JOURNAL OF MATERIALS SCIENCE 16 (1981) 3283–3291

Electron irradiation damage in TiC

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Electron irradiation experiments were carried out on (100) $TiC_{0.93}$ thin foils inside an electron microscope operated at 100 kV at room temperature. Both graphite rings and extra diffraction spots were observed as irradiation continued. The extra diffraction spots correspond to an ordered cubic superstructure having a composition near $TiC_{0.5}$, as determined by Goretzki. These extra spots were disrupted with continued irradiation. These results are discussed in the light of displacement damage in TiC.

1. Introduction

TiC is a stoichiometric compound consisting of two different atoms, one metallic and the other non-metallic, having very different atomic masses. This material has the NaCl structure, with carbon atoms occupying octahedral sites in the metal atom substructure, and can exist over a wide range of substoichiometry. A long-range ordered carbon atom distribution near the composition $TiC_{0.5}$ was determined by Goretzki [1] in a neutron diffraction study. Bell and Lewis [2] have confirmed Goretzki's observation of a cubic superstructure through the use of electron microscopy and diffraction.

Electron irradiation experiments on stoichiometric TiC having two widely differing atomic masses make it possible to selectively displace one species through a careful choice of incident electron energy. For example, irradiation experiments can be designed such that only the lighter carbon atoms will be displaced, not the heavier titanium atoms. This can be achieved easily by using an accelerating voltage which is lower than the threshold displacement voltage for titanium but higher than that for carbon. Irradiation under such conditions enables one to investigate the damage resulting from the displacement of carbon atoms rather than titanium atoms. If sufficient numbers of carbon atoms are displaced from their octahedral sites and are removed, the area under irradiation will gradually become increasingly more substoichiometric and carbon atom ordering may take place when the composition is near $TiC_{0.5}$. It will be shown that the carbon atom ordering does indeed take place during irradiation at room temperature where diffusion of carbon is too slow to effect ordering. It has also been observed that disordering of the ordered structure takes place with continued irradiation. Irradiation enhanced ordering and disordering in alloys have been observed [3–5]. Disordering in V_6C_5 was also observed during electron irradiation [6]. In addition, vacancies may agglomerate to form dislocation loops and voids as commonly observed in quenching and irradiation experiments in metals and alloys. Indeed, voids in electron-irradiated TiC at high temperatures have been observed recently by Chatterjee and Lipsitt [7]. Results of the present study suggested that the displaced carbon atoms diffuse to the surface during irradiation and agglomerate to small crystallites.

2. Experimental procedure

TiC single crystals* having near-stoichiometric composition ($TiC_{0.93}$) were grown by the floating zone method in an electron-beam zone refiner. Thin slices about 500 μm thick and 3 mm in diameter were cut parallel to the (100) plane of the

*The $TiC_{0.93}$ single crystal was grown by Mr W. Precht of Martin Marietta Laboratories, Baltimore, and the boule was donated by Dr J. D. Venables.

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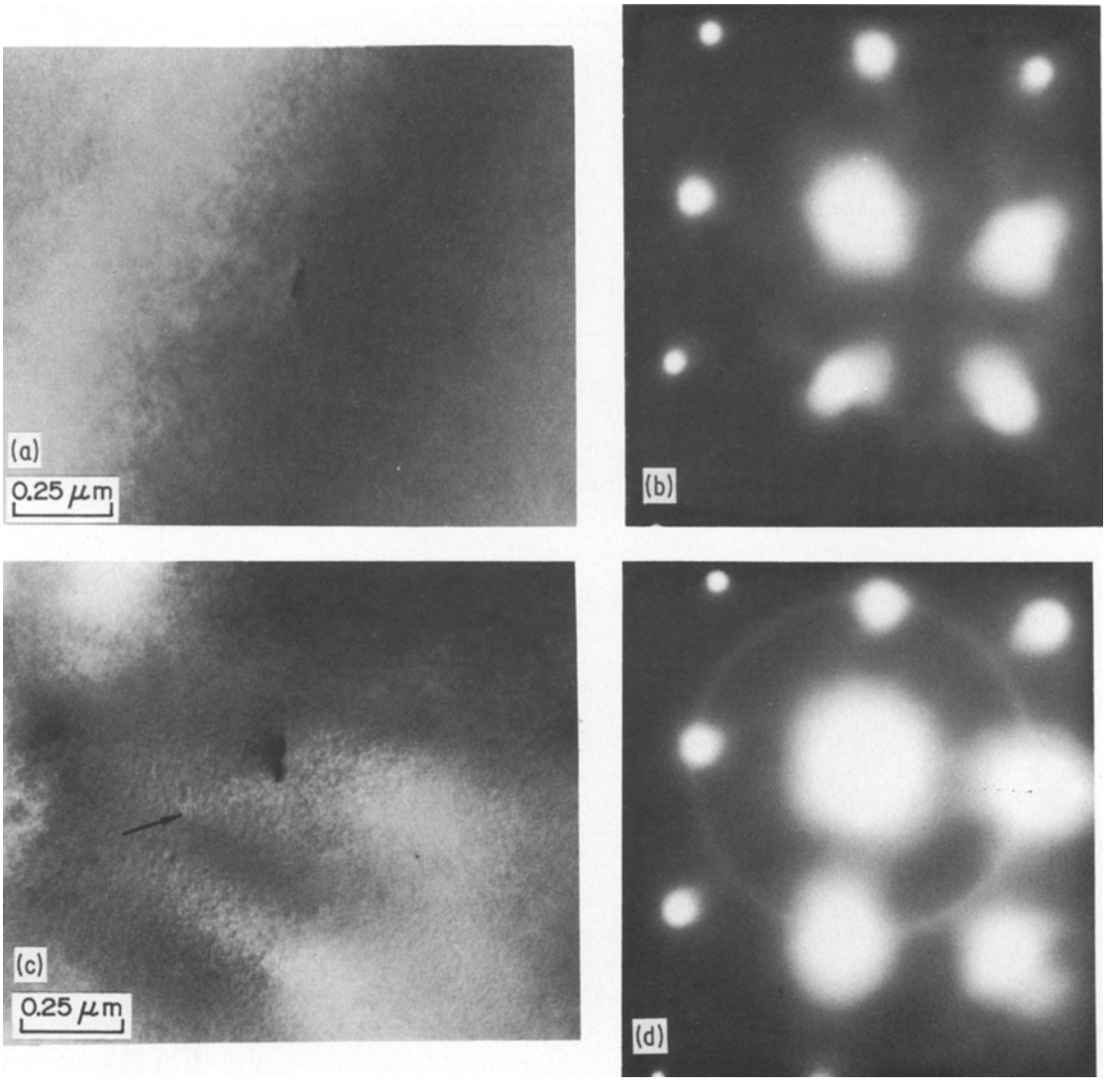


Figure 1 Electron irradiation damage in a (100) $TiC_{0.93}$ foil at 100 kV at room temperature: (a) Bright-field (BF) image, before irradiation; (b) SAD of (a); (c) BF image after 30 min of irradiation, showing the appearance of a new feature indicated by arrow; (d) SAD of (c) showing the appearance of diffuse graphite rings; (e) BF image after 60 min of irradiation showing the bend contours; (f) SAD of (e) showing the sharp graphite rings; (g) BF image after 130 min of irradiation; (h) SAD of (g) showing the presence of extra diffraction spots (circled) due to the formation of superstructure; (i) BF image after 150 min of irradiation, showing the formation of black spot damage; (j) SAD of (i); (k) schematic diagram of (h) illustrating the identification of different matrix spots, graphite rings and the superlattice spots; (l) BF image after 170 min of irradiation; (m) SAD of (l); (n) dark-field (DF) image after 170 min of irradiation, taken with the superlattice spot (marked by x in Fig. 1m). Light areas in (n) are ordered regions corresponding to $TiC_{0.5}$ in the TiC matrix. Inset in Fig. 1l shows the same area taken at a slightly different tilt to reveal the double-arc contrast of several small defect clusters, (o) BF image after 215 min of irradiation; and (p) SAD of (o) showing the disappearance of the superlattice spots.

single crystal. The thickness was reduced to about 250 μm by mechanical polishing. These discs were electropolished using a twin-jet electropolisher in an electrolyte consisting of a mixture of perchloric acid, butanol and methanol in a ratio of 1:4:10 by volume at 20 V and -20° C. Thin foils were irradiated with a fully-focused beam in a Philips EM-300 electron microscope operated at 100 kV at room temperature. The electron flux was measured by means of a Faraday cage located at the specimen level.

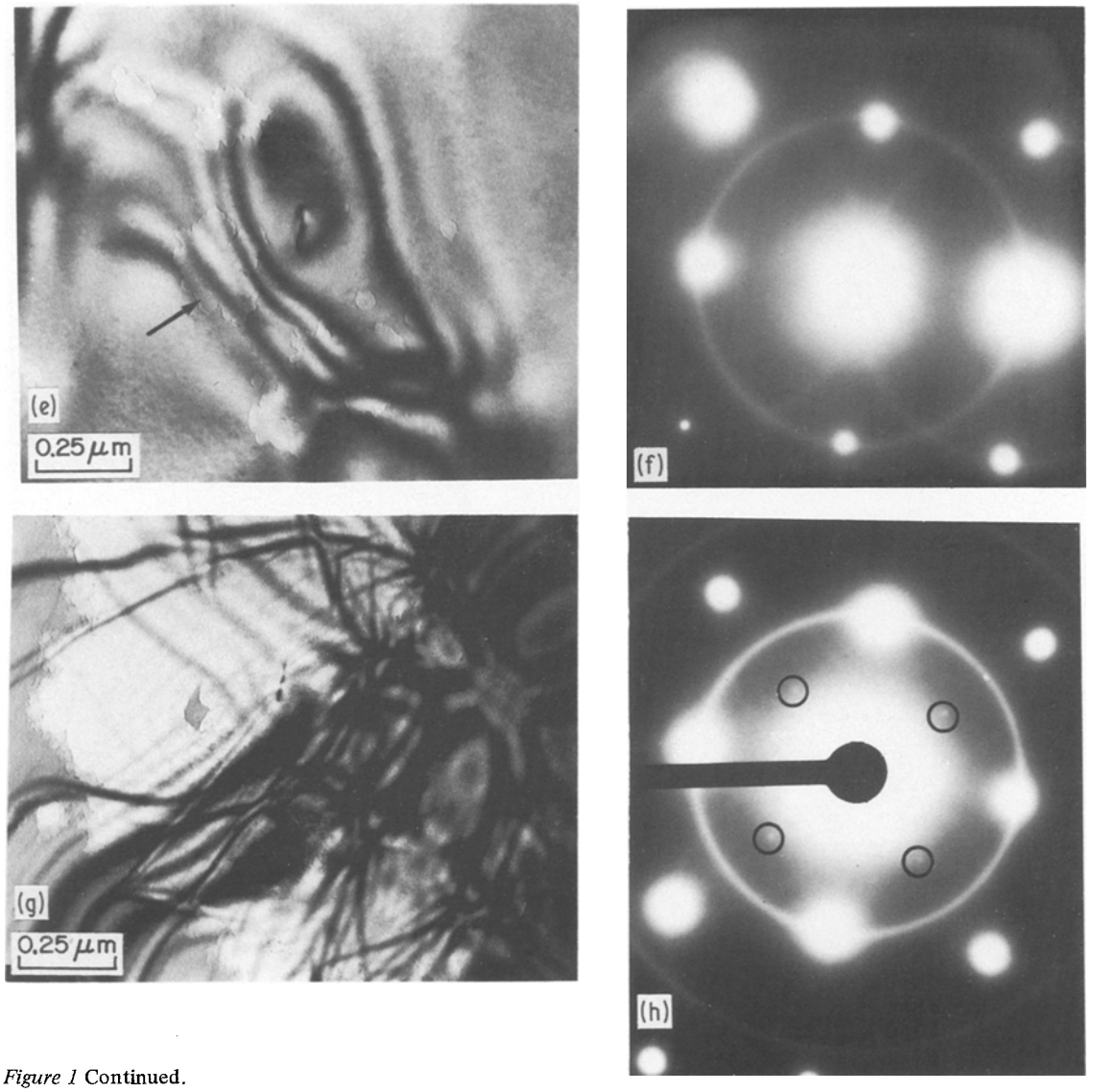
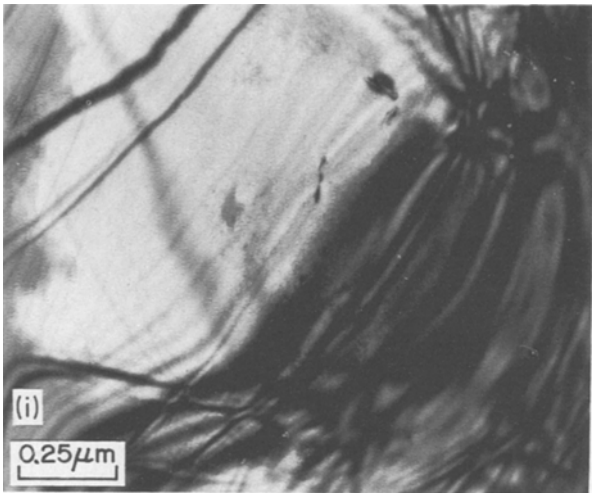


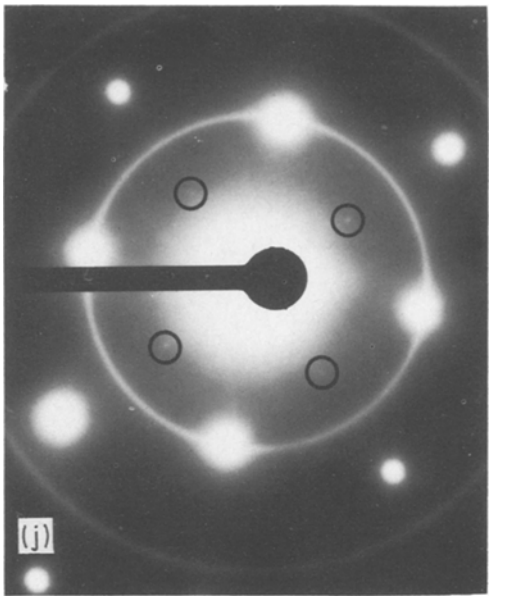
Figure 1 Continued.

3. Results

The effects of electron irradiation at 100 kV at room temperature as a function of dose in a (100) foil are illustrated in Fig. 1 which shows a series of electron micrographs and corresponding selected-area diffraction patterns (SAD) taken from the same area under irradiation. Several minutes after irradiation was initiated, diffuse rings gradually appeared along with the matrix diffraction spots shown in Fig. 1d. The intensity and the sharpness of these rings increased with increasing irradiation, as shown in Fig. 1f. An analysis of the ring pattern was made, and it was determined to be due to graphite. The development of graphite rings around the diffracted beams is due to double diffraction. With continued irradiation, after 130 min, extra diffraction spots (circled) gradually became visible together with matrix spots and the graphite ring pattern formed earlier (Fig. 1h). These extra diffraction spots make a square pattern, and the individual spot was not located exactly at the midpoints of the (220) reflections of the irradiated TiC. They could be matched with a cubic superstructure having a lattice parameter of 0.92 nm, which is somewhat larger than twice that of the unirradiated TiC*, as determined by Goretzki [1] in his studies of $TiC_{0.5}$ by neutron diffraction. Fig. 1k is a schematic representation of Fig. 1h, illus-

*Lattice parameter of TiC is taken to be 0.4328 nm [8].





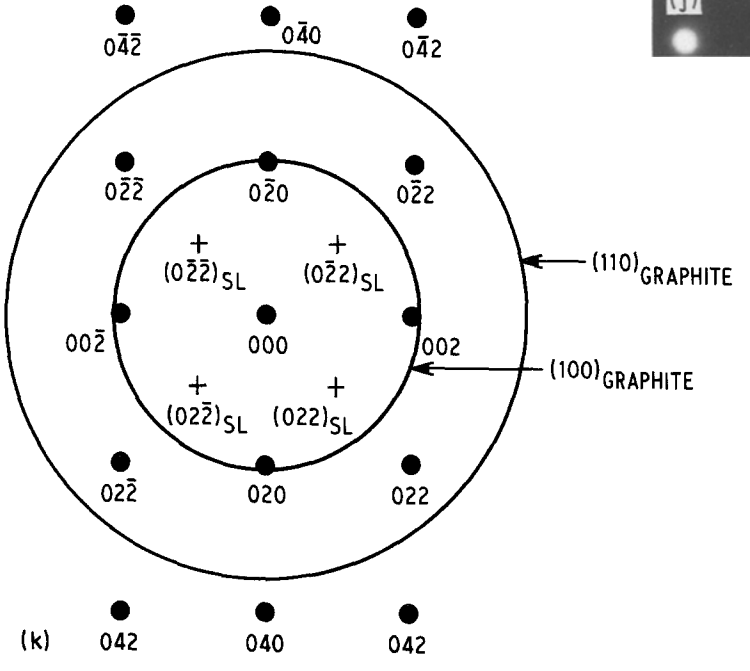
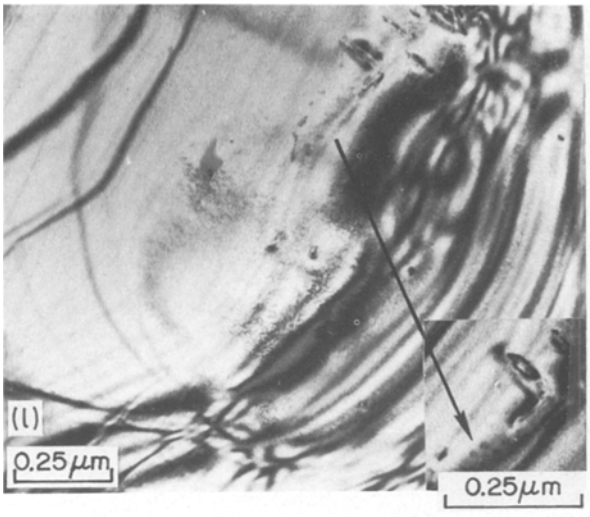
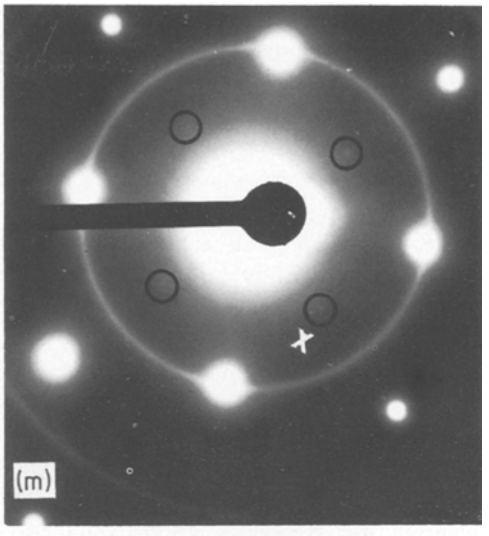


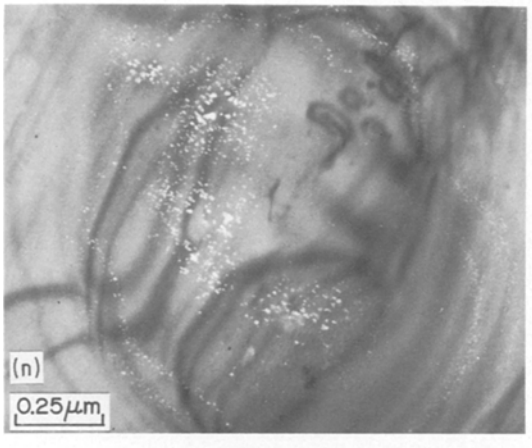
Figure 1 Continued.

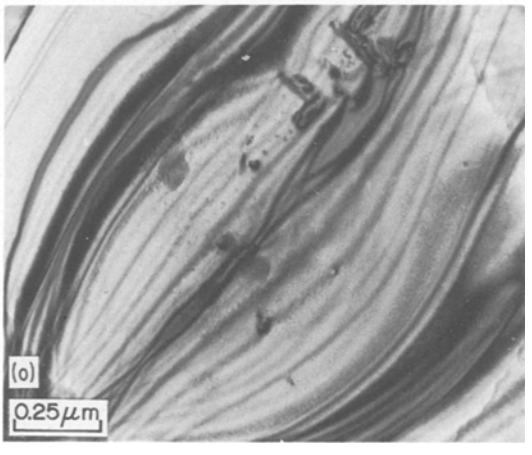
trating the identification of various matrix and extra diffraction spots as well as graphite rings. With continued irradiation, a gradual destruction of these spots was observed, and they completely disappeared after irradiation for 215 min (Fig. 1p).

As in the case of the SAD, there is a progressive change in the irradiated area as revealed by electron micrographs shown in Fig. 1c, e and g. A new feature began to develop in the irradiated area during the initial stages of irradiation (indicated by arrows). It was observed that these features grew during irradiation, coalesced with others, and spread throughout the irradiated area. The final appearance left one with an impression that material had been scooped out from the irradiated area (Fig. 1g). In addition, the irradiated area underwent severe bending, as evidenced by the formation of bend contours. This may be due to a build-up of stress in the irradiated area during irradiation. After 150 min irradiation, black spot-like features began to appear in the irradiated area (Fig. 1i). With continued irradiation some of these grew rather rapidly and were found to coalesce with others, resulting in a needle-like shape with strain contrast around them. The others grew at a slower rate, with a few of them exhibiting double-arc contrast, and could be resolved as dislocation loops (see inset in Fig. 1l).









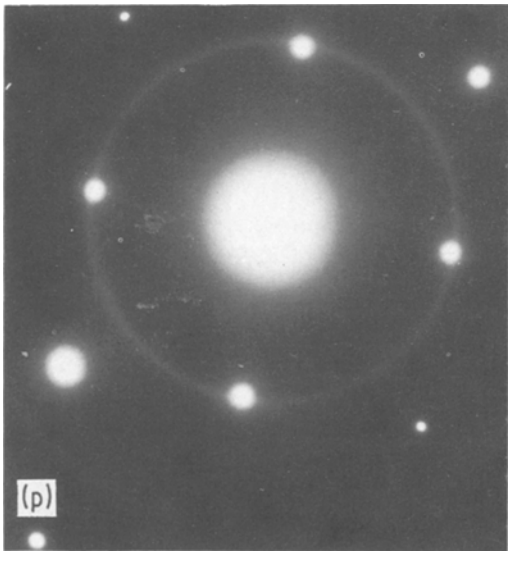


Figure 1 Continued.

As described earlier, extra diffraction spots corresponding to a cubic superstructure appeared in the diffraction pattern after 130 min of irradiation. A dark-field electron micrograph (Fig. 1n) taken using the extra diffraction spot (marked by x) as shown in Fig. 1m revealed light areas within the irradiated matrix. These are the ordered regions corresponding to the $TiC_{0.5}$ superstructure in the TiC matrix. A gradual disordering of these ordered domains took place, as evidenced by the gradual disappearance of the extra diffraction spots as irradiation continued. Finally, the ordered domains underwent complete disordering after 215 min of irradiation. Possible reasons for the appearance of the superstructure and the effects of irradiation upon it will be presented in the discussion section.

4. Discussion

4.1. Displacement damage

TiC has the NaCl structure, with carbon atoms occupying octahedral sites in the metal atom substructure. This material can exist over a wide range of substoichiometry where some of the carbon atom sites remain vacant. However, when a composition near $TiC_{0.5}$ is achieved, a cubic superstructure is formed by an ordered arrangement of carbon atoms in octahedral voids of the metal substructure. This structure (space-group $Fd3m$) may be described with 1/6 and 5/6 occupancy of alternate octahedral {1 1 1} carbon layers. The lattice parameter of the superstructure is twice as large as that of the subcell. Goretzki [1] determined this superstructure using neutron diffraction; his determination was confirmed by Bell and Lewis [2] using electron microscopy and diffraction. When TiC is subjected to bombardment by energetic electrons, both Ti and C atoms may be displaced from their normal lattice positions, provided the respective atoms receive energies through elastic collisions with the incident electrons which exceed their threshold energies for atomic displacement. According to Seitz and Koehler [9], the maximum amount of energy, E_m, which can be transferred by elastic collisions between the incident electrons and the target atom is given (in eV) by

$$E_m = 2148\, E_0\, (E_0 + 1.022)/A, \qquad (1)$$

where E_0 is the kinetic energy of an incident electron (in MeV) and A is the atomic weight of the target atom. The incident electron beam used in the present study had an energy of 100 kV which is capable of transferring a maximum energy of 20 eV and 5 eV to carbon and titanium atoms, respectively. The threshold displacement energy for titanium determined by high-voltage electron microscopy studies is 23 eV [10] which is much higher than that received by titanium atoms under present irradiation conditions. The most energetic primary displaced carbon atoms can, in turn, transmit up to 13 eV to titanium atoms in secondary collisions; this energy is also insufficient to produce displacement of titanium atoms. Thus, the energy received by the titanium atoms from the incident electron beam will increase the temperature of the specimen only, leaving the titanium sublattice undisturbed.

The threshold displacement damage in graphite has been determined by a number of investigators [11–13] using electron irradiation at sufficiently high temperature inside an electron microscope to cause the lattice defects to agglomerate into resolvable clusters. The values determined for the threshold displacement energy in graphite varied between 24.5 and 43.7 eV. If one assumes the lowest value of 24.5 eV to be the threshold displacement energy in graphite, the maximum energy received by carbon atoms (20 eV) through direct collisions in the present study is still lower than the 24.5 eV required for displacing carbon atoms from their lattice sites. As a result, one should not expect any displacement of either carbon or titanium atoms during electron irradiation at 100 kV. It should be noted, however, that the displacement threshold values for titanium and carbon in the above discussion are based upon displacements in titanium and graphite lattices and would be different if the determination were made on TiC since bonding in TiC [14] is different from that in titanium and graphite lattices.

Observation of the formation of the cubic superstructure, as suggested by Goretzki [1], in the irradiation area in the present study lends credence to the suggestion that the displacement of carbon atoms has indeed taken place at 100 kV in TiC. However, the superstructure formation requires the removal of displaced carbon atoms from the irradiated area to insure that the area under irradiation will attain a composition very near that of $TiC_{0.5}$. It is believed that the displaced carbon atoms diffuse to the foil surfaces which act as sinks. Moreover, the observation of the formation of graphite rings during irradiation strongly supports the idea that carbon atoms are displaced. The diffusion of displaced carbon atoms to the surface may be aided by the vacancies already present in $TiC_{0.93}$ and enhanced by the radiation-enhanced diffusion process [15]. As the composition of the irradiated area approaches a value near $TiC_{0.5}$ during irradiation, ordering of carbon atoms gradually takes place, leading to the formation of the cubic superstructure. Again, ordering of carbon atoms in the octahedral voids must be enhanced by irradiation since the diffusion of carbon atoms at room temperature in the $TiC_{0.93}$ lattice is extremely slow.

Goretzki [1] observed that the ordered superstructure is stable up to 1900° C. However, in the present study it has been observed that the superlattice reflections exhibited by the ordered $TiC_{0.5}$ were disrupted by continued electron irradiation (see Fig. 1p). The temperature rise in the foil due

to beam heating is too small to cause disordering of the ordered superstructure. This disordering effect may be attributed to the disordering of the carbon sublattice which results from the displacement of carbon atoms by the impinging electrons. Similar radiation-induced disordering of the ordered V_6C_5 has been studied by Venables and Lye [6] using electron irradiation inside a microscope at room temperature. They concluded that the displacement energy of carbon atoms in V_6C_5 has a surprisingly low value of 5.4 eV. From the similarities in the crystal structure and bonding in TiC and V_6C_5, it can be speculated that the threshold displacement energy in TiC is much lower than 20 eV and may be in the range similar to that observed by Venables and Lye [6].

Black spot damage began to appear after 150 min irradiation (see Fig. 1i). Some of these black spots grew rather rapidly, while others grew at a much lower rate. The observation of a cubic superstructure with continued irradiation strongly suggests that carbon atoms are displaced and removed from the irradiated area, leaving behind vacancies in the octahedral sites of the metal substructure. Although the mobility of vacancies in TiC at room temperature is extremely low, irradiation may enhance the mobility of the vacancies and thereby their tendency either to cluster in the form of vacancy loops or to form voids. Chatterjee and Lipsitt [7] have observed void formation in $TiC_{0.93}$ irradiated with 100 kV electrons at 800° C and above, the mobility of the vacancies being much higher than that of the room-temperature irradiation carried out in the present investigation. The appearance of defect clusters and the observation of strain fields around them led to speculation that these defect clusters are vacancy loops.

4.2. Graphite rings

The formation of graphite rings in the diffraction pattern was observed in (100) $TiC_{0.93}$ foils as a result of irradiation at 100 kV at room temperature. Furthermore, the experimental observation of the formation of the cubic superstructure indicates that a composition near $TiC_{0.5}$ was achieved in the irradiated area. It is believed that the displaced carbon atoms must find their way to the foil surfaces which act as sinks. This process is probably enhanced by the vacant sites already present in $TiC_{0.93}$ and by radiation-enhanced diffusion since the temperature used in this experiment is too low for diffusion of carbon atoms in TiC to take place.

As irradiation continues, the displaced carbon atoms diffuse to the foil surfaces, and it appears that they initially grow in the form of amorphous layers as evidenced by the diffuse nature of the graphite rings. As an increasing number of carbon atoms are available to these layers at the foil surfaces during irradiation, the layers will grow and may undergo irradiation-induced recrystallization, as supported by the formation of sharp continuous graphite rings. Radiation-induced recrystallization has been observed in amorphous ZrO_2 [16]. Alternatively, the appearance of graphite rings may be explained as resulting from epitaxial growth of graphite crystallites on the foil surfaces. At the beginning, these rings show up as diffuse rings; and as the crystallites grow further, the rings will become sharper, as observed.

A further explanation concerning surface graphite formation during irradiation can be given, based upon momentum transfer. In this case, enhanced diffusion in the electron beam direction will produce an excess of carbon atoms on the bottom of the thin foil and a deficiency of carbon atoms on the top surface. Stereomicroscopy of the irradiated area could have clarified the concept involving momentum transfer. Unfortunately, this technique was not used in the present investigation.

4.3. Radiation enhanced diffusion

From the experimental results, it is evident that radiation enhanced diffusion must have taken place during electron irradiation since the thermal diffusion coefficient is too low at room temperature to give rise to the observed effects. Vansant and Phelps [17] have used layer growth experiments to determine the diffusion coefficient in TiC, and the extrapolated value of the diffusion coefficient to room temperature is about 4.6×10^{-47} cm^2 sec^{-1} with an activation energy for diffusion of carbon in TiC of about 2.7 eV.

When irradiation is carried out at a temperature at which the radiation produced defects are mobile, a balance is reached between the rate of defect production and defect annealing at sinks. During this process an excess steady-state concentration of defects will be present in the sample, and the diffusion coefficient will be increased accordingly. Dienes and Damask [15] have proposed that the amount of enhancement in diffusion is a strong function of the mechanism by

which the excess defects are removed from the lattice. They considered a simplified theory in which it is assumed that the defects anneal at internal or external surfaces and their mutual annihilation is unimportant. The diffusion coefficient in the radiation field, D_{rad}, under such conditions can be given by

$$D_{rad} = D + \frac{K}{\alpha}, \qquad (2)$$

where D is the thermal diffusion coefficient, K is the defect production rate in dpa sec^{-1}, α is the sink concentration and $(D_{rad} - D)$ is the measure of diffusion enhancement.

In order to determine D_{rad}, the D, K and α values of Equation 2 must be known. Only a crude estimation of the D_{rad} under the present irradiation condition will be attempted because: (1) the displacement cross-section value for TiC required for calculation of K is not available; and (2) the diffusion coefficient measured by the layer growth technique [17] will provide only an average value of the diffusion coefficient in TiC. The extrapolated value of D to room temperature where the irradiation experiment was carried out is about 4.6×10^{-47} cm^2 sec^{-1} which is negligibly small. The determination of K requires knowledge of the displacement cross-section (σ_d), of the damage process in TiC, and of the electron flux used in the experiment. The value of the displacement cross-section in TiC is not available in the literature. However, it is assumed to be the same as that for V_6C_5 [6] which has a similar crystal structure and bonding characteristics [18], and the atomic weights of V and Ti are nearly the same. According to Venables and Lye [6] the value of σ_d in V_6C_5 for a displacement threshold energy of 5.4 eV and 100 kV incident electron energy is about 200 barns (2×10^{-22} cm^2). The electron flux used in the present study was about 10^{19} e cm^{-2} sec^{-1}. Thus, a value of K of $\simeq 2 \times 10^{-3}$ dpa sec^{-1} is obtained.

Assuming that the external surface is the only sink, the sink concentration, α, can be evaluated for simple geometric shapes by solving the diffusion equation with appropriate boundary conditions [19]. For a rectangular parallelepiped of dimension $A \times B \times C$

$$\alpha = \pi^2 \left(\frac{1}{A^2} + \frac{1}{B^2} + \frac{1}{C^2} \right). \qquad (3)$$

A and B are taken to be 3×10^{-4} cm (electron beam diameter), and C is 3×10^{-5} cm (foil thickness). The value of the sink concentration, α, is evaluated to be about 10^{10} cm^{-2}.

At room temperature the thermal diffusion is negligibly small and, thus, $D_{rad} = K/\alpha$. D_{rad} is determined to be 2×10^{-13} cm^2 sec^{-1} during irradiation at room temperature compared with 4.6×10^{-47} cm^2 sec^{-1} in the absence of electron irradiation. It represents a significant enhancement of the diffusion coefficient under irradiation. The estimated D_{rad} corresponds to a value of the thermal diffusion coefficient at about 890° C in the absence of irradiation [17]. A determination of the diffusion distance under irradiation can be made by the following relationship:

$$L = \left(\frac{K}{\alpha} \right)^{1/2} t^{1/2}, \qquad (4)$$

where L is the diffusion distance, K is the defect production rate, α is the sink concentration and t is the duration of irradiation. For example, a diffusion distance of 0.14 μm will be obtained after irradiation for 1000 sec at room temperature. Thus, the observed effects can be attributed to radiation induced diffusion.

It should be pointed out, however, that a precise estimation of the D_{rad} should incorporate the effect of mutual annihilation of vacancies and interstitials as well as the annihilation of defects to internal sinks such as dislocation loops, etc.

5. Summary and conclusion

Radiation damage in (100) $TiC_{0.93}$ foils was studied using a transmission electron microscope operated at 100 kV at room temperature. At first, diffuse rings were observed which, upon further irradiation, became sharp and were determined to be due to graphite. During irradiation, extra diffraction spots gradually became visible in the diffraction pattern, together with graphite rings formed earlier. The extra diffraction spots correspond to a cubic superstructure having a lattice parameter of 0.92 nm which is similar to the one observed by Goretzki [1] in his studies of $TiC_{0.5}$ by neutron diffraction. The formation of these extra diffraction spots strongly suggests that the irradiated area had attained a composition near $TiC_{0.5}$. It is suggested that the displaced carbon atoms must diffuse to the foil surfaces acting as sinks, thereby leaving an increasingly substoichiometric composition in the irradiated area. The present irradiation experiments were conducted at

room temperature where the thermal diffusion of carbon atoms is extremely slow. It is shown that the diffusion of carbon atoms can be enhanced sufficiently by irradiation, thus accounting for the observed effects.

With continued irradiation, the extra diffraction spots due to the ordered $TiC_{0.5}$ were disrupted. This effect may be attributed to the disordering of the carbon sublattice which results from the displacement of carbon atoms by the impinging electrons. Similar radiation-induced disordering of the ordered V_6C_5 has been observed by Venables and Lye [6].

Acknowledgements

The authors are grateful to Dr Moshe Ish-Shalom, Israel Ceramic and Silicate Institute, for critical reading of the manuscript and fruitful discussions. Thanks are also due to Dr D. B. Williams, Lehigh University, for making available his Faraday cage for use in the present study.

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Received 12 August 1980 and accepted 30 April 1981.