JOURNAL OF MATERIALS SCIENCE 25 (1990) 4992–4996

Formation of TiN whiskers from oxide-containing cyanide melts

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It has been found that the formation of TiN whiskers by reaction of molten alkali metal (sodium, potassium) cyanide with TiN powder or with TiO_2 is effected by the presence of alkali metal oxides. This has led to the successful use of reactions of molten cyanide with several sodium and potassium titanates for the formation of TiN whiskers.

1. Introduction

Our earlier finding that TiN whiskers can be formed by reaction of sodium–titanium bronze with sodium cyanide by means of a mechanism apparently other than growth on dislocations or vapour–liquid–solid (VLS) reactions [1], led us to explore the possibility of forming TiN whiskers using a variety of alternate titanium compounds. Exploratory tests were made to determine if TiN powder could be recrystallized into whiskers when contacted/reacted with molten NaCN. Only in a few instances was a very small number of whiskers observed to form. This result was, nevertheless, considered encouraging because it indicated that the conversion of TiN powder to whiskers was possible. Experimental conditions that could make the process reproducible and increase its yield were sought and tested. The results led to alternative reactions, described below, for the preparation of TiN whiskers.

2. Experimental procedure

The reagents consisted of analytical grade TiO_2, Na_2CO_3, $K_2CO_3 \cdot 1.5\ H_2O$, NaCN, and KCN. The titanates Na_2TiO_3, $Na_2Ti_6O_{13}$, and $Na_8Ti_5O_{14}$ were synthesized from mixtures of Na_2CO_3 and TiO_2, and were characterized as described previously [2]. $K_2Ti_6O_{13}$ acicular crystals were prepared by the method described by Berry *et al.* [3] and $K_2Ti_2O_5$ by reaction of TiO_2 and KNO_3 at 1000° C. TiN powder 99.8% from two sources (Atlantic Equipment Engineers, Bergenfield, New Jersey and Cotronics Corporation, Brooklyn, New York) were used. In preliminary experiments the mixtures of reagents were contained in boats made of alumina or vitreous carbon. These were placed in alumina combustion tubes and heated in a horizontal furnace under a stream of nitrogen. Subsequently, the experiments were scaled up and the reagents were contained in crucibles of 35 mm i.d. and at least 35 mm height. These crucibles were made of graphite, nickel, copper, or vitreous carbon, with the latter the preferred material. The crucibles were placed in nickel containers of typically 45 mm i.d. × 450 mm height, which were topped by a No. 50 "Ace" glass joint to which one No. 11 and two No. 7 joints were attached. The latter served to connect, respectively, a Teflon exit tube, a nickel thermocouple well and a nickel tube used to introduce the cover gas, usually nitrogen, at about $300\,\mathrm{ml\,min^{-1}}$. The assembly was placed in a vertical tubular furnace connected to a temperature controller. In order to examine the products of the reactions, the assembly was cooled under flowing inert gas. In cases where condensation of decomposition products prevented removal of the crucible, those products (one of which was Na_2C_2) were carefully dissolved with a jet of cold water from a washing bottle. (The reaction of H_2O with Na_2C_2 produces H_2C_2 which ignites spontaneously in air.) No identification of other decomposition products was attempted on a regular basis because it was considered that they would be similar to those obtained when reacting sodium–titanium bronze with sodium cyanide [1]. The contents of the crucible were removed with hot water and digested over a hot plate for times ranging from 15 to 60 min. The solids were recovered by centrifugation, washed with water until alkalinity had been removed, rinsed with ethanol or acetone and dried in an oven at 110° C for 1 to 2 h.

The residues were weighed and examined by a variety of techniques: (a) optical microscopy, (b) scanning electron microscopy (SEM), (c) transmission electron microscopy (TEM), and (d) X-ray diffraction (XRD). For SEM the specimens were prepared by gently mulling a small subsample in isopropanol using a mortar and pestle, and then dispersing a portion of the resulting suspension on an SEM planchet. Scanning electron microscopy was performed in a Hitachi S-800 SEM utilizing low accelerating voltages (typically 5 kV or less) to enhance surface detail and to minimize electrical charging. Transmission electron microscopy specimens were prepared by placing several whiskers on a flat substrate, embedding them in epoxy cement and polishing and dimple grinding in such a manner that a thin region (about 25 μm thick) containing whiskers was produced. The specimens were then ion-milled to perforation and observed in a Jeol 2000FX TEM equipped with a Kevex Quantum/Delta V energy dispersive X-ray analyser (EDXA).

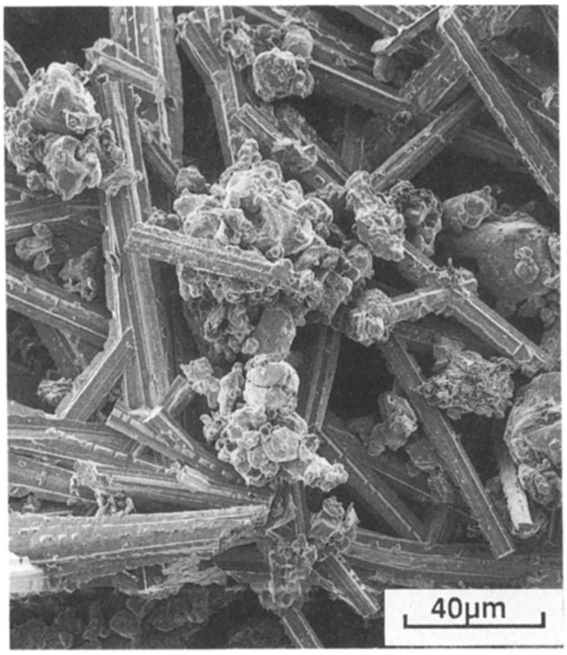

Figure 1 TiN whiskers recrystallized from a melt consisting of 0.5 Na_2CO_3 and 18 NaCN (the quotients are in mmol referred to one mmol titanium).

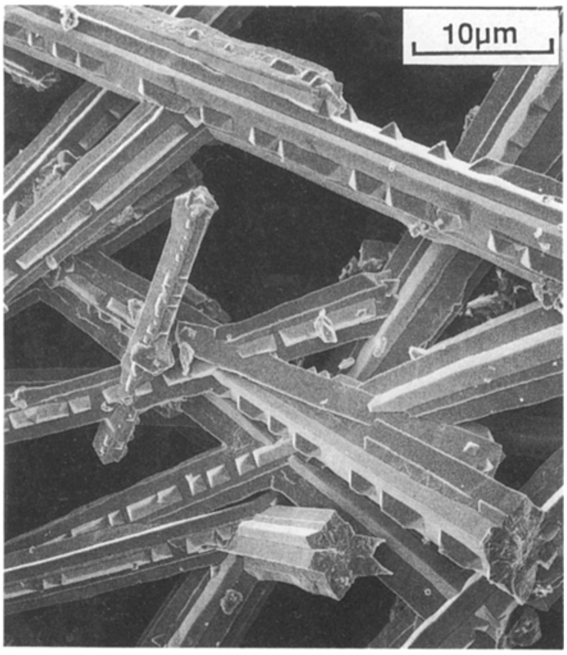

Figure 2 Higher magnification of TiN whiskers shown in Fig. 1.

3. Results and discussion

In earlier tests in which TiN powder was contacted with NaCN at 1000° C, we observed that TiN whiskers had occasionally formed in graphite crucibles and in Al_2O_3 boats, but not in copper crucibles. The graphite crucibles had been used previously with NaCN and, although they had been thoroughly washed with water, on drying in air at 110° C they usually developed a white coating on the surface. Raman spectroscopy of this coating indicated that it was Na_2CO_3. We speculated that this Na_2CO_3, was occluded in the graphite pores and had originated by hydrolysis of the NaCN previously diffused as a liquid into the graphite at high temperature. When Al_2O_3 was exposed to NaCN at 1000° C it was, very likely, corroded by formation of sodium aluminates. The latter and Na_2CO_3, in the case of graphite crucibles, may have acted as sources of oxide ions. All the above observations suggested to us that the common denominator in the more successful tests was the contamination of the NaCN melt with oxide ions. Thus, it was decided to test the effect, on the conversion of TiN powder into whiskers, of controlled additions of Na_2O. These were made using mainly Na_2CO_3. High NaCN/Ti ratios were used because they were indicated by our experience to be a requisite for high yields of TiN [1]. A series of experiments (shown in Table I) was performed at ~ 1000° C; the reaction times generally ranged from 20 h, for 3 to 10 mmol Ti, to 90 h for 15 or more mmol Ti.

It can be seen in Table I that a product consisting of only golden acicular crystals was not common and did not appear to depend on the variables studied. Examination by SEM showed that a variety of morphologies was produced in these batches. All batches contained elongated whisker-like objects, as well as more equiaxed particulate material. Both geometries are shown in Fig. 1, an example of a typical preparation (TiN + 0.5 Na_2CO_3 + 18 NaCN). The elongated objects are nearly identical in morphology to objects identified previously as TiN whiskers [1]. Thus the morphological evidence supports the conclusion that these acicular crystals are primarily single-crystal whiskers. Fig. 2 shows another example, at higher magnification, of these whiskers with very little particulate material present. Noteworthy are the presence of very well developed faces, apparently conforming to crystallographic planes and the presence of surface facets. These results were very encouraging because they suggested new alternatives to the production of TiN whiskers.

TABLE I Reaction of TiN powder with Na_2CO_3 and NaCN at ~ 1000° C

Ti* (mmol)	NaCN/Ti	Na_2CO_3/Ti	Container	Products†
3.2 (1)	12.4	0	Al_2O_3	Very few golden acicular crystals (AC)
23.0 (1)	9.3	0.33	New graphite	Mainly light brown powder
17.7 (1)	18.3	0.33	Vitreous carbon	Light brown powder and golden AC
7.3 (2)	18.1	0.48	Used graphite	Golden and colourless AC
7.1 (1)	18.2	0.48	Used graphite	Golden AC
7.5 (2)	23.9	0.50	Vitreous carbon	Light brown powder and golden AC
16.8 (2)	18.1	0.50	Vitreous carbon	Mainly brown powder
15 (2)	19.4	0.75	Vitreous carbon	Short golden AC, some brown powder
10 (1)	27.2	1.00	Vitreous carbon	Long golden AC, some white crystals

*(1) and (2): different sources of TiN.
†Observed by optical microscopy.

Figure 3 Electron-transparent region of TiN whisker, its ⟨1 1 1⟩ zone axis is aligned with the electron optical axis. The inset shows an electron diffraction pattern comprised of (2 2 0) reflections.

The crystallography and orientation of the TiN whiskers were determined from TEM results. Although it has so far been impossible to prepare large electron-transparent areas of these relatively large needles to make them suitable for TEM viewing, small areas were successfully thinned and analysed. Electron diffraction confirmed that all thin regions observed were single crystals with the ⟨1 1 0⟩ crystallographic axes aligned parallel to the long axis of the whiskers. Fig. 3 shows a typical thin region having ⟨1 1 1⟩ zone axis orientation as shown by the inset diffraction pattern. The ⟨2 2 0⟩ reflections are clearly parallel to the whisker axis. Thus we concluded that the needle-shaped objects are single crystals and can be correctly termed "whiskers". The source of the contrast within the thin regions is presently unknown but could be related to unresolved defects present due to growth or introduced by the ion-milling.

Although we were unable to identify all the by-products by XRD or Raman spectroscopy in preparations purposely stopped before completion, we speculated that the recrystallization of TiN powder may proceed through stages involving the formation of titanates and alkali metal-titanium bronze. If this were the case, then possibly our previous results [4] in which mixtures of TiN and sodium titanates were obtained from reacting TiO_2 with 1 or 2 mol NaCN could be drastically improved to yield TiN whiskers by increasing significantly the ratio NaCN/Ti. The product of reacting TiO_2 with a large excess of NaCN (NaCN/Ti = 10 to 25) was TiN powder, indicating that the amount of oxide ions in the system was inadequate for the

TABLE II Reaction of TiO_2 with A_2O and ACN (A = Na, K) at ~1000° C

Ti (mmol)	NaCN/Ti	A_2O/Ti*	Products[†]
4.3	9.5	0	Powder
11.9	9.5	0	Powder
4.7	26.3	0	Powder
4.9	25.9	0.20^{a}	Brown whiskers
11.2	21.4	0.50^{a}	Golden whiskers
5.1	24.2	0.50^{a}	White crystals; few golden whiskers
4.4	26.0	0.51^{a}	Golden whiskers
4.7	24.7	0.51^{a}	Golden whiskers; white and grey fragments
11.8	15.2	1.00^{a}	Mainly white particles; few golden whiskers
11.6	18.3	1.00^{a}	Large golden and brown whiskers
7.8	27.5	1.00^{a}	Lots of white particles; golden whiskers
2.2	25.1	0.80^{b}	Long golden whiskers
5.2	25.4	0.80^{b}	Golden whiskers, brown powder
10.7	25.3	0.80^{b}	Golden whiskers
1.7	25.2	0.33^{c}	Golden whiskers
2.1	25.2	0.17^{d}	Golden whiskers
4.6	34.0	$0.17^{d‡}$	Long golden whiskers
7.0	31.8	0.65^{e}	Golden whiskers
17.0	16.0[§]	$0.17^{d†}$	Dark brown and black whiskers
6.3	34.0	0.50^{f}	Golden whiskers

*A_2O added as: (a) Na_2CO_3, (b) $Na_8Ti_5O_{14}$, (c) $Na_2Ti_3O_7$, (d) $Na_2Ti_6O_{13}$, (e) mixture of $Na_{0.23}TiO_2$ and Na_2CO_3 and (f) $K_2Ti_2O_5$.

[†] Observed by optical microscopy.

[‡] $K_2Ti_6O_{13}$ used.

[§] KCN used.

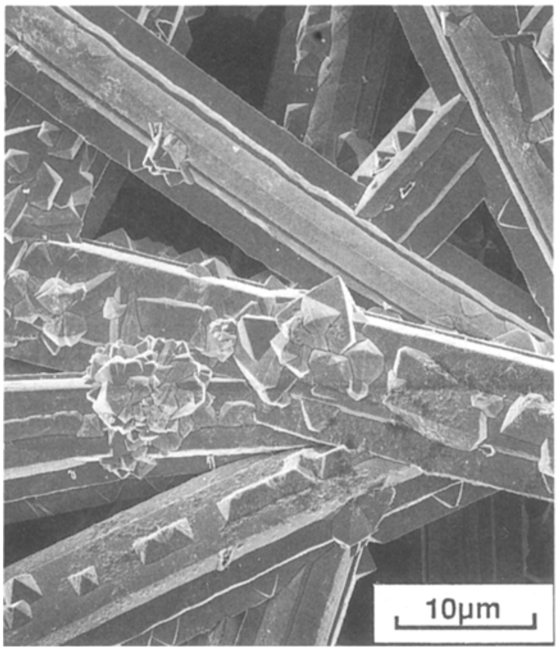

Figure 4 TiN whiskers obtained by reaction of $Na_8Ti_5O_{14}$ with NaCN (NaCN/Ti = 25).

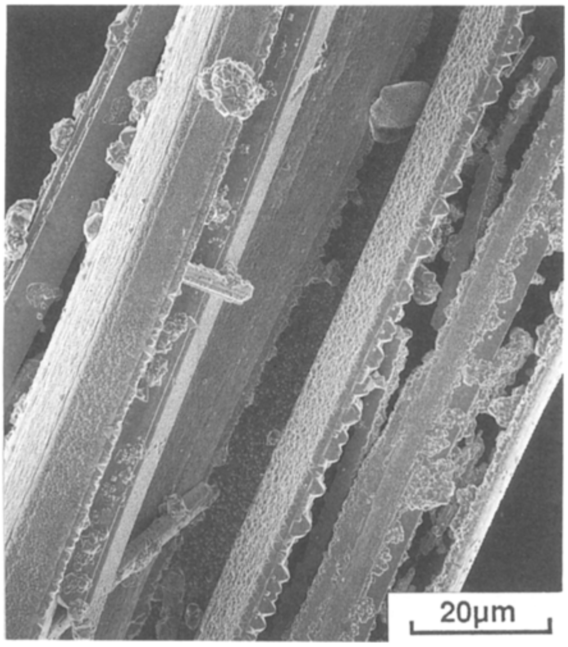

Figure 6 TiN with elongated platelet morphology obtained by reaction of $K_2Ti_6O_{13}$ with NaCN (NaCN/Ti = 34).

formation of TiN whiskers. The addition of different amounts of Na_2CO_3 resulted in the production of TiN whiskers together with other phases (Table II). This, however, confirmed that the presence of oxide was necessary for the formation of TiN whiskers from NaCN melts and led us also to test the reactions of several sodium titanates with excess NaCN. The results were an improvement over the earlier ones because a larger fraction of the preparations yielded products which consisted predominantly of whiskers (Table II).

The use of reciprocal systems resulting from the replacement of sodium titanates, e.g. $Na_2Ti_6O_{13}$, by acicular crystals of $K_2Ti_6O_{13}$ or of $K_2Ti_2O_5$, or the replacement of NaCN by KCN, in general, did not produce significant changes in regard to the product. On very few occasions, however, when using KCN, the product, after extracting with hot water, consisted mainly of white needles which were amorphous by XRD. Annealing at 850° C for a few hours provoked crystallization which allowed for their identification as $K_2Ti_6O_{13}$. This and recently completed studies on the synthesis and hydrolysis of potassium titanates [5] leads us to conclude that the amorphous needles stemmed from the hydrolysis of $K_2Ti_2O_5$ whiskers formed in the melt. The products from reacting alkali metal titanates, some in reciprocal cyanide systems, are illustrated in the Figs 4 to 9. Fig. 4 shows TiN whiskers, obtained by reaction of $Na_8Ti_5O_{14}$ with NaCN, with well-developed faces, similar to those in

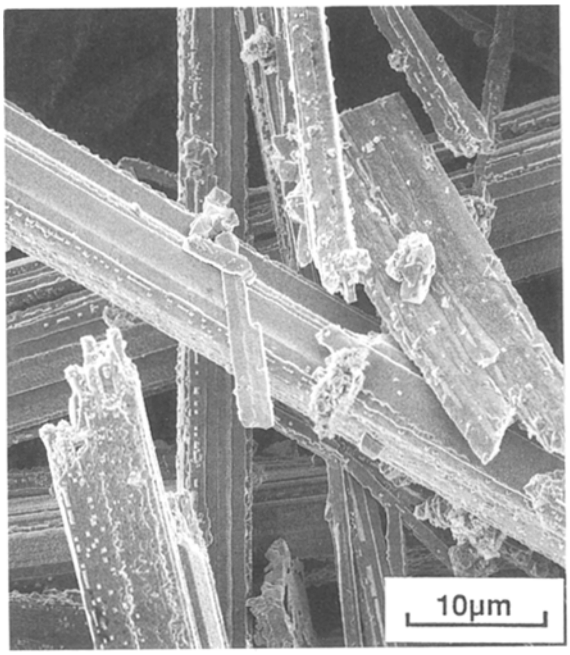

Figure 5 TiN with elongated platelet morphology obtained by reaction of $Na_2Ti_3O_7$ with NaCN (NaCN/Ti = 25).

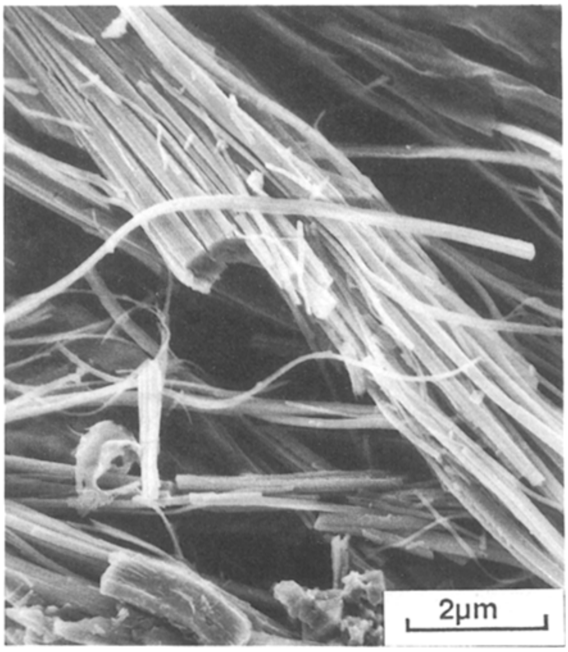

Figure 7 Fibrils obtained by reaction of $Na_2Ti_6O_{13}$ with KCN (KCN/Ti = 16).

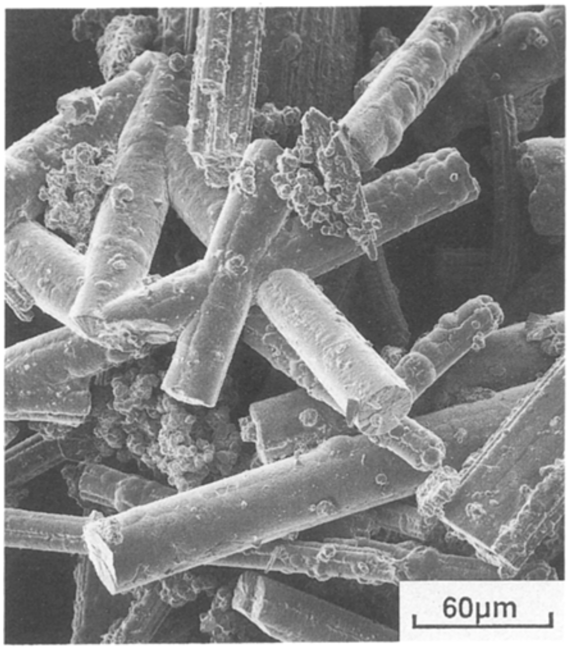

Figure 8 TiN needles with circular cross-section, obtained by reaction of $K_2Ti_2O_5$ with NaCN (NaCN/Ti = 34).

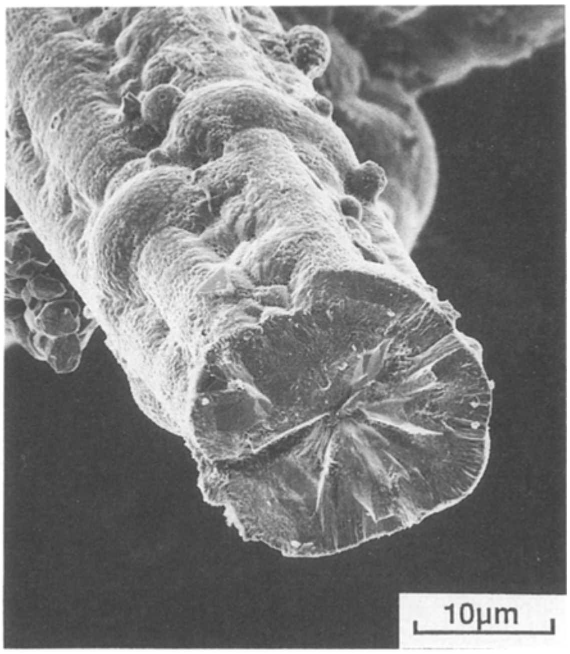

Figure 9 Higher magnification of needle with circular cross-section (Fig. 8).

Fig. 2 obtained from the recrystallization of TiN. Several other morphologies were also observed by SEM; Figs 5 and 6 show lath-like or elongated platelet structures obtained, respectively, by reaction of NaCN with $Na_2Ti_3O_7$ and with $K_2Ti_6O_{13}$. These laths often appear to be composed of many small crystals bonded together with some long-range crystallographic order present. In another preparation, obtained from reacting $Na_2Ti_6O_{13}$ with KCN, very fine fibrous needles (Fig. 7) were present in a few isolated clumps. Finally, a preparation based on the reaction of $K_2Ti_2O_5$ with NaCN consisted primarily of rounded needles, often having nearly circular cross-sections (Figs 8 and 9).

4. Conclusions

While the micrographs shown (Figs 1, 2, 4 to 9) were selected to illustrate the variety of morphologies obtainable with the reactions described above, it should be noted that a given morphology was not consistently obtained with a specific combination, alkali metal titanate/cyanide. As observed by SEM the predominant morphologies were whiskers and elongated platelets. The only common denominator qualitatively observed was that whiskers were more often obtained when the amount of reactants was relatively small, e.g. equivalent to less than 10 mM Ti. This observation implies that there is a relationship between the mass of reactants and the reaction area available. The mechanism of crystal growth still needs to be elucidated; at present, based on crystallized products identified in incomplete reactions, we can only speculate that the formation of TiN from mixtures of alkali metal cyanides with oxides of alkali metals and of titanium proceeds through stages involving the formation of alkali metal titanates and alkali metal-titanium bronze.

Acknowledgements

We thank George M. Begun for his assistance with the Raman spectroscopic identification of several intermediate chemical species. This research was sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, US Department of Energy under contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

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Received 8 August 1989
and accepted 9 January 1990