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Formation of Titanium Nitride Whiskers by Reaction of Sodium Titanium Bronze with Molten Sodium Cyanide

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The production of titanium nitride, TiN, whiskers by reaction of sodium titanium bronze, Na_xTiO_2 (STB), with excess sodium cyanide, NaCN, at 1000°C is reported. The solubility of Ti from a STB in molten NaCN has been estimated experimentally. The TiN whiskers obtained under different experimental conditions have been examined by scanning electron microscopy and analyzed by analytical electron microscopy. [Key words: whiskers, titanium nitride, formation, chemistry.]

I. Introduction

TITANIUM NITRIDE, TiN, is a material of promising technological importance because it has a high melting point (2950°C), high hardness (8 to 9 on the Mohs scale), and high electrical conductance. It is stable at high temperatures in inert atmospheres, but air, oxygen, and oxidizing acids (e.g., HNO_3) convert TiN into TiO_2 above ambient temperature. Thermochemical calculations indicate that TiN should be compatible with SiC, Al_2O_3, or ZrO_2; it should also be stable toward Si_3N_4 and TiB_2. These materials (SiC, Si_3N_4, Al_2O_3, ZrO_2, etc.) are presently gaining importance in high-temperature applications; however, applications such as internal combustion engines could be expanded if the strength of the fabricated parts could be increased. One method for imparting more strength to ceramic objects is to make composites of the matrix materials with whiskers.

The literature on TiN whiskers shows that their preparation is essentially based on one set of reagents: $TiCl_4$, N_2, and H_2. The reaction of gaseous $TiCl_4$ with N_2 and H_2 has been used at 1400°C by Aivazov and Melekhin[1] for growing large, millimeter-sized crystals of TiN. Kato and Tamari[2] used the same reactants at 1200° to 1300°C to grow TiN "needle crystals," very likely whiskers, on graphite plates. Sugiyama *et al.*[3] studied the effect of Au droplets on the growth of TiN whiskers on quartz surfaces. The reactants consisted of a mixture of $TiCl_4$, N_2, and H_2, and whisker growth was detected at 1050° to 1065°C. Bojarski *et al.*[4] have studied the morphology of TiN whiskers formed on a W substrate by gaseous mixtures of $TiCl_4$, N_2, and H_2 at temperatures above 1300°C.

In general, all of the above-mentioned researchers observed stringent purity requirements for the gases employed. The effect of impurities in the system, except for the finding that graphite substrates act as a source of contamination,[5] does not seem to have been studied. Kamiya *et al.*[6] have recently reported on the preparation of TiN fibers (presumably polycrystalline) by the nitridation with NH_3 of TiO_2 fibers prepared by a sol–gel method; for a 5-h exposure to NH_3, the nitriding reaction started at 900°C and was complete at 1100°C.

Based on our earlier work on the production of TiN powders by reacting NaCN, sodium cyanide, at ≈1000°C with several Ti compounds (TiO_2,[7] TiP_2O_7, $(TiO)_2P_2O_7$, $NaTi_2(PO_4)_3$, and $Na_4(TiO)(PO_4)_2$[8]), it was decided to extend the study of such reactions to include sodium titanium bronze, Na_xTiO_2 (STB). This species occurs as crystalline, nonstoichiometric phases containing Na, O, and Ti, the latter in more than one oxidation state, e.g., Ti^{3+} and Ti^{4+}. Their composition can be visualized as if in TiO_2 some Ti^{4+} has been replaced by an equiatomic number of Ti^{3+} and Na^+.[9] Testing the reaction of NaCN with STB was motivated by the finding of STB among the products of earlier reactions with Ti compounds.[7,8] When STB was reacted with NaCN, it was surprisingly found that, under some conditions, the TiN formed had the morphology of needles or whiskers. Because of the technological importance of ceramic whiskers, their formation from molten NaCN was studied and is reported here.

II. Reaction of STB with NaCN

Preparations of Na_xTiO_2 (with $x = 0.18$ to 0.25)[9] were reacted with different amounts of NaCN at high temperatures under flowing N_2 for periods ranging from 16 to 67 h. The container materials used, in the shape of crucibles or boats, were alumina, BN, vitreous carbon, and graphite. They were placed in Ni or fused silica apparatuses provided with a thermocouple well and gas inlet and outlet ports. The silica apparatus, used in exploratory tests, was attacked by the NaCN and Na_2C_2 and cracked and crumbled on cooling in a manner similar to that reported in Ref. 10. Thus, the majority of the reactions were performed using the Ni apparatus.

The effects of the following variables were examined: temperature, time of reaction, and the ratio NaCN/Ti. It was found that for a 20-h reaction time, temperatures below 1000°C were not satisfactory; i.e., not all the bronze was converted to TiN. At 1000°C the conversion was generally complete and yielded a mixture of whiskers with some powder. The effect of time at temperature was examined cursorily at ≈1000°C because it had been observed that the amount of whiskers, determined visually with an optical microscope, was dependent on the total amount of bronze–NaCN loaded and the duration of the reaction. Typically, mixtures containing 0.2 g of bronze were converted to TiN whiskers in 17 h; larger amounts of bronze, e.g., 0.3 to 0.4 g, required 40 h or more. The container material had no effect on whether or not whiskers were obtained; however, it was noted that "high-fired" alumina and BN were, respectively, somewhat corroded and exfoliated by the treatment with NaCN. Vitreous carbon was the best container material among those used in this work. The most significant variable was the ratio NaCN/Ti; values of 4 yielded only a small fraction of whiskers with the balance being mainly TiN powder, whereas values in the neighborhood of 20 yielded the largest fraction of whiskers.

III. Characterization of the TiN Whiskers

Because the various preparations of TiN whiskers varied between golden and brown, we thought that this could be indicative of changes in composition. After reviewing the available literature,[2,5,11] we concluded that there is no relationship between the color of TiN and its composition.

A lack of agreement on the lattice parameter (a_0) of TiN is also apparent in the literature; this is illustrated in a compilation of X-ray diffraction (XRD) data listing values of a_0 for TiN which range from 4.230×10^{-1} to 4.249×10^{-1} nm (4.230 to 4.249 Å).[12]

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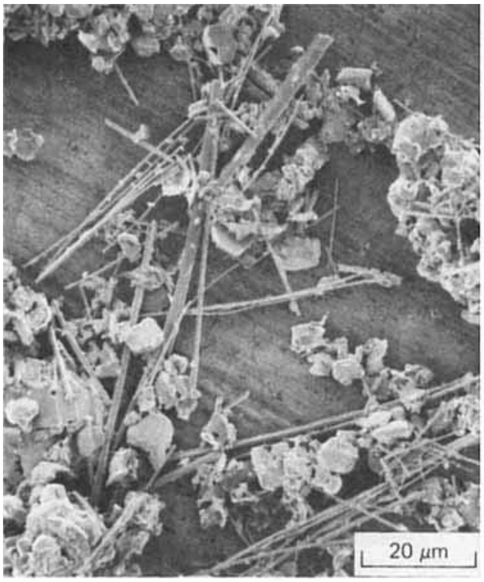

Fig. 1. SEM photograph of a mixture of whiskers and particles of TiN formed by reaction of $Na_{0.25}TiO_2$ with NaCN in a BN crucible at 1027°C for 15 h. The product was first extracted with hot water, followed by boiling in ≈1*M* HCl, washed with water, and dried (NaCN:Ti = 4).

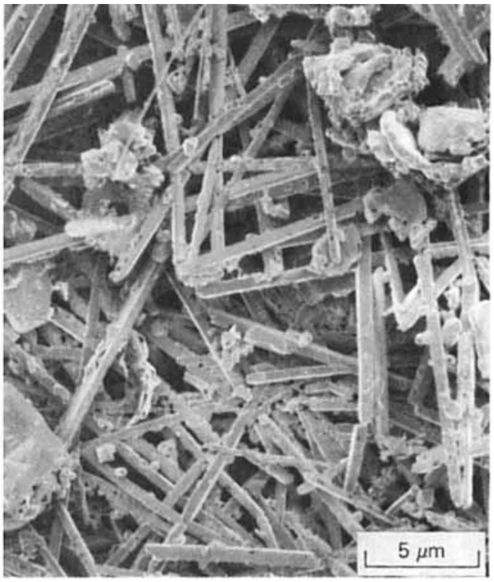

Fig. 2. Another portion of the product shown in Fig. 1 highlighting mats of whiskers containing few particulates (NaCN:Ti = 4).

The authors of a 1987 study of equilibrium between the various phases in the system Ti–N[13] collected additional values for the lattice parameters of cubic TiN_x as a function of x and concluded that $a_0 = (4.2398 \pm 0.0005) \times 10^{-1}$ nm (4.2398 ± 0.0005 Å) for $x = 1$. It is very likely that the lack of agreement reflects more the uncertainty of the analytical methods used to determine the composition than that of the method used to measure a_0.

‡Model S-800, Hitachi, Mountain View, CA.
§Model EM400T/FEG, Philips Electronics Instruments, Inc., Mahwah, NJ.
¶Model EM430T, Philips Electronics Instruments, Inc.
**Model 6585, Philips Electronics Instruments, Inc.
††Model EDAX 9100/70, Philips Electronics Instruments, Inc.
‡‡Model 607, Gatan, Inc., Warrendale, PA.
§§Gatan, Inc.

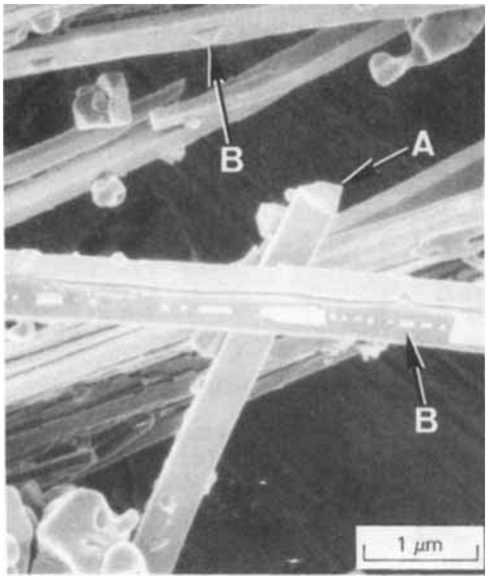

Fig. 3. High-magnification image of whiskers showing their angular shape, as evidenced by the fracture at *A*, and their sharp surface facets, shown at *B* (NaCN:Ti = 4).

In view of the above-mentioned ambiguities and the need to confirm that the whiskerlike material indeed consisted of TiN whiskers, the products were examined by scanning electron microscopy (SEM) and were characterized by techniques of analytical microscopy (AEM). The SEM work was conducted using a high-resolution field emission scanning electron microscope,‡ and the AEM work was conducted using electron microscopes operated at 100 kV§ and 300 kV.¶ Both analytical microscopes were equipped with a scanning transmission electron microscope (STEM),** an X-ray energy dispersive spectrometer (EDS),†† and an electron energy loss spectrometer (EELS).‡‡ A double-tilt liquid-nitrogen-cooled holder§§ was used to minimize contamination or volatilization of the specimen during the EDS and EELS analyses. The EELS experiments were performed in the image mode (diffraction coupled) with a collection aperture of 8.11 mrad. Specimens for viewing by SEM were prepared by gently milling a small subsample in isopropyl alcohol with mortar and pestle and then dispersing a portion of the resulting suspension on an SEM planchet. For transmission electron microscopy (TEM), the specimens were prepared in a similar fashion by depositing a droplet of the suspension on a holey carbon film or on a Be grid.

Although many whisker products were examined, we report here on two that are representative of different preparation conditions: CN^-/Ti ratios of 4 and 16. Secondary electron image investigation of the preparation with CN^-/Ti = 4 revealed the presence of two primary morphologies of material, one a needlelike morphology and the other particulate. Figure 1 is a low-magnification view of a typical area showing both morphologies. In some regions agglomerates of needlelike material with particulate material were observed (Fig. 2). At very high magnifications the needlelike material was observed to be angular in cross section (note the fractured needlelike material at *A* in Fig. 3) and to have a few angular facets on the surfaces (see *B* in Fig. 3). Measurements from the micrographs indicate that the needlelike materials were typically from 0.5 to 1 μm in diameter and had aspect ratios typically greater than 50. AEM analyses of specimens of the CN^-/Ti = 4 preparation revealed that the preparation consisted of whisker, particulate, fiber, and agglomerate materials. Microdiffraction was used to determine if various materials, described as needlelike, were actually single crystals and thus could be termed whiskers. This technique was necessary since the whiskers were usually bent along their axes, and other techniques, such as centered-beam dark-field microscopy, were not applicable. Whiskers of at least two different morphologies were observed. One set of whiskers

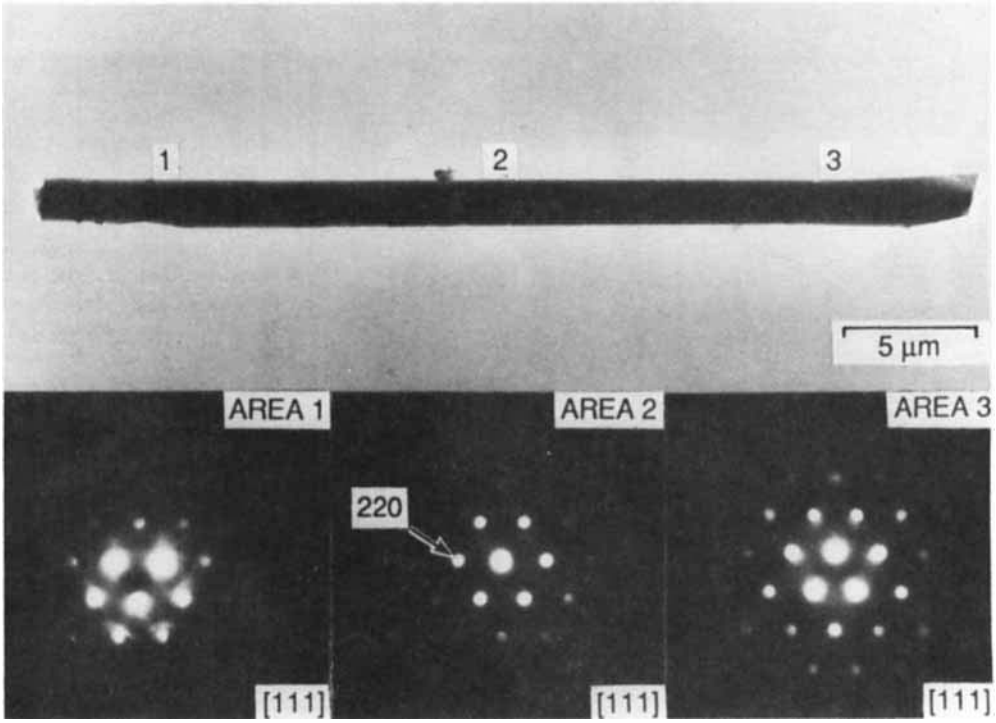

Fig. 4. Face-centered cubic TiN solid single-crystal whisker and three microdiffraction patterns. The axis of the whisker is parallel to the ⟨110⟩ type direction (NaCN:Ti = 4).

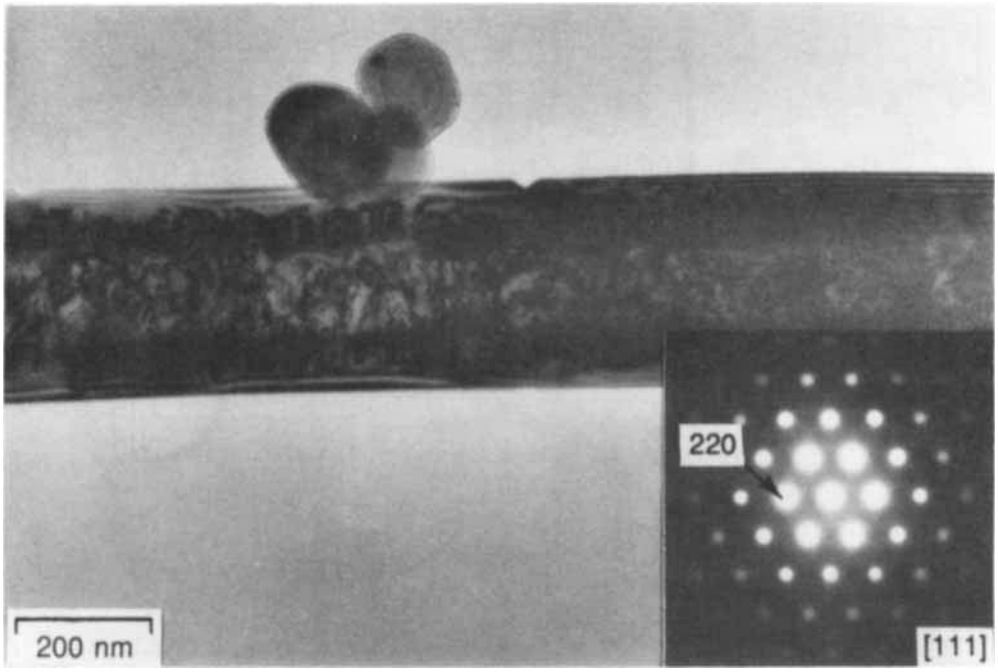

Fig. 5. Facetted TiN whisker with a central cavity along the ⟨110⟩ direction. Insert: microdiffraction pattern indicating face-centered cubic structure (NaCN:Ti = 4).

was facetted with solid cores. A micrograph and corresponding microdiffraction patterns for this type of whisker are shown in Fig. 4. The diffraction patterns were indexed as (111)-type zones of a face-centered cubic structure having a lattice parameter of $a_0 \approx 4.26 \times 10^{-1}$ nm (4.26 Å).[¶¶] The axis of the whisker was determined to be along a ⟨110⟩-type direction. The second type of whisker was also facetted but contained a central cavity. The wall thickness was found to vary along the length, and the surface was irregular and facetted. Micrographs of this type of whiskers are presented in Fig. 5. These whiskers had a structure, lattice parameter, and growth axis identical with those of the first type of whiskers.

The whiskers contained various defects including voids and dislocations. Results of EELS experiments showed the presence of N and Ti (Fig. 6). The composition, determined using EELS with standardless quantification techniques,[14] was $TiN_{(0.99)}$.[***] C was not detected. It is not clear, from EELS data, whether or

[¶¶]This and other lattice parameters obtained by AEM and reported below have an uncertainty estimated at ±1%.

[***]This and other compositions determined by EELS, reported below, have estimated uncertainties of ±10%.

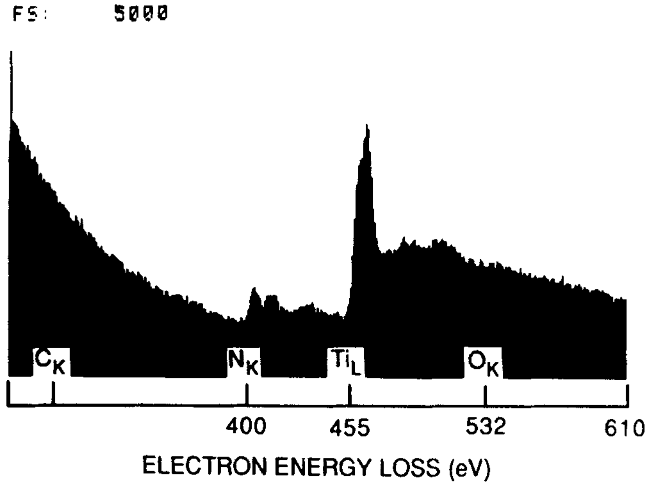

Fig. 6. Electron energy loss spectroscopy (EELS) of TiN whisker taken at 300 kV and at 77 K. C was not detected; the presence of small amounts of O is not certain (NaCN:Ti = 4).

not O was present, since the Ti L-core absorption edge interferes with the oxygen K-core absorption edge. Ti was also detected using EDS[15] and was the major element present with atomic number (Z) greater than 11, as shown in Fig. 7. Fe and Cu were also detected in some whiskers at levels near the detectability limits (0.2 at.%) of the EDS technique. Another type of whisker was also observed which had both a central cavity on one half (left side of whisker shown in Fig. 8) and a seemingly solid core on the other half (right side of whisker shown in Fig. 8). The central cavities were observed by the use of bright-field TEM and by the use of EDS X-ray line scans taken across the diameter of the whiskers as measured in the STEM mode. The occurrence of this particular type of whisker is an indication that the two basic types of whiskers mentioned earlier have related structures, and the growth preference depends upon the preparation process.

SEM and AEM of the preparation with $CN^-/Ti = 16$ revealed primarily whisker morphology with only a small amount of particulate material. Typical regions (shown in Figs. 9 and 10) reveal the whiskers to have diameters ranging from less than 0.5 μm to greater than 2 μm, and aspect ratios up to about 30. Larger diameter entities appear to be several whiskers grown together with nearly

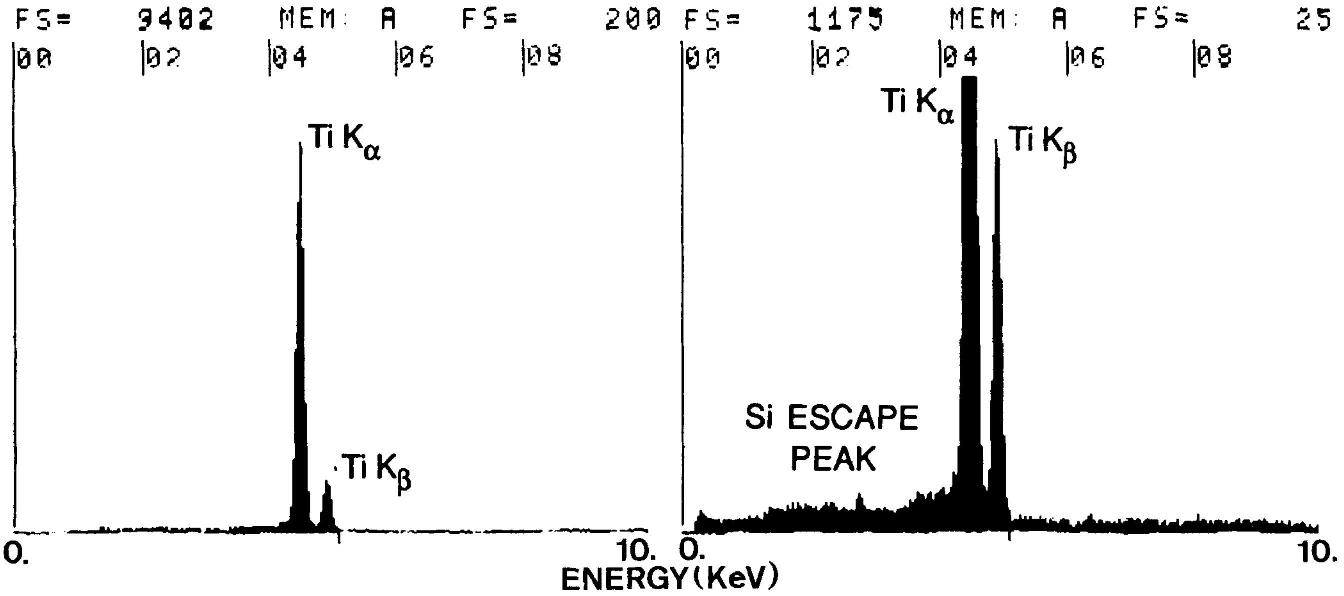

Fig. 7. X-ray energy dispersive spectroscopy (EDS) of whisker in Fig. 6. No Na was detected (NaCN:Ti = 4).

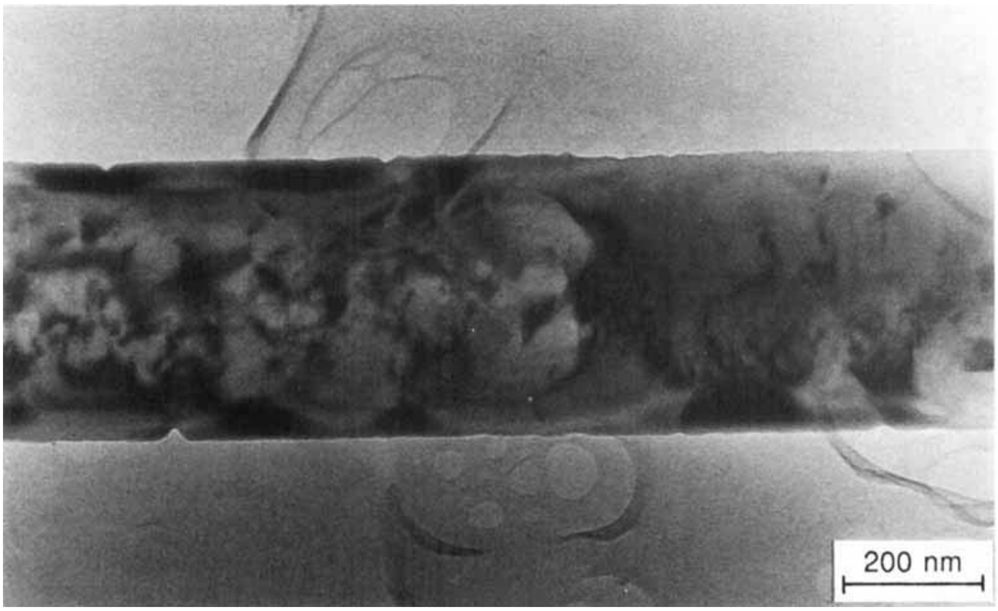

Fig. 8. Single-crystal whisker of TiN with both a void and a solid central core (at right side of micrograph). The surface is observed to be facetted (NaCN:Ti = 4).

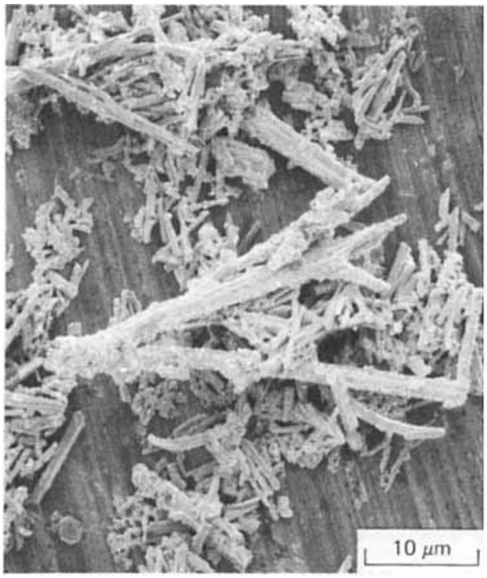

Fig. 9. SEM photograph of TiN whiskers and agglomerates of whiskers formed by reaction of $Na_{0.25}TiO_2$ with NaCN in a glassy carbon boat at 1030°C for 15 h (NaCN:Ti = 16).

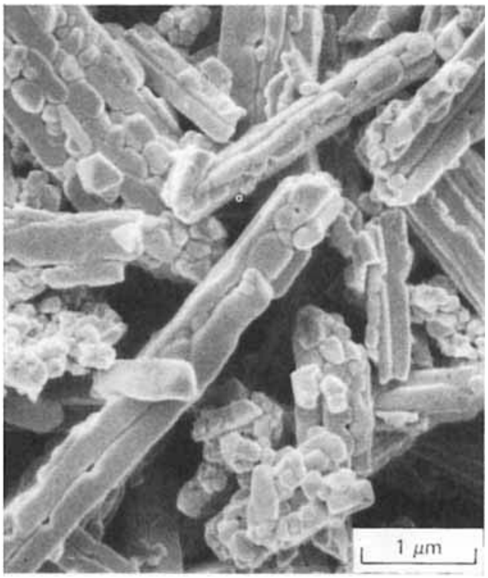

Fig. 10. High-magnification image of some of the whiskers showing numerous rounded facets on their surface.

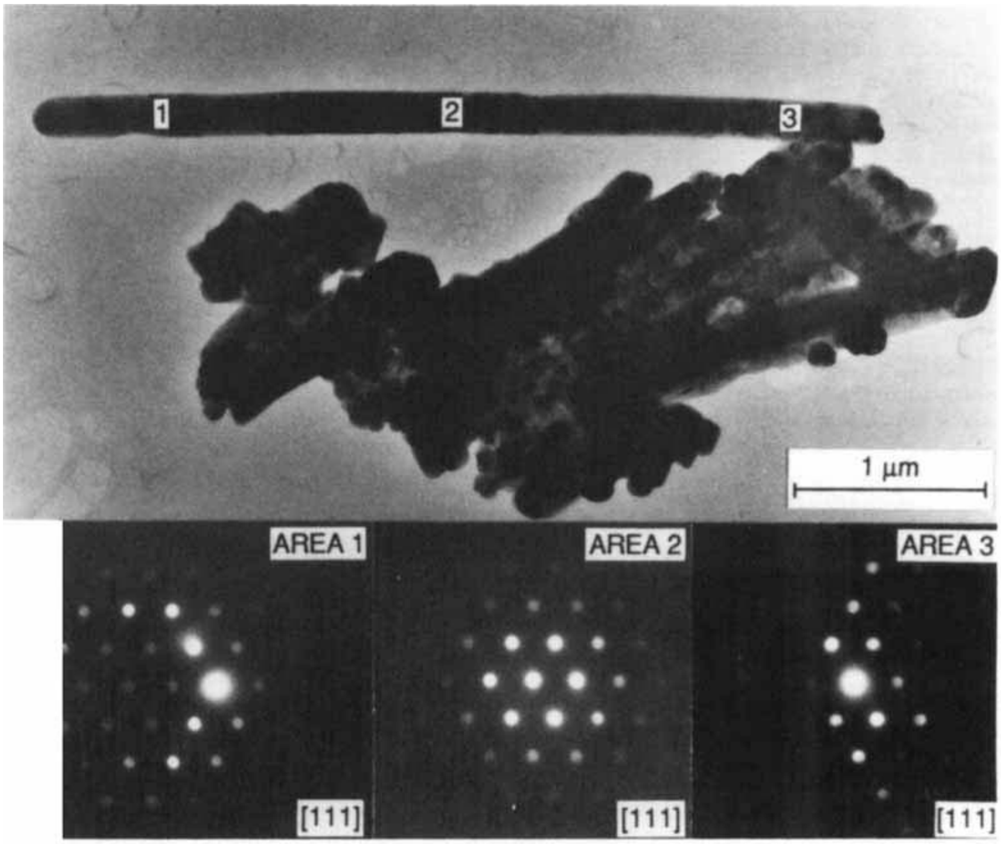

Fig. 11. Agglomerates of whiskers, polycrystalline fibers, and particulate material. The electron microdiffraction patterns confirm the presence of single-crystal TiN whiskers (NaCN:Ti = 16).

parallel crystallographic axes. Whisker ends are rounded and whisker surfaces have many somewhat rounded facets. The AEM analyses of the CN^-/Ti = 16 preparation showed the material to consist of whisker, particulate, fiber, and agglomerate material as shown in Fig. 11.

Electron microdiffraction was used to evaluate whether the needlelike material was composed of single-crystal whiskers or polycrystalline fibers. The microdiffraction patterns shown in Fig. 11 were taken at various positions along the axis of a whisker as marked in Fig. 11. All of the diffraction patterns showed an orientation near (±5°) a (111)-type zone from a face-centered cubic crystal structure with a lattice parameter of $\approx 4.23 \times 10^{-1}$ nm (4.23 Å). These results show that the material is clearly a single crystal and, thus, a whisker. As indicated in Fig. 11, the axes of the whiskers were parallel to a ⟨110⟩ direction. Whiskers did not have well-defined facetted surfaces but were generally round in cross section and contained both dislocations and voids. EDS analyses of these whiskers showed results similar to those shown in Fig. 7. The EDS results show whiskers to be relatively free of high-Z impurities although in some cases Fe and Cu were detected at concentration levels near the detectability limits of the technique. EELS was performed to identify the light elements and their amounts. The light elements of interest were C, N, and O because they were the major light elements present in the initial reactants. The major elements identified with the use of EELS were Ti and N. The composition was determined to be $TiN_{(0.9)}$, quantified using standardless techniques; C was not detected.

EDS analysis of the particulate material also showed the presence of Ti, with both Fe and Cu detected at a concentration level near detectability limits in certain particulates. Both Ti and N were detected by EELS. The composition determined from EELS data was $TiN_{(0.90)}$. C was not detected with the use of EELS.

IV. Possible Mechanism of the Reaction

The stoichiometry of the reaction between STB and NaCN was deduced from measurements of weight loss on heating and by water extraction of the products.

$$Na_{0.25}TiO_2 + 3NaCN \rightarrow TiN + 2CO + 0.5Na_2C_2 + 2.25Na + N_2 \quad (1)$$

TiN was identified by XRD, and unreacted NaCN and Na_2C_2 were identified qualitatively by means of wet tests. On occasion, NaCN was identified by XRD of products before water extraction. Since only traces of CO_2 (or none at all) were evolved, it was concluded that the O was evolved as CO. A confirmation of the volatilization of elemental Na, an effect concluded from a material balance calculation, was not sought experimentally.

Because all the Ti compounds (TiO_2,[7] TiP_2O_7, $(TiO)_2P_2O_7$, $NaTi_2(PO_4)_3$, and $Na_4(TiO)(PO_4)_2$[8]) reacted earlier with NaCN, yielded TiN powder, and only the STB yielded TiN whiskers, it was speculated that the presence of Ti^{3+} in the bronze may have enhanced the initial concentration of Ti in NaCN. Attempts made to measure the solubility of bronze in NaCN consisted of equilibrating the bronze in powder form with an excess of NaCN (NaCN/Ti = 16). The mixture was contained in a glassy carbon crucible placed in a flanged-top Ni container which was provided with gas inlet and exit ports, a thermocouple well, and a sampling port with a ball valve. "Filter sticks," made of stainless steel or Cu,[16] were used for obtaining samples of filtered molten NaCN. For the sampling operation, the filters were flushed with N_2 and lowered into the Ni container to attain thermal equilibrium, then pushed into the melt and a sample withdrawn by applying vacuum. After removal from the system, the exteriors of the filters were cleaned with emory cloth and the frozen salt crushed out for the determination of Ti. Samples obtained after 47 h at 900°C and 21 h at 1000°C were analyzed, and, although the results showed considerable scatter, they indicated that the solubility of Ti in NaCN was less than 1 mg Ti/g NaCN at both temperatures. Although this value is relatively low, it may be the controlling factor in the formation of whiskers, provided that the dissolution–exsolution process is fast.

In most of the experiments, the original bronze was completely consumed. This suggested that whisker growth due to dislocations on the bronze crystals was not the mechanism. Since the yields of the reactions producing TiN were always close to 100%, it can be implied that whisker formation did not involve a volatile Ti species. An alternative experiment in which STB was reacted with gaseous NH_3 for 24 h at 900°C and yielded quantitatively TiN powder, strongly suggests that the molten NaCN is involved in the crystal-growth process. Further work is necessary to identify the mechanism of whisker formation in the system STB–NaCN.

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