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# Characterization of recent silicon carbide whiskers

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SiC whisker surface chemistry and morphology can strongly impact composite processing and properties. We report here the surface chemistry and morphology of SiC whiskers received during late 1987 and 1988 from five sources. Comparisons are made with previously characterized whiskers.

## 1. Introduction

SiC whiskers are currently being used for the development of new high-temperature ceramic matrix composites with enhanced toughness. Whisker chemistry and morphology can affect final composite properties and can impact processing [1, 2]. Because the synthesis of these whiskers is in a state of development itself, differences can be seen among products from different manufacturers and among different batches from the same producer [3–11].

In our previous work we have characterized the chemistry and morphology of a number of commercially available SiC whiskers. The results of whisker characterization efforts on a number of recently produced SiC whiskers, designated AM5, AM6, CN1, KS2, LA1, TK3, TK4C, and TK5 are reported here (see Table I). Comparisons are made to whiskers analysed earlier [3, 4], designated AC1, AM1, AM3, AM4, KS1, TA1, and TK1.

## 2. Experimental procedure

Whisker surface chemistry was performed by means of X-ray photoelectron spectroscopy (XPS), using a Hewlett–Packard 5950A XPS. Calibration of the energy scale was accomplished by assigning the most intense carbon peak to SiC. Normally, a broad-energy low-resolution "survey scan" is taken to determine where peaks are located. This is followed by narrow-width high-resolution scans about the peaks observed in the survey scan. The data presented here are taken from these higher accuracy scans.

For scanning transmission electron microscopy (STEM) sample preparation, a carbon-coated copper

TABLE I

| SiC whisker | Supplier | Date received |
|---|---|---|
| AC1 – ACMC SC-9 | Advanced Composite Materials Co. (ACMC), formerly ARCO Chemical Co. | February 1985 |
| AM1 | American Matrix Co. | February 1987 |
| AM3 | American Matrix Co. | September 1987 |
| AM4 | American Matrix Co. | December 1987 |
| AM4C | American Matrix Co. with manufacturer-applied carbonaceous surface layer | December 1987 |
| AM5 | American Matrix Co. | March 1988 |
| AM6 | American Matrix Co. | June 1988 |
| CN1 – SCW-0011 | Alcan | August 1988 |
| KS1 | Kobe Steel | August 1987 |
| KS2 – W880104-RT | Kobe Steel | August 1988 |
| LA1 – VLS | Los Alamos National Lab | August 1988 |
| TA1 – Tateho SCW no. 1 | Tateho Chemical Industries | March 1985 |
| TK1 – Tokai Tokamax | Tokai Carbon Co. | May 1985 |
| TK3 – Grade 3 | Tokai Carbon Co. | March 1988 |
| TK4C – Grade 4 | Tokai Carbon Co. with manufacturer-applied carbonaceous surface layer | March 1988 |
| TK5 – Lot 30301 | Tokai Carbon Co. | April 1988 |

0022–2461/91 $03.00 + .12 

TABLE II American Matrix SiC whisker XPS data. B.E. = binding energy

| Species | AM6 | | AM5 | | AM4C | | AM4 | | AM3 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | at. % | B.E. (eV) | at. % | B.E. (eV) | at. % | B.E. (eV) | at. % | B.E. (eV) | at. % | B.E. (eV) |
| Si peak 1 | 33.1 | 100.4 | 15.9 | 100.5 | 18.9 | 100.5 | 17.9 | 100.5 | 12.2 | 100.3 |
| Si peak 2 | 6.2 | 101.7 | 17.3 | 103.2 | 2.4 | 101.9 | 14.6 | 103.3 | 19.2 | 103.5 |
| C peak 1 | 34.4 | 282.4 | 13.6 | 282.4 | 16.3 | 282.4 | 15.9 | 282.4 | 10.2 | 282.4 |
| C peak 2 | 8.6 | 284.1 | 2.8 | 283.9 | 35.3 | 284.5 | 4.8 | 284.6 | 7.0 | 284.3 |
| C peak 3 | | | 1.9 | 285.3 | 6.1 | 286.9 | | | | |
| O peak 1 | 11.6 | 531.9 | 8.1 | 531.3 | 18.3 | 532.6 | 44.6 | 532.4 | 51.4 | 532.6 |
| O peak 2 | | | 37.5 | 532.4 | | | | | | |
| Ca peak | 1.0 | 349.0 | 1.7 | 347.9 | 1.3 | 348.6 | 1.2 | 347.8 | | |
| Mg peak | | | 1.2 | 50.6 | | | | | | |
| Fe peak | 0.4 | 713.5 | | | | | | | | |
| N peak 1 | | | | | 0.8 | 397.9 | 0.8 | 397.8 | | |
| N peak 2 | | | | | 0.6 | 400.3 | 0.2 | 400.2 | | |
| F peak | 4.7 | 685.8 | | | | | | | | |

TABLE III Alcan and Kobe Steel SiC whisker XPS data

| Species | KS2 | | KS1 | | CN1 | |
|---|---|---|---|---|---|---|
| | at. % | B.E. (eV) | at. % | B.E. (eV) | at. % | B.E. (eV) |
| Si peak 1 | 23.5 | 100.4 | 18.6 | 100.6 | 32.0 | 100.5 |
| Si peak 2 | 10.9 | 101.7 | 17.6 | 102.7 | 6.4 | 101.9 |
| Si peak 3 | 2.7 | 103.1 | | | | |
| C peak 1 | 31.1 | 282.4 | 15.9 | 282.4 | 31.5 | 282.4 |
| C peak 2 | 5.5 | 283.8 | 4.8 | 283.7 | 6.2 | 284.1 |
| C peak 3 | 2.9 | 285.4 | | | | |
| O peak | 21.4 | 531.5 | 43.2 | 531.8 | 19.2 | 531.8 |
| Ca peak | | | | | 0.4 | 346.9 |
| Fe peak | 0.7 | 712.5 | | | 0.3 | 710.8 |
| Ni peak 1 | 0.8 | 855.0 | | | | |
| Ni peak 2 | 0.6 | 860.4 | | | | |

TABLE IV General surface chemistry categories

| Category | Description |
|---|---|
| A | Whiskers such as the TK1 have a high surface oxygen level, and the oxide resembles $SiO_2$ |
| B | Whiskers such as the TA1 have a low surface oxygen level, and the oxide resembles a Si–O–C glass |
| C | Whiskers such as the AM1 have a carbonaceous hydrocarbon surface |
| D | The AC1 whisker had a high oxygen level surface, and the oxide resembles a Si–O–C glass |

grid was pre-wet with isopropanol. A scoop of whiskers was placed on to the grid and isopropanol was again applied. After drying, excess whiskers were removed by gently tapping the tweezers holding the grid. The sample was then inserted into the STEM. A VG HB-5 dedicated STEM was used.

XPS was run on the AM5, AM6, CN1, and KS2 whiskers. TK3, TK4C, and TK5 whiskers were not characterized by XPS, because it was not believed that their morphology warranted further study (for the present applications). The LA1 whiskers are available in such small quantities (and this will continue) that we limited their analysis.

STEM analysis was performed on the AM5, CN1, KS2, LA1, TK3, TK4C, and TK5 whiskers. The AM6 whiskers differed little from the AM5 morphologically.

## 3. Results and discussion

### 3.1. Surface chemistry

The surface chemistries of the AM5 and AM6 are given in Table II along with data for the AM4, AM4C, and AM3 whiskers analysed earlier. The XPS results for the CN1 and KS2 SiC whiskers are given in Table III as well as data for the KS1 whisker characterized earlier.

In our previous whisker characterization work [3, 4] we have found that the major component

TABLE V Major component XPS data for SiC whisker examples

| Species | TK1 | | TA1 | | AM1 | | AC1 | |
|---|---|---|---|---|---|---|---|---|
| | at. % | B.E. (eV) | at. % | B.E. (eV) | at. % | B.E. (eV) | at. % | B.E. (eV) |
| Si peak 1 | 21.4 | 100.5 | 27.3 | 100.4 | 18.9 | 100.5 | 19.3 | 100.5 |
| Si peak 2 | 14.7 | 103.0 | 8.5 | 101.6 | 2.4 | 102.8 | 15.3 | 102.2 |
| C peak 1 | 17.3 | 282.4 | 28.1 | 282.4 | 20.4 | 282.4 | 16.8 | 282.4 |
| C peak 2 | 12.9 | 283.9 | 19.7 | 284.2 | 26.6 | 284.7 | 12.8 | 283.9 |
| C peak 3 | | | | | 13.8 | 286.6 | | |
| O peak | 33.7 | 532.2 | 14.9 | 531.6 | 16.9 | 532.4 | 35.0 | 531.6 |
| Whisker surface Chemistry category | A | | B | | C | | D | |

Note: total percentages shown may be less than 100 due to presence of impurity species which are not shown.

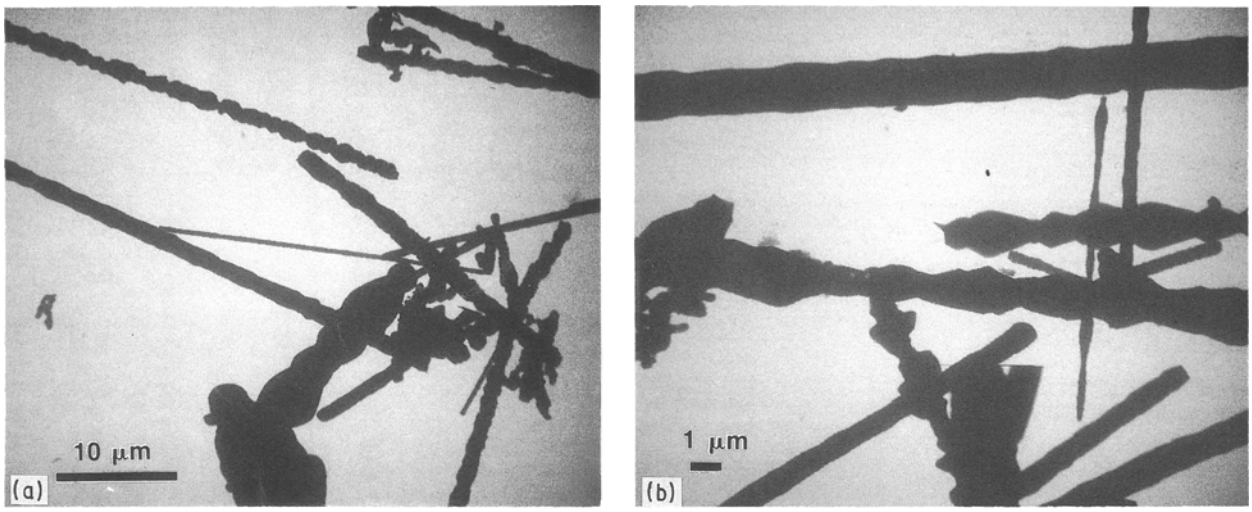



*Figure 1* (a, b) AM5 SiC whisker morphology.

surface chemistries can be classified into four groups (Table IV). As examples, the XPS results for the TK1, TA1, AM1, and AC1 SiC whiskers are given in Table V. Only the major components (silicon, oxygen and carbon) are presented in this table.

The AM5, AM4, and AM3 whiskers are very similar and fall in category A. They all exhibit significant amounts of surface $SiO_2$. The silicon and carbon contents attributable to SiC (first silicon and carbon peaks) are low. The second silicon peak is dominated by the $SiO_2$, while the small amount of carbon in the second and third carbon peaks probably indicates the presence of some Si–O–C glass. The AM6 whiskers had been given a treatment by the manufacturer to reduce surface $SiO_2$. This treatment clearly had a significant effect upon the AM6 surface chemistry, as the whisker falls in category B. The oxygen level is one of the lowest that we have observed on SiC whiskers. Silicon and carbon contents corresponding to SiC are high with the remaining silicon and carbon species attributable to Si–O–C.

Calcium is clearly a common impurity for the AM manufacturer. Magnesium was noted only on the AM5 whisker. The sizable fluorine level on the AM6 whisker is consistent with an HF-based etch to remove $SiO_2$. This removal may have uncovered some remnant catalyst as indicated by the iron impurity.

The major component (silicon, carbon, oxygen) surface chemistries of the KS2 and CN1 whiskers are very similar, although the KS2 whisker surface is slightly more oxygenated. Both fall into category C. However, the oxygen levels are slightly higher than we have seen for other whiskers in this category. The surface of the KS2 whisker is quite different from that of the earlier KS1 whisker. The KS1 surface was dominated by $SiO_2$ and fell into category A.

Both the KS2 and CN1 whiskers have significant amounts of iron and/or nickel surface impurities. The surface nitrogen content of the CN1 whiskers is sizeable. It may indicate bulk nitrogen content, and, if so, this might increase the electrical conductivity of the whiskers (extrinsic conductivity of a semiconductor, SiC, due to an impurity).

## 3.2. Morphology

The morphology and size of the AM5 whiskers (Fig. 1) was similar to the AM4 analysed earlier. Diameters ranged from 0.2 to 5 μm with the average being a little less than 1 μm. Whisker lengths varied from 5 to 50 μm. As in the past, the knobbly surface morphology was dominant; the irregularities tended to match the stacking faults (Fig. 2). For AM5 there seemed to be a greater fraction of smooth surfaced whiskers than for previous sets. Whiskers tended to be straight although there were some branched and bent whiskers. Whisker tips tended to be blunt (Fig. 3). (They were more rounded, however, than, for example, the AC1 whisker tips.) Some debris was present, and the amount was similar to that of AM4. A few 10 nm Fe–Ni–Ca particles were found attached to the whisker (Fig. 4). Calcium-rich particles were typically found as unattached debris.

A wide variety of morphologies was found for the CN1 SiC whiskers (Fig. 5). The whiskers were generally straight, but there were some contortions and

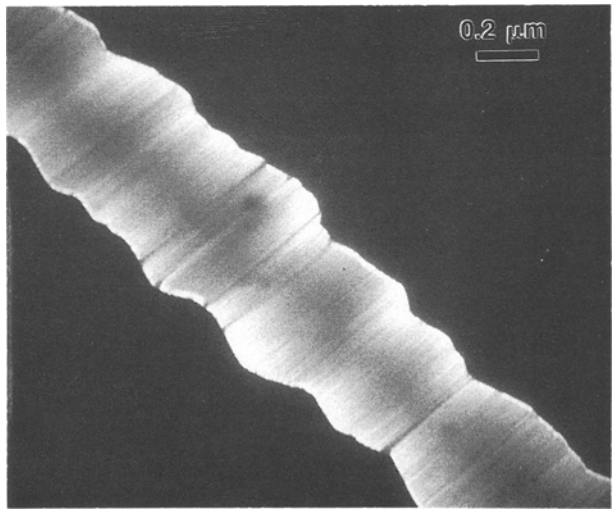



*Figure 2* Stacking faults matching surface irregularities in AM5 whisker. (*d*-spacing diffraction disc = 0.24 nm.)

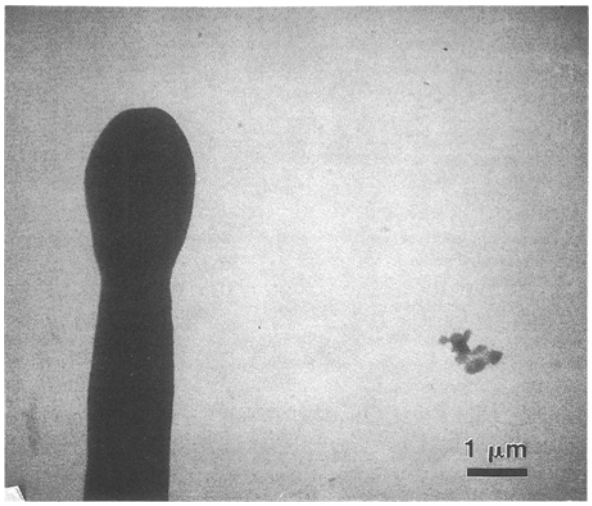



*Figure 3* Blunt tip end for AM5 whisker. Note calcium-rich particle on the right.

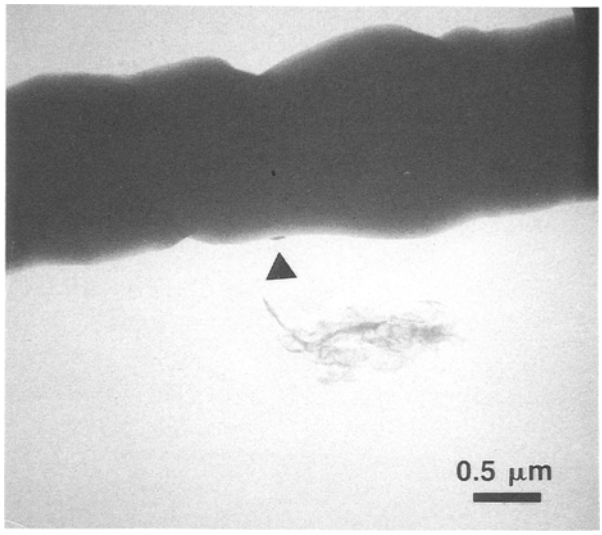



*Figure 4* Fe–Ni–Ca particle (arrow) on AM5 whisker. Particle off whisker is calcium-rich.

many had varying diameters (Fig. 6). Also fairly common was a shish-kebab (Fig. 7) morphology. Much debris was present as well (Fig. 8). Whisker diameters ranged from 0.1 to 2.5 μm, and some lengths were over 100 μm. Most of the whiskers had stacking-fault-type defects; occasionally a calcium impurity particle would be associated with disruption of the stacking faults (Fig. 9). Morphologically, the CN1 whiskers appear to be in an early stage of development.

The large variety of morphological whisker shapes seen in the earlier KS1 version has been reduced in the KS2 whisker. In general the whiskers are fairly straight (Fig. 10) with only a few irregularly shaped whiskers (Fig. 11). Diameters ranged from 0.1 to 5 μm. The longest observed whisker was 30 μm. The amount of debris has been reduced from that seen in the KS1. Nickel-rich particles were found (Fig. 12) as well as Raney-like nickel-rich particles (Fig. 13). Presumably the nickel was being used as a catalyst. Both Iwanga-type stacking faults were present, sometimes on the same whisker (Fig. 14). The KS2 SiC whiskers have an improved morphology but further development would be beneficial. In particular, longer whiskers and elimination of the nickel catalyst would be highly desirable.

The LA1 SiC whiskers were generally straight and quite long. Diameters ranged from 0.25 to 5 μm (Fig. 15). Many of the whiskers had lengths in excess of 100 μm. Some variation in diameter was noted (Fig. 16). Impurity particles of iron, nickel and cobalt were observed at the end of some whiskers (Fig. 17). Similar morphology was reported by Milewski *et al.* [12] for whiskers grown by the vapour–liquid–solid (VLS) process using stainless steel particles as the catalyst. Stacking faults were noted for most whiskers but gaps between some stacking faults were quite common (Fig. 18). Because of the whisker lengths, dispersion of the whiskers during sample preparation was a problem. A similar agglomeration problem might occur when mixing the whiskers with the $\alpha$-$Si_3N_4$ powder. The iron impurities need to be eliminated.

The TK3 and TK4C SiC whiskers had very similar morphologies. Because the TK4C whiskers were

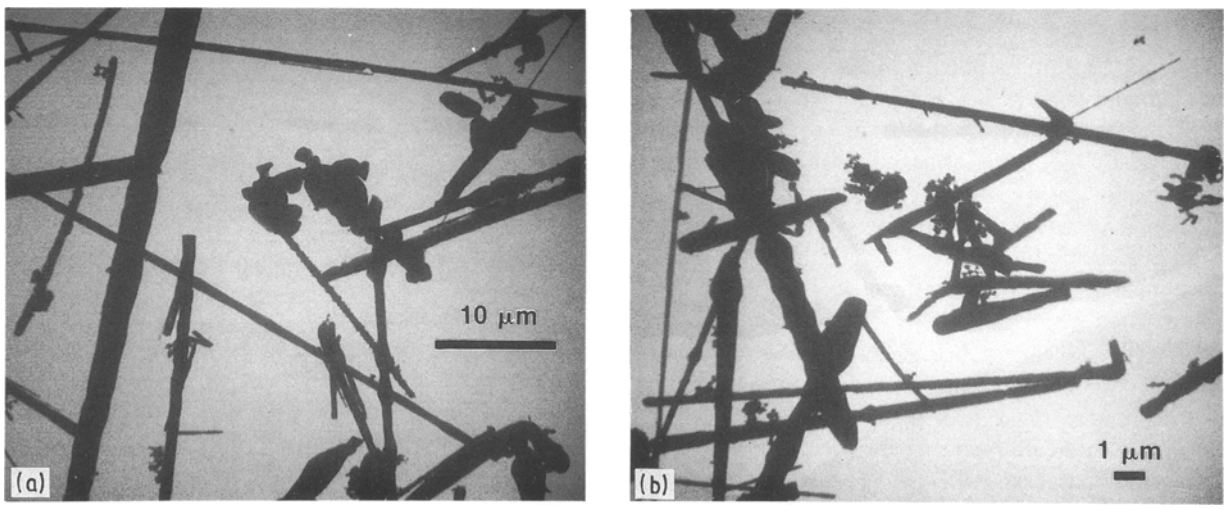



*Figure 5* (a, b) Morphology of CN1 whiskers.

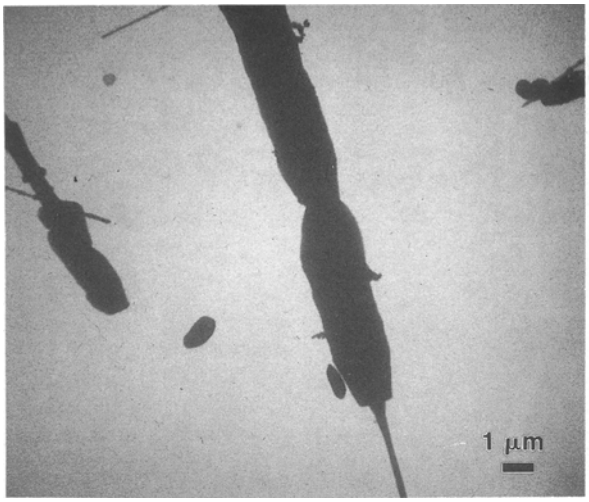



*Figure 6* Variation in diameter of a CN1 whisker.

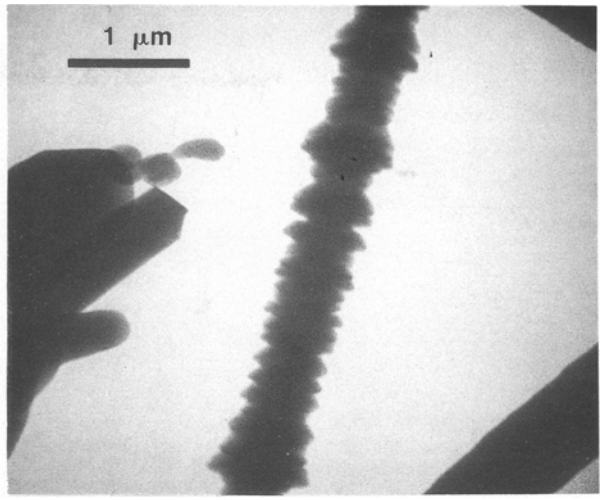



*Figure 7* Shish-kebab morphology in a CN1 whisker.

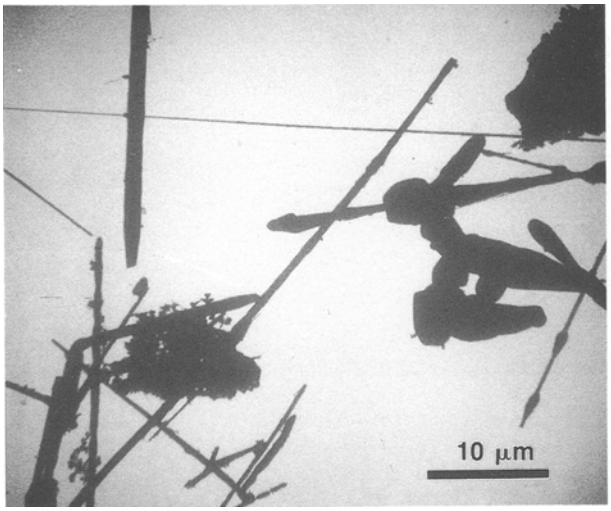



*Figure 8* Debris in CN1 whiskers.

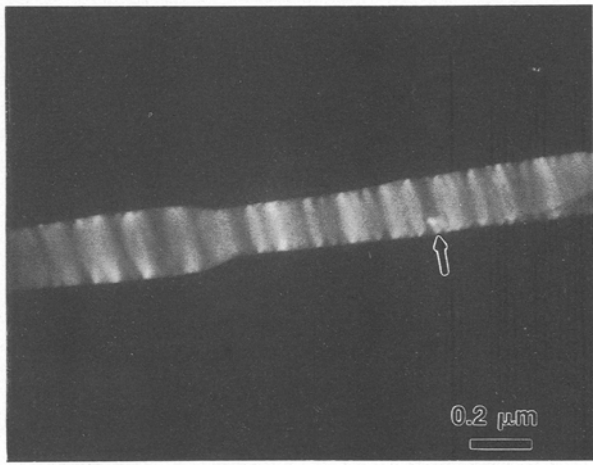
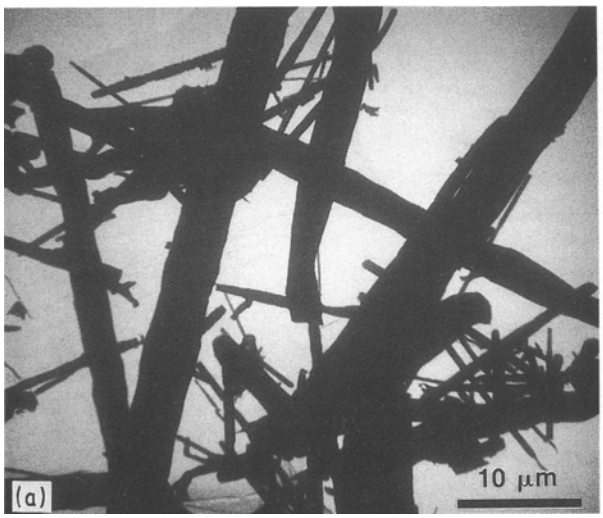



*Figure 9* Stacking faults in CN1 whisker; arrow points to calcium-rich impurity. (*d*-spacing diffraction disc = 0.15 nm.)



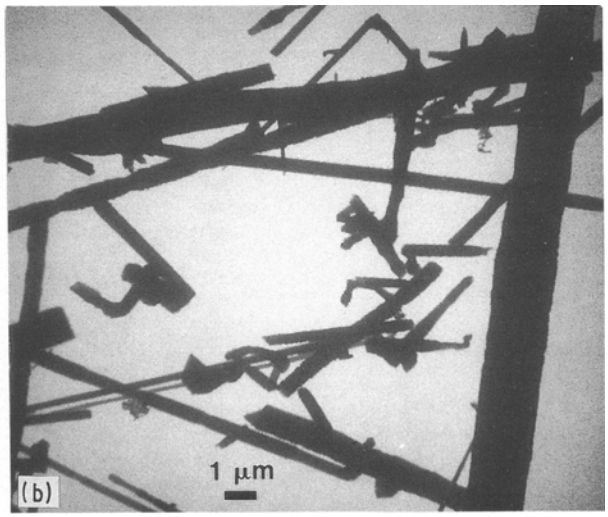




*Figure 10* (a, b) Morphology of KS2 whiskers.

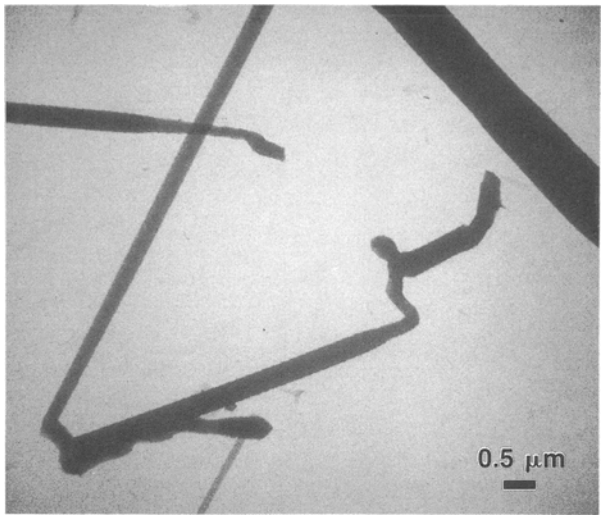



*Figure 11* Contorted morphology of some KS2 whiskers.

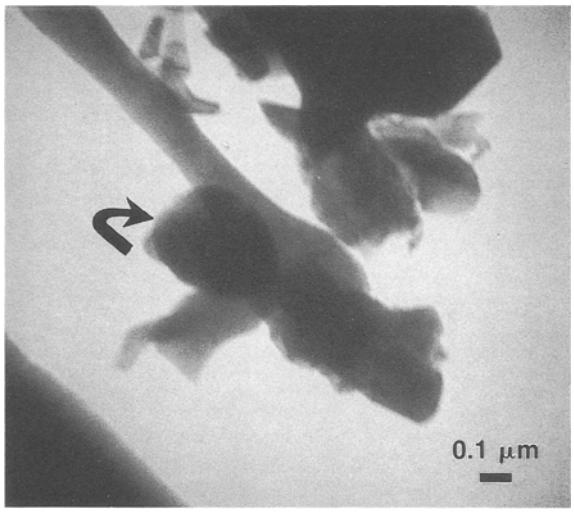



*Figure 12* $Ni_{95}Co_5$ particle (arrow) associated with KS2 whisker.

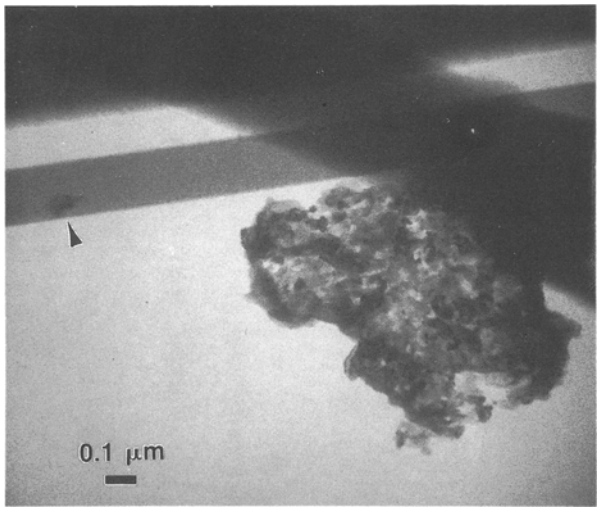



*Figure 13* Nickel particle (arrow) and Raney nickel catalyst on whisker. A trace of iron was detected in the Raney particle.

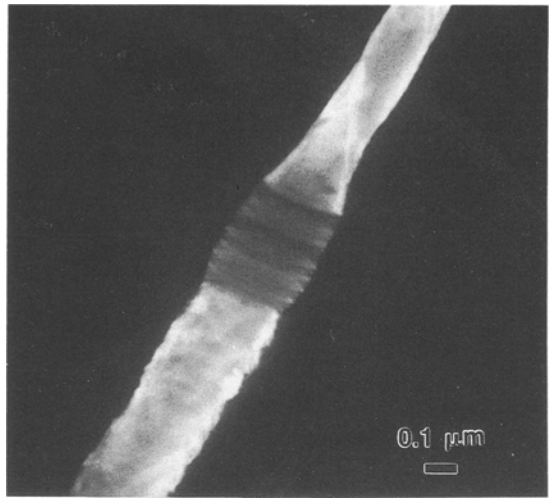



*Figure 14* Both types of Iwanga stacking faults in KS2 whisker (*d*-spacing diffraction disc = 0.15 nm.)

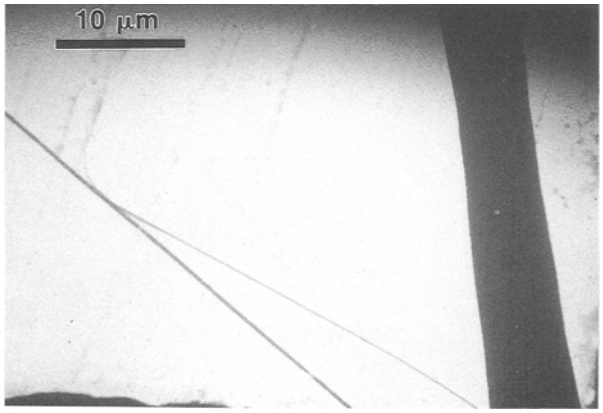



*Figure 15* Morphology of LA1 whiskers.

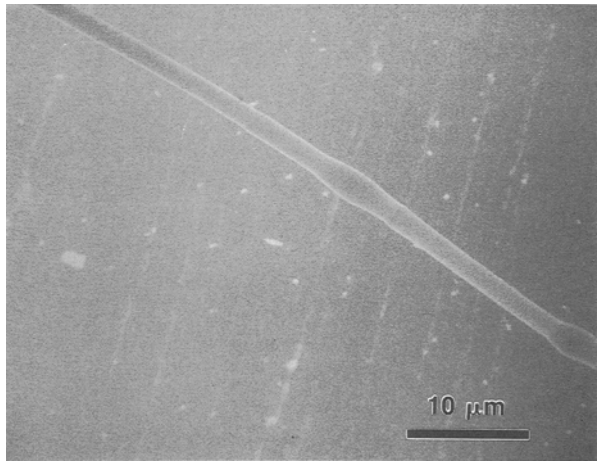



*Figure 16* Variation in diameter in LA1 whisker.

specified to have a 5.5 nm carbon coating, the TK4C whisker may have been a coated version of the TK3 whisker. One concern with coatings is how uniform they are; for example, are there some regions which are much more thickly coated than others? We were unable to resolve the coating layer on the TK4C whisker, indicating that we saw no regions which had coating thicknesses much greater than the 5.5 nm

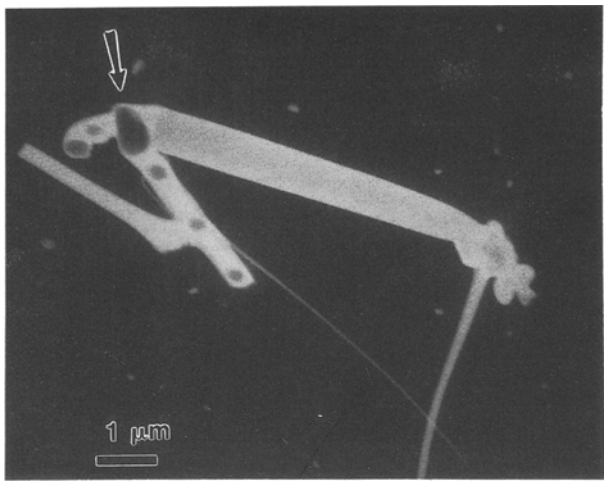



*Figure 17* Impurity particles (arrow) on LA1. Annular dark-field microscopy. (41.6 at. % Si, 29.9 at. % Fe, 16.1 at. % Co, 13.3 at. % Ni.)

specified. Fig. 19 shows the general morphology of the TK4C whiskers. Fig. 20 gives a more highly magnified view of some TK3 whiskers. These whiskers resemble the earlier TK2 version. Although they may appear to be fairly straight at low magnification, closer examination reveals that they have a warped and twisted morphology. Diameters range from 20 nm to 0.6 μm. Lengths are between 5 and 100 μm. A small amount of particulate debris was observed. We saw a few whiskers that had remnant cobalt-based catalyst particles attached.

The TK5 SiC whiskers tended to be irregularly shaped (Fig. 21). Whisker diameters of 0.2 to 2 μm with lengths up to 100 μm were observed. These whiskers were larger in diameter than the TK3 and TK4C. A fair amount of micrometre-sized debris was present (Fig. 22). Most of the TK5 SiC whiskers had a type-a defect structure (Fig. 23). Catalyst particles rich in

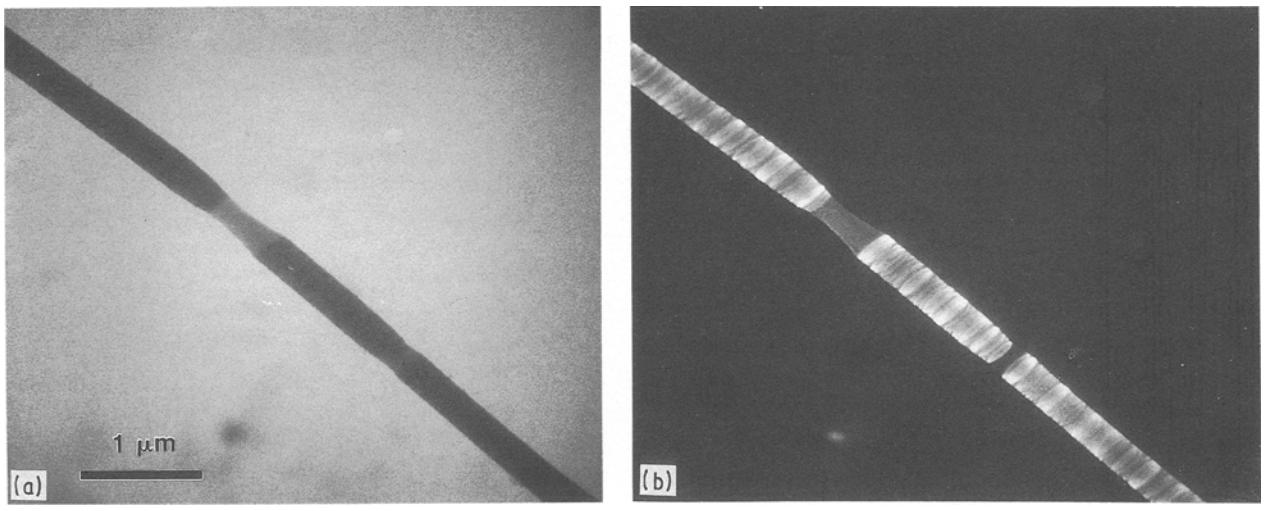



*Figure 18* (a, b) Variation in stacking faults for LA1 whisker. (*d*-spacing diffraction disc = 0.25 nm.)

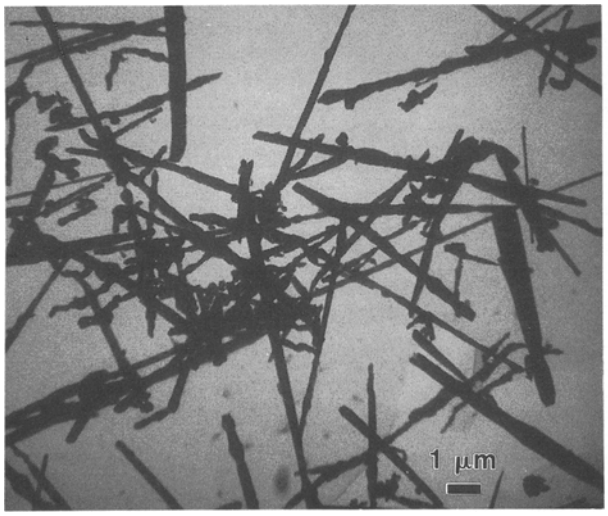



*Figure 19* Morphology of TK4C whiskers.

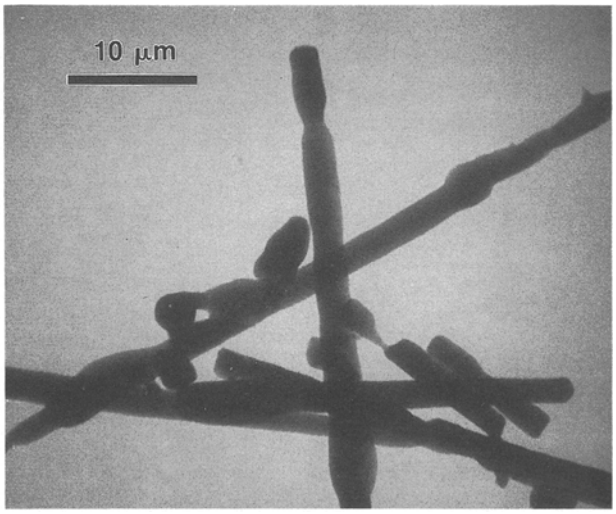



*Figure 20* Morphology of TK3 whiskers.

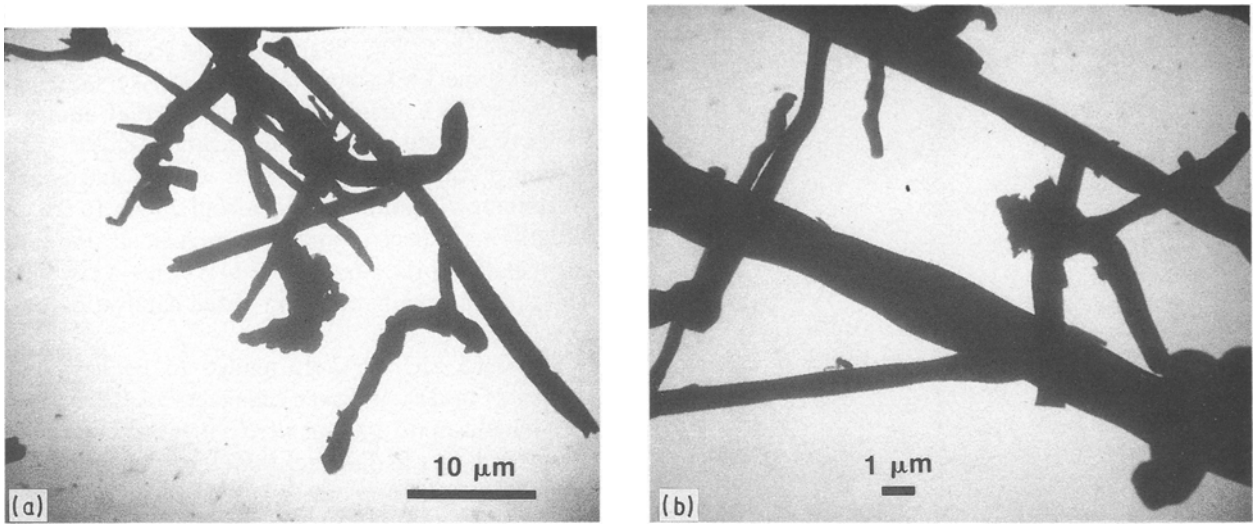



*Figure 21* (a, b) Morphology of TK5 whiskers.

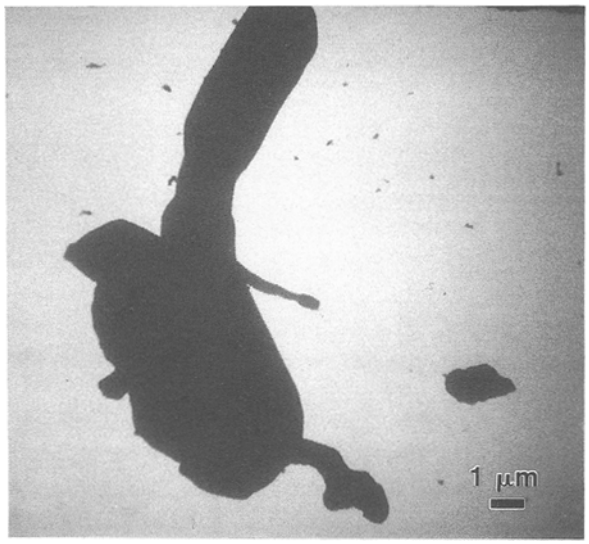



*Figure 22* Debris present on TK5.

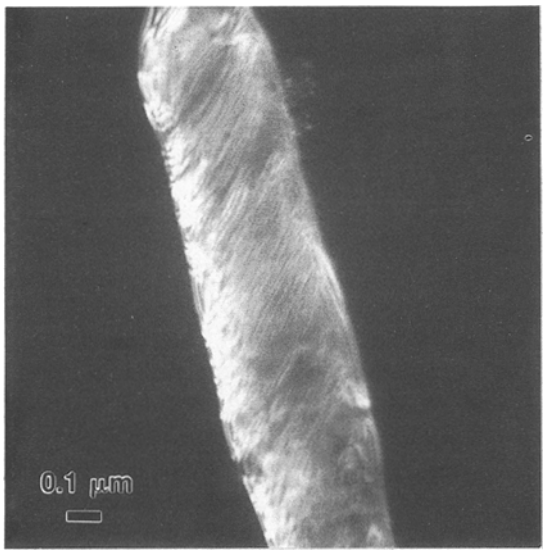



*Figure 23* Type-A defect structure in TK5 whisker. (*d*-spacing diffraction disc = 0.22 nm.)

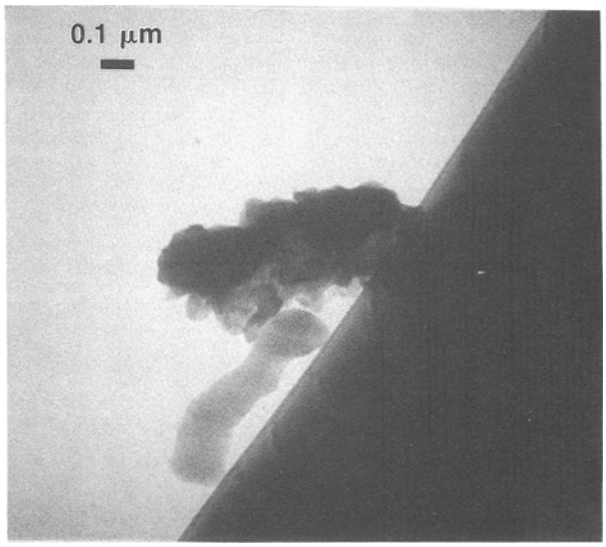



*Figure 24* Catalyst particle $Co_{95}Fe_5$ attached to the side of a TK5 whisker.

cobalt were found attached to the sides of a few whiskers (Fig. 24). These whiskers have been improved over earlier versions, but they still have a substantial fraction of irregularly formed whiskers.

## 4. Conclusions

Two of the manufacturers of whiskers examined here have been providing whiskers for some time. The morphology of the AM5 and AM6 whiskers is little changed from the past, but this manufacturer has shown that it can vary the surface chemistry. The TK3, TK4C, and TK5 all show morphological defects similar to those seen in previous versions. Although we did not perform surface chemistry analyses on these recent samples, it appears that they also can provide whiskers with different surface chemistries.

The relatively new whiskers, the KS2 and CN1, are generally straight. The KS2 whiskers are among the shortest available, and the Fe/Ni level on the surface is

quite high. The major drawback for the CN1 whiskers in comparison with the KS2 whiskers is that they have much more debris. The major component surface chemistries of both of these whiskers are fairly low in oxygen content.

The LA1 whiskers have an excellent morphology, as expected. If they would ever become available for a cost comparable to the other whiskers, they would probably be an excellent choice. One concern is the presence of catalyst particles. Another potential problem is agglomeration.

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