JOURNAL OF MATERIALS SCIENCE 24 (1989) 1617-1622

Composition and microstructure of silicon carbide whiskers

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The bulk and surface chemistries of four sets of commercially available SiC whiskers made by three manufacturers were determined. The oxygen content varied significantly, ranging in the bulk from 1.9 to 0.6 at.% and on the surface from 35 to 15 at.%. Surface analysis as obtained by X-ray photoelectron spectroscopy also indicated that the oxygen species differed significantly with whisker supplier; each of three of the whisker sets contained a surface species that is very similar to that found in a Si–O–C glass, while one whisker surface appeared to have a silica-rich surface. Surface carbon concentrations varied significantly, while silicon concentrations did not. Scanning transmission electron micrographs indicate significant morphological variations (i.e., twinning, branching, kinks, surface roughness, etc.) occur in all of the whisker types.

1. Introduction

SiC whiskers are being extensively evaluated for ceramic matrix composites. These reinforcements are synthesized by pyrolizing materials containing silica and carbon (e.g. rice hulls). SiC whisker toughened alumina [1–6] has received much of the attention so far; similar composites have been commercialized for machine tool applications.* Work has been performed with mullite [6, 7] and zirconia [8]. The addition of SiC whiskers to toughen and strengthen Si_3N_4 [9–12] is being pursued for high temperature applications. Some differences in surface chemistry have been noted for SiC whiskers from different sources [13, 14]. The chemical and morphological properties of these SiC whiskers would be expected to affect the processing and mechanical properties of the resulting composites. For example, dispersion of whiskers in a slip casting slurry or injection moulding polymer will depend upon the whisker morphology and surface chemistry. Later, during high temperature sintering, hot pressing, and/or hot isostatic pressing processes, both the surface and bulk whisker chemistries may cause the whiskers to interact and react with the sintering aids, silicon nitride, and gas atmosphere. The objective of this work has been to characterize several of the SiC whiskers currently being considered for high temperature Si_3N_4 matrix composite development.

Silicon carbide whiskers are currently available from several manufacturers. In this paper we present the characterization of four sets of whiskers: Tateho Chemical Industries SCW#1 (TA1), Tokai Carbon Co. Tokamax (TK1), Advanced Composite Materials Co. SC-9 (AC1), and Tateho Chemical Industries Co. SCW#1-S (TA2). The whisker types and the dates when they were received are listed in Table I. A number of techniques have been utilized in order to evaluate the chemistry and whisker morphology in order to assist our development of silicon nitride matrix composites.

2. Experimental procedure

Bulk chemical analysis was accomplished through emission spectroscopy. Since this technique can only detect a number of metallic cations, a separate bulk carbon analysis was also performed. The carbon content is obtained by pyrolizing the sample in an oxidizing atmosphere and measuring the amount of CO given off by infrared detection. A similar oxygen fusion analysis (performed by LECO Corp., St. Joseph, Michigan) was used for bulk oxygen determination. Surface analysis was done on a Hewlett-Packard 5950A X-ray photoelectron spectroscopy (XPS) unit. Calibration of the energy scale was accomplished by assigning the most intense carbon peak to SiC.

Scanning transmission electron microscopy (STEM) sample preparation was performed by prewetting a carbon-coated nylon grid with isopropanol, placing a scoop of whiskers onto the grid, and then rewetting the mass with isopropanol. Dried and excess whiskers were removed by gently tapping the tweezers holding the grid. Care was exercized so as not to break or reduce the length of any of the whiskers. The sample was then inserted into a Vacuum Generators HB-5 dedicated STEM for analysis. Some whiskers were examined in cross-section. Ultramicrotomed thin sections were prepared by concentrating the whiskers

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TABLE I Silicon carbide whiskers characterized

Whisker manufacturer	Designation	Date received	Author's symbol
Tateho Chemical Industries Co.	SCW#1	March 1985	TA1
Tateho Chemical Industries Co.	SCW#1-S	April 1986	TA2
Tokai Carbon Co.	Tokamax	May 1985	TK1
Advanced Composite Materials Co. (formerly a division of ARCO Chemical Co.)	SC-9	February 1985	AC1

in acrylic. After trimming the block, thin sections of 90 nm thickness were made. The samples were then examined on the STEM.

Several whisker samples were examined by X-ray diffraction. The whiskers were placed in a rectangular channel in the sample holder (a thin sheet of aluminium) and held in place by two thin pieces of glass placed on either side of the aluminium. Although an effort was made to randomly distribute the whiskers, some preferred orientation was unavoidable. The X-ray diffractometer utilized copper $K\alpha$ radiation

3. Results and discussion

3.1. Chemical analysis

The data from emission analysis, the bulk carbon test, and the bulk oxygen analysis are given in Tables II and III. (No emission analysis was run on the TA2 whiskers.) Whiskers TA1 and AC1 have similar impurities; both manufacturers use rice hulls as a starting material [15, 16]. The TK1 whisker manufacturer, on the other hand, specifies very pure starting materials in their patent [17], and the whiskers are very clean. It should be noted, however, that they do contain rather large amounts of cobalt and titanium. Cobalt is specified in the manufacturer's patent as a possible catalyst. The TK1 and AC1 whiskers contain much more oxygen than either TA1 or TA2 whiskers, while the carbon contents are similar for all of the whisker types.

3.2. Surface analysis

Although there were few major variations in bulk chemical composition, the surface chemistries differed significantly among the whiskers.

TABLE II Emission analysis of silicon carbide whiskers

Element	TA1 whiskers (wt %)	TK1 whiskers (wt %)	AC1 whiskers (wt %)
Ca	0.099	–	0.16
Mn	0.015	< 0.005	0.11
Al	0.12	< 0.05	0.081
Fe	0.045	0.023	0.050
Mg	0.007	< 0.005	0.059
Cr	–	–	< 0.014
Na	< 0.4	< 0.4	< 0.4
Co	–	0.29	–
Zr	0.11	–	–
Ni	< 0.014	< 0.014	< 0.014
Cu	< 0.005	< 0.005	< 0.005
Zn	–	–	< 0.18
Ti	0.090	0.14	–

– indicates that test yielded no trace. Tests were made for V, Sn, Pb, Mo, B, Ba, and Sr, but none of these were detected in any of the three sets of whiskers.
(< X) indicates trace amount below detection limit of X wt %.

High resolution scans were obtained for regions around the carbon 1s, silicon 2p, and oxygen 1s peaks for each of the whisker types as well as for the calcium $2p_{3/2}$, iron $2p_{3/2}$, and tin $3d_{5/2}$ where necessary. Table IV gives the surface compositions for each of the whiskers and the binding energies for the carbon, silicon and oxygen peaks (in parentheses). Two species each of silicon and carbon are present.

As noted earlier, the first carbon peak was assigned the energy (282.4. eV) of carbon in SiC for calibration purposes. The second carbon peak can be attributed to several other possible sources. One is adventitious carbon which is present on most surfaces due to normal exposure to the atmosphere. This binding energy is also similar to that seen for graphite [18]. The second carbon peak is also similar to that observed for XPS analysis of a Si–O–C glass in which the carbon is incorporated into the glassy network [19].

For silicon the lower energy peak was found to correspond to SiC [18], confirming the calibration step. For all but the TK1 whisker sample, the second silicon peak is at an energy that is slightly higher than that seen for the Si–O–C glass [19] and lower than that seen for SiO_2 [18]. As in the bulk analysis, the oxygen levels for TK1 and AC1 whiskers are significantly higher than for the TA1 and TA2 whiskers. Both the oxygen binding energy and the second silicon binding energy peak for the TK1 whiskers were much closer to the values appropriate [18] for SiO_2 than those of the other whiskers, indicating the presence of a more SiO_2-like species.

The surface impurity levels were lowest for the TK1 whiskers. The iron levels in both TA1 and TA2 whisker types were significantly higher than that found in the AC1 type. Iron can be a catalyst in the synthesis of SiC whiskers [16].

3.3. Oxide levels

It is clear from both the bulk analyses and the surface analyses that both TA1 and TA2 whiskers have much lower oxygen contents than either the TK1 or AC1 whiskers. It also appears that the oxide layers for the various whiskers are somewhat different. The TK1

TABLE III Bulk carbon and oxygen analyses

Whisker	Carbon (wt %)	Oxygen (wt %)
TA1	29.2 ± 0.2	0.56 ± 0.4
TK1	28.6 ± 0.2	1.85 ± 0.4
AC1	29.0 ± 0.2	1.40 ± 0.7
TA2	29.1 ± 0.2	0.76 ± 0.1
SiC theoretical value	30.0	–

TABLE IV Surface composition and binding energies from XPS

	TA1 Whiskers at % (eV)	TK1 Whiskers at % (eV)	AC1 Whiskers at % (eV)	TA2 Whiskers at % (eV)
C peak 1	28.1 (282.4)	17.3 (282.4)	16.8 (282.4)	28.9 (282.4)
peak 2	19.7 (284.2)	12.9 (283.9)	12.8 (283.9)	14.6 (284.1)
Si peak 1	27.3 (100.4)	21.4 (100.5)	19.3 (100.5)	29.0 (100.4)
peak 2	8.5 (101.6)	14.7 (103.0)	15.3 (102.2)	8.5 (101.8)
O	14.9 (531.6)	33.7 (532.2)	35.0 (531.6)	17.5 (531.5)
Ca	0.5	–	0.6	0.9
Fe	0.9	–	0.2	0.5
Sn	0.2	–	–	–

For carbon and silicon two peaks are listed. Each peak represents a different atomic species and, hence, are additive.

TABLE V Surface chemistry of whiskers

Whisker type	Oxygen level	Surface oxide resembles
TA1 & TA2	Low	Si-O-C Glass
TK1	High	SiO_2
AC1	High	Si-O-C Glass

surface is very much like SiO_2, while the TA1 and TA2 whiskers seem to have an oxide which resembles that of a Si-O-C glass. The AC1 whisker surfaces have a high oxygen content like the TK1 whiskers, but the oxide resembles a Si-O-C glass like the TA1 and TA2 whiskers. Table V summarizes these results.

The appearance of an oxide similar to that of a Si-O-C glass is not entirely without precedent. Yavuz and Hench [20] reported the formation of an intermediate Si-O-C phase underneath an SiO_2 layer during low temperature (1100° C) oxidation of SiC. Their work was based upon infrared spectroscopy data. The bulk oxygen content of the TK1 whiskers (about 1.85 wt %) is greater than that of the AC1 whiskers (about 1.4 wt %) which in turn is greater than that of either TA1 or TA2 whisker grade (0.5 to 0.8 wt %). If oxidation of the SiC whiskers proceeds by first forming a Si-O-C phase, all of the whiskers may contain this material. Since XPS is only sensitive to the 3 to 10 nm nearest the surface, such an analysis would not see as much Si-O-C phase in a heavily oxidized SiC sample compared to one less oxidized. The fact that these whiskers have differing amounts of Si-O-C surface phase as detected by XPS may merely reflect the relative degrees of oxidation.

3.4. Whisker morphology

The TA1 and TA2 whiskers exhibited the greatest variety of morphologies among all the whiskers studied. The two grades looked very similar, although the extent of the defects was greater for the TA2 whiskers. A general view of the TA1 whiskers is illustrated in Fig. 1. The whisker diameter ranged from 50 to 1000 nm. The majority of the TA1 and TA2 whiskers had smooth, undulating surfaces (Fig. 2). Most of the whiskers exhibited stacking faults normal to the whisker axis (Figs 3a and b), spaced 2 to 20 nm apart. Similar stacking faults were observed by Nutt [21], Comer [22], and Iwanaga *et al.* [23]. The {1 1 1} twins result in double diffraction spots. Faulting similar to the type-b reported by Iwanage *et al.* [23] could also be seen. A number of defects such as distorted structures, branching, and particulate debris were observed. The ultramicrotomed samples illustrated a rather unique defect seen in this manufacturer's whiskers; as depicted in Fig. 4, some of the whiskers were hollow.

The TK1 whiskers consisted of both smooth and contorted or irregular shaped whiskers (Fig. 5). Whisker diameter ranged from 50 to 500 nm. On a few

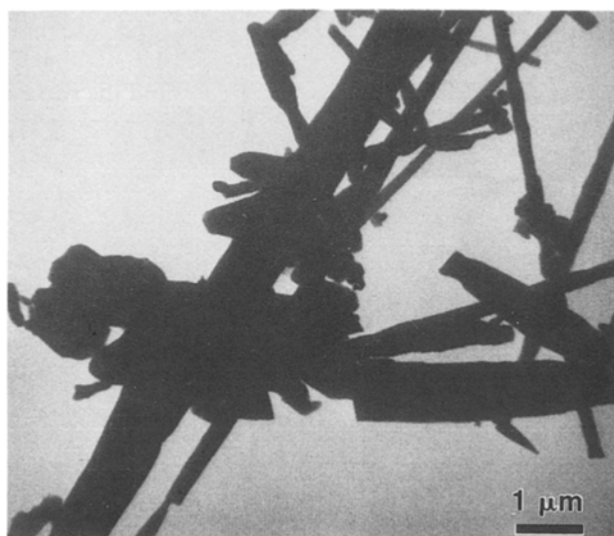


Figure 1 Variety of morphologies for TA1 SiC whiskers.

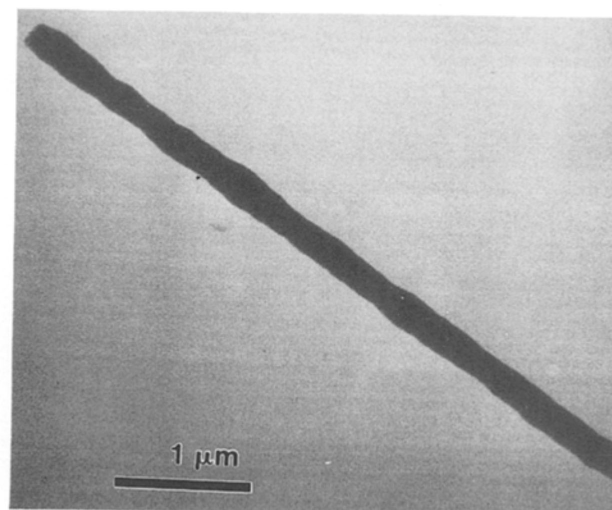
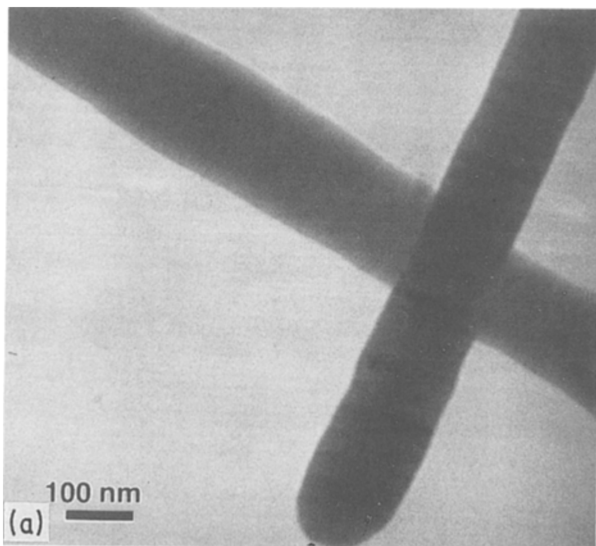


Figure 2 Smooth, undulating surface for TA1 SiC whiskers.



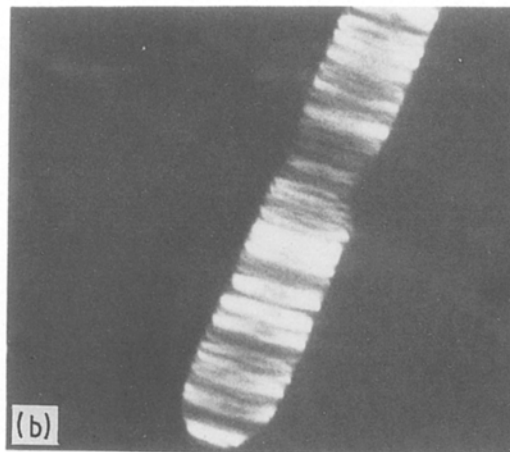


Figure 3 (a) TA1 SiC whiskers with (b) axial dark field. (d-spacing diffraction disk = 0.25 nm).

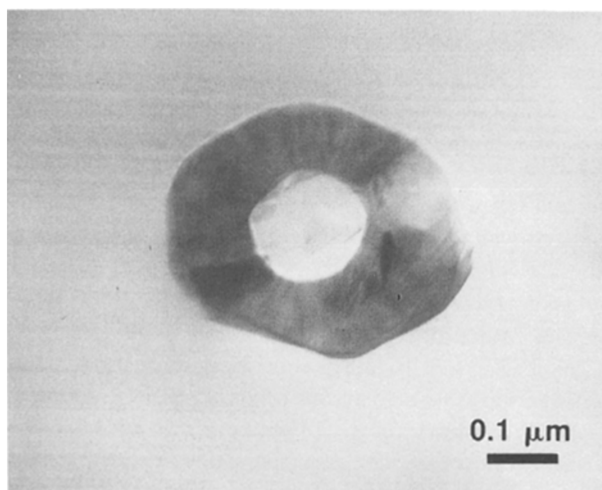


Figure 4 STEM photograph of TA1 whisker cross section.

whiskers a cobalt-rich catalyst particle (20 nm) was found (Fig. 6). Stacking faults were common, but not universal. Particulate and non-crystalline debris could be seen. Some of the whiskers appeared to be hexagonal and (a few) triangular (Figs. 7a and b) when viewed in cross section.

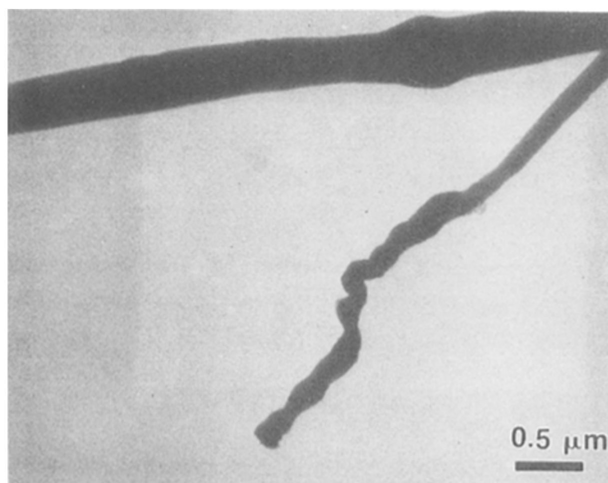


Figure 5 Contorted shapes of TK1 SiC whiskers.

The AC1 SiC whiskers exhibited a variety of morphologies (Fig. 8). Compared to the other whiskers examined, the AC1 whiskers were the straightest and exhibited the fewest defects. Nevertheless, numerous defects could be seen. Surface morphologies varied from a smooth to a knobbly appearance. Diameters of the whisker ranged from 50 to 500 nm. Most of the whiskers contained stacking faults; this included both smooth surfaced whiskers (Figs 9a and b) and those consisting of irregularly stacked SiC lamellae (Figs 10a and b). Many whiskers had a polygonal-shaped tip (Fig. 11) with the sides making an angle of about 60° C. Some debris was present.

3.5. Crystal structure: X-ray diffraction

Comparing the diffraction patterns for the as-received samples, the TK1 whiskers were almost entirely cubic (β-SiC), while both TA1 and TA2 whisker types and, to a lesser extent, the AC1 whiskers contained a minor amount of hexagonal (α-SiC) phase.

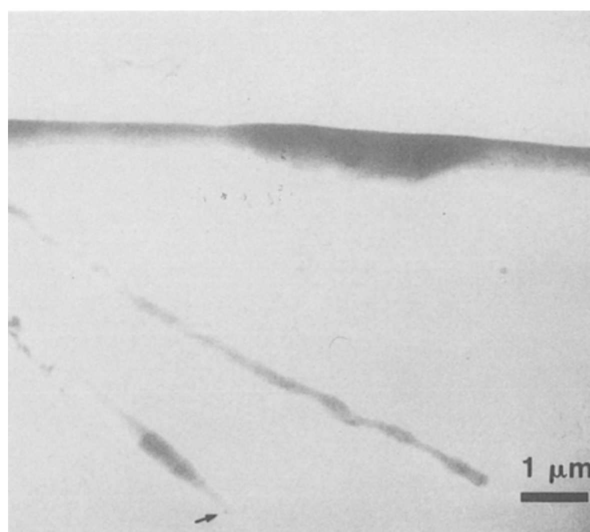
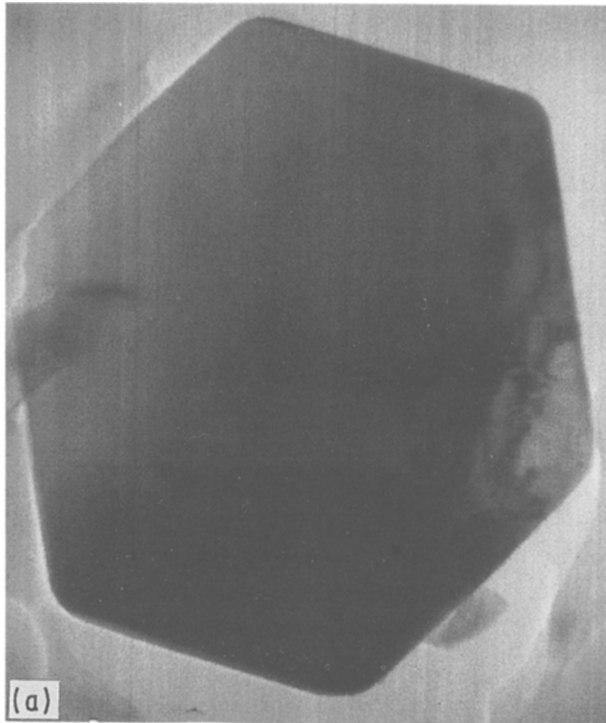


Figure 6 Variations in morphology for TK1 whiskers. The arrow points to a cobalt rich particle.



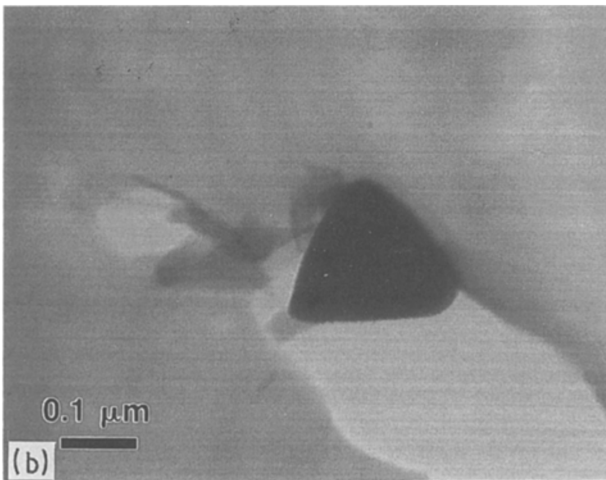


Figure 7 TK1 whiskers with (a) hexagonal and (b) triangular cross sections.

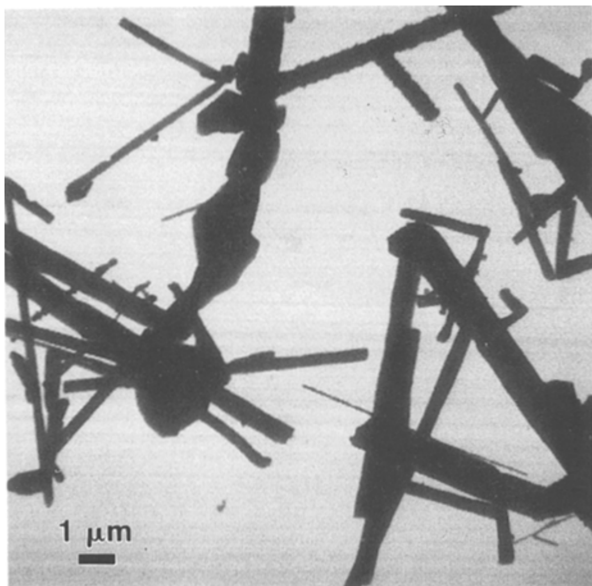
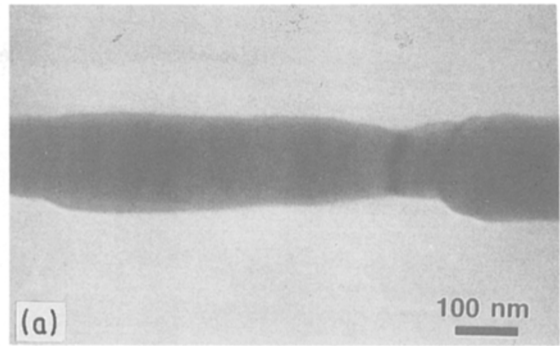


Figure 8 General view of AC1 SiC whiskers.



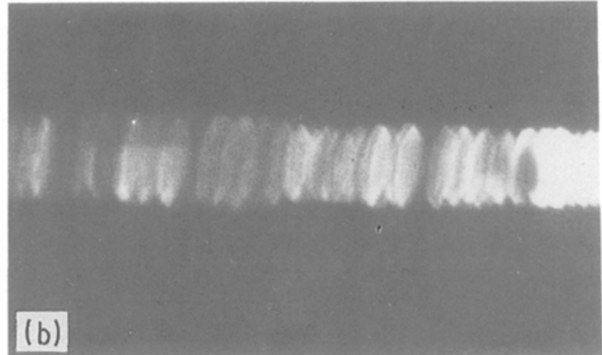


Figure 9 (a) AC1 SiC whisker with (b) axial dark field.

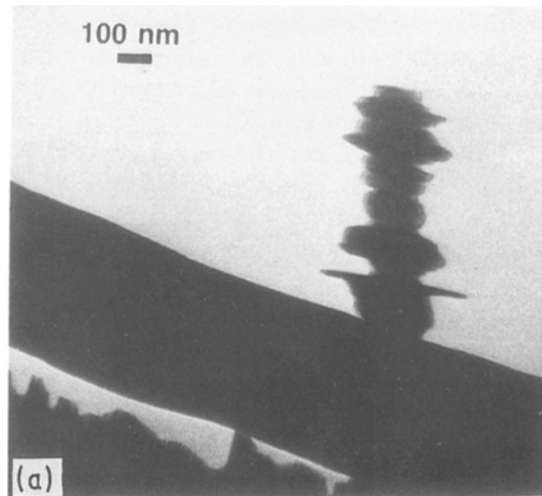


Figure 10 (a) Irregular stacking of SiC lamellae for AC1 SiC whiskers with (b) axial dark field. (d-spacing diffraction disk = 0.24 nm).

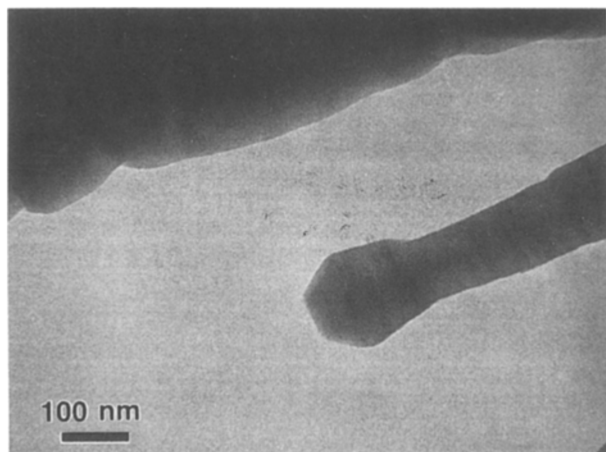


Figure 11 Tip of AC1 SiC whisker.

4. Conclusions

(1) Significant chemical and morphological differences can be seen among commercially available silicon carbide whiskers.

(2) The impurity content of the TK1 whiskers is less than that of the other whiskers, probably due to starting materials with higher purity levels. The TK1 whiskers do, however, contain the largest single impurity – cobalt.

(3) The major differences between the whiskers produced by the three different manufacturers are oxygen content (both bulk and surface) and the surface oxide chemistry. TA1 and TA2 whiskers have less oxygen than AC1 whiskers which have less oxygen than TK1 whiskers. The surface oxides for the TA1, TA2, and AC1 whiskers resemble that of a Si–O–C glass in which the carbon is dispersed on an atomic scale, while the TK1 oxide resembles SiO_2.

(4) Extensive morphological variations have been found in all of the batches of SiC whiskers examined.

Acknowledgements

The authors would like to thank M. A. Vanek for the X-ray diffraction runs, N. L. Dietz for the ultramicrotomy of the whiskers, R. J. Kot for the atomic emission experiments, and J. W. Souza for the XPS runs.

This work was partially supported under ORNL subcontract No. 86X-22008C.

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Received 18 March and accepted 28 July 1988