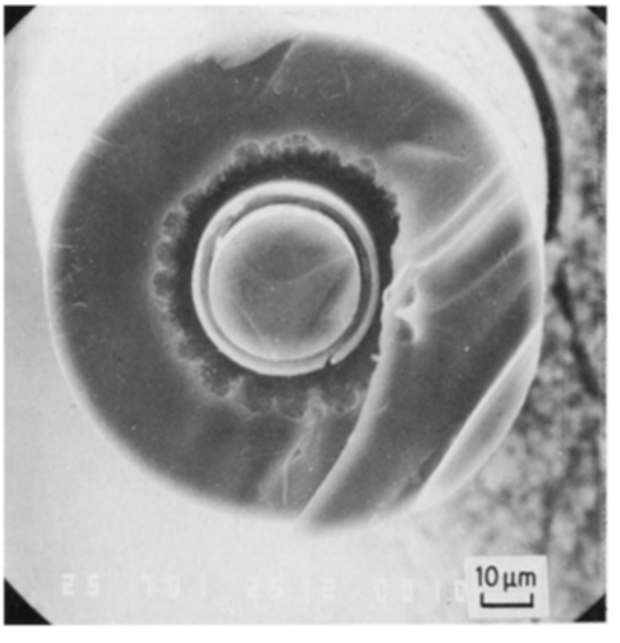

Figure 5 Interfacial void formation in B/C filament heated to 1200° C for 5 min.

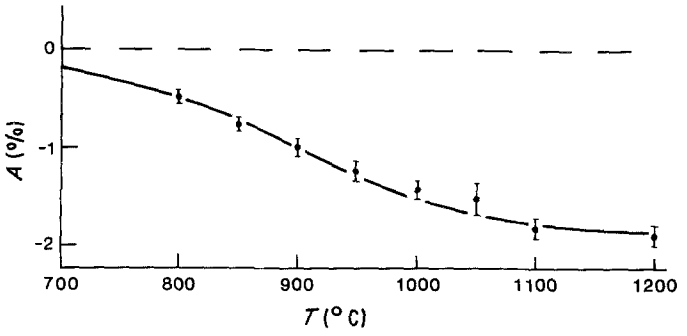

Figure 6 Elongation against annealing temperature for B/W filament. $[O_2]$ as in air, time 300 sec.

Considering the previously mentioned observations of boron oxide condensation on the chamber walls, smoothing of the filament surface and no void formation when annealed in a vacuum or an impurity-free inert gas, one can conclude that the void formation must occur as a result of surface removal of the boron atoms and their subsequent replacement from within.

3.3. Void formation mechanism

The above observations indicate that there is a net outward diffusion of boron atoms and an inward diffusion of vacancies which coalesce at the interface to form the internal voids. This type of phenomenon has previously been observed in boron filaments when fabricated in a titanium matrix composite at 1000° C for 10 min [9, 10]. It was also noted in one of these studies [10] that the boron fibre diameter did not change significantly. This is also the case in the present study.

A critical factor in understanding all diffusion phenomena is the dependence on temperature. Many boron filaments were annealed in dry air at constant periods of time (300 sec), at temperatures ranging from 800 to 1200° C. The lower limit of 800° C was imposed by the optical pyrometer and the upper limit of 1200° C was due to the transformation of amorphous boron to a crystalline phase or phases. The results from these experiments are shown in Fig. 6. The solid circles on the graph are the mean values of contraction, with bars representing the standard deviation for each set of experiments. The solid line represents an exponential decay (see Equation 2 below), which allows for contraction to take place even at room temperature.

Figs. 3 and 6 both exhibit an exponential decay toward equilibrium. This is common in nature (radioactive decay, amplitude of vibration of a string, diffusion, etc.); therefore a simple exponential decay was postulated

$$A = A_\infty(1 - e^{-Kt}) \quad (1)$$

where A is the percentage contraction of boron filament, A_∞ is the asymptotic value of contraction at infinite time, K is a rate constant dependent on boundary conditions and t is annealing time.

In order to fit the experimental data, K was found to be a product of two rate constants K_1 and K_2

$$K_1 = \nu e^{-E/kT}$$

$$K_2 = K_0(1 - e^{-\alpha[O_2]})$$

By substitution, one obtains the equation

$$A = A_\infty\{1 - \exp[-tK_0\nu e^{-E/kT}(1 - e^{-\alpha[O_2]})]\} \quad (2)$$

Fitting this equation to the experimental data gave values for E, A_∞, $K_0\nu$ and α shown below

$$A_\infty = -1.89\%$$

$$K_0\nu = 37.87\,\text{sec}^{-1}$$

$$\alpha = 40$$

$$E = 0.97\,\text{eV}$$

It must be emphasized that Equation 2 is an empirical relationship constructed to fit the experimental data presented, and that the physical meaning of the values found is as yet not completely known. An interesting point to note was that the effective activation energy determined by the present work (0.97 eV) was near the midpoint of the range in activation energies determined by DiCarlo and Wagner [11] in similar experiments.

3.4. Additional void observations

All SEM observations of void formation in different filaments were basically similar, differing only in magnitude and shape. Fig. 7 depicts a higher magnification of an interfacial region, showing hemispherical

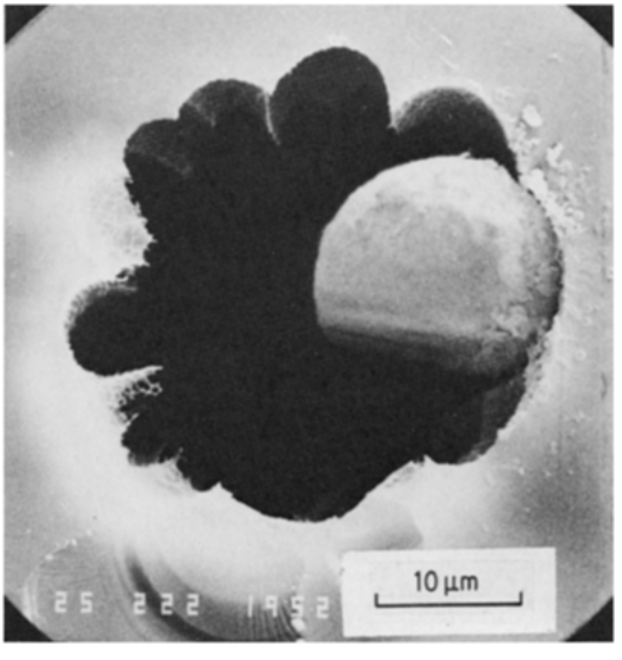

Figure 7 Interfacial void region showing β-rhombohedral fibrils.

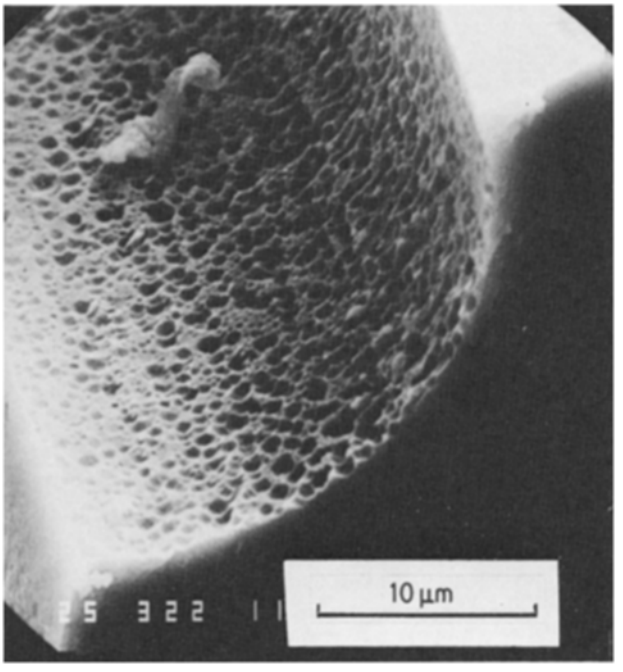

Figure 8 Split B/W filament heated to 1200° C for 3 min with core etched away. Note aligned voids.

voids surrounding the core with networks of small fibrils.

Of particular interest were observations made on a filament that was split longitudinally into three sections prior to annealing, annealed in air, and then had the core removed by chemical etching. Fig. 8 is a scanning electron micrograph of the interior surface of the boron after the core was removed. The voids in the figure appear to be aligned axially, quite similar to the initial growth characteristics along die marks on the tungsten substrate [1]. This indicates that there is a possible relationship between interfacial void formation, nucleation and growth of the boron deposit and the formation of "proximate voids" [6].

3.5. Structural observations

Electron diffraction studies were conducted in a transmission electron microscope. A thinned boron filament characteristically yielded a pattern of broad haloes describing microcrystalline or "amorphous" boron throughout the bulk material. After annealing and the development of interfacial voids with the fibrils previously described, the diffraction patterns showed that the fibrils consisted of β-rhombohedral boron. This is consistent with earlier observations [12] that "amorphous" boron crystallizes by surface migration and nucleation rather than by nucleation in the bulk. The internal surface created by the voids obviously activated this process. X-ray energy dispersive analysis of this region showed no tungsten, eliminating it as a catalyst for crystallization.

4. Conclusions

Experiments have shown that when boron filaments are heated in an environment containing a reactive species such as oxygen, formation of boron oxide on the surface and subsequent vaporization causes removal of boron atoms from the surface. Removal of this material results in a contraction in the filament which is due to redistribution of internal stresses and anelastic recovery. The magnitude of the contraction observed is far greater than expected, since the sheath material is normally well bonded to the tungsten boride core. Examination of the interior of the filaments showed massive void formation around the core and hence separation of core and sheath.

An empirical relationship was constructed to fit the contraction data, based on an exponential relationship. Activation energies were determined and were reasonable when compared with similar studies. A possible mechanism for the observed phenomena is that there is a net outward diffusion of boron atoms to the surface, and an inward diffusion of vacancies which coalesce at the interface between sheath and core to form the voids. The structure of the vapour-deposited boron (i.e. microcrystalline with crystallite size 2 to 4 mm and highly disordered) is such that it contains many vacancies.

Electron diffraction of fibrils on the void surfaces showed that they were of β-rhombohedral structure, verifying that the "amorphous" or microcrystalline boron crystallizes by surface migration and nucleation rather than by nucleation in the bulk as suggested by Gillespie [12].

Acknowledgment

The authors wish to acknowledge the partial support of the Office of Naval Research.

References

1. F. E. WAWNER, Jr, in "Composite Materials", edited by L. Broutman and R. Krock (Addison-Wesley, Reading, Massachusetts, 1967), p. 244.
2. V. KRUKONIS, in "Boron and Refractory Borides", edited by V. Matkovich (Springer-Verlag, New York, 1977), p. 517.
3. L. LINE and U. HENDERSON, in "Handbook of Fiberglass and Advanced Plastics Composites", edited by G. Lubin (Krieger Publishing Co., Huntingdon, New York, 1969), p. 201.
4. D. BEHRENDT, Calculation of Residual Principle Stresses in CVD Boron on Carbon Filaments, NASA Report TM–81456 (Lewis Research Center, Cleveland, Ohio, USA, 1980).
5. J. DICARLO, Time–Temperature–Stress Dependence of Boron Fibre Deformation, NASA Report TM–X–71908 (Lewis Research Center, Cleveland, Ohio, USA, 1976).
6. J. VEGA-BOGGIO and O. VINGSBO, *J. Mater. Sci.* **11** (1976) 273.
7. J. VEGA-BOGGIO, O. VINGSBO and J. CARLSSON, *ibid.* **12** (1977) 1750.
8. J. EASON, R. JOHNSON and F. WAWNER, *Ceram. Eng. Sci. Proc.* **1** (1980) 693.
9. A. G. METCALFE in "Metal Matrix Composites", edited by K. G. Kreider, Vol. 4 (Academic Press, New York, 1974) p. 269.
10. J. THEBAULT, R. PAILLER, G. BONTEMPS-MOLEY, M. BOURDEAU and R. NASLAIN, *J. Less-Common Metals* **47** (1976) 221.
11. J. DI CARLO and T. WAGNER, Oxidation Induced Contraction and Strengthening of Boron Fibers, NASA Report TM–82599 (Lewis Research Center, Cleveland, Ohio, USA, 1981).
12. J. S. GILLESPIE, *J. Amer. Chem. Soc.* **88** (1966) 2423.

Received 25 March
and accepted 22 April 1985