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RADIATION DAMAGE IN BORON CARBIDE

By

C. W. Tucker, Jr.

and

P. Senio

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General Electric Company
KNOLLS ATOMIC POWER LABORATORY
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Introduction

X-ray diffraction studies of radiation damage in boron carbide have previously been made on single crystal and polycrystalline specimens irradiated in the Brookhaven reactor at approximately 175°C for integrated thermal neutron fluxes of 6.4×10^{18} and 1.4×10^{19} neutrons/cm^2. The results of these studies have been reported in KAPL-710, pp. 42-47, KAPL-750, pp. 57-58, KAPL-749, KAPL-807, pp. 72-83, and KAPL-845, p. 60. This work has now been extended by irradiation of similar specimens for an integrated thermal neutron flux of 3×10^{20} neutrons/cm^2 in the MTR reactor. The temperature of the specimens during this irradiation is not accurately known but probably is not seriously different from that of the previous irradiations. To give an order of magnitude idea of the burnup during the MTR irradiation, neglecting absorption effects, the irradiation was somewhat longer than necessary to burn out the natural B-10 isotope concentration of 18.8%.

Dimensional Changes

Due to difficulties in removing the specimens from the irradiation capsule only part of the gross dimensional change measurements originally planned could be completed. Enough work could be done, however, to establish the order of magnitude of the dimensional changes to be expected in hot pressed boron carbide at this rather large burnup. For example, a thin disk of the hot pressed material about 0.02 inches thick and 0.5 inches in diameter was found to have increased its diameter 1.0% due to the irradiation. Similarly, a cylinder approximately 0.25 inches long and 0.25 inches in diameter increased its diameter 0.7% on irradiation. Unfortunately no measurements could be made in the direction of the axis of the cylinder after irradiation. In view of the X-ray lattice parameter changes to be discussed presently, it may be that the cylinder would have shown little or no expansion (or even a contraction) in this direction. One expects a contraction of about 0.3% because the irradiated hot pressed cylinder showed a 1.1% density decrease relative to a similar (and presumably identical) but unirradiated specimen. In connection with the dimensional changes, it may be important to note that the single crystals of boron carbide fragmented considerably during this irradiation. This may have been due to thermal stresses, inhomogeneity of the irradiation, or the very large anisotropy in the lattice expansion to be discussed presently. The last named seems the most probable cause. The hot pressed samples did not fragment during the irradiation but seemed mechanically much weaker.

It is also of interest to note that the hot pressed disk showed no weight change due to the irradiation. Apparently the weight increase due to the absorption of neutrons (about 3 milligrams) is offset by the loss of about one fourth of the helium formed (about 12 milligrams) by the reaction of the B-10 nucleus with the slow neutrons absorbed. The retention of the helium by the hot pressed material may even have been better since some weight loss may have resulted from chemical attack on the specimen when it was being removed from the irradiation capsule. The probability of this occurring is difficult to assess but leaves the figure of 25% as an upper limit to the helium loss during irradiation.

Inspection of the X-ray diffraction powder patterns from the irradiated and unirradiated hot pressed samples immediately showed considerable changes in the lattice parameters of the irradiated material. Measurement of the lattice parameters showed an expansion of 0.63% in the a_o-direction and a contraction of 0.83% in the c_o-direction*. These unusual results were confirmed semi-quantitatively using irradiated and unirradiated single crystals. The single crystal work not only confirmed the a_o-direction expansion and the c_o-direction contraction, but also showed that the change going from the one direction to the other was continuous, passing through zero at approximately the expected direction. These results show that the lattice dimensional changes in boron carbide are more anisotropic than in any other material thus far studied. Graphite is the next most anisotropic material in that it expands in the c_o-direction and contracts very slightly in the a_o-direction.

The reason for the large anisotropy of the lattice dimensional changes in boron carbide is not yet well understood. It is quite possibly due to anisotropic bonding of the interstitial atoms. Based on the geometry of the lattice this conclusion seems quite reasonable. It does not seem likely that depletion of the boron content would cause the observed parameter changes, as the work of Glaser, Moskowitz, and Post[1] shows that the lattice undergoes a nearly isotropic contraction on decreasing the boron content. The work of the Norton Company[2] on the effect of boron on the lattice parameters does not cover the boron deficient region, but they have found that excess boron expands the lattice almost isotropically. It seems rather certain that the quite different lattice changes (compared to variation of boron content) observed on irradiation are due to the interstitial atoms and perhaps also due

* Boron carbide has a rhombohedral crystal structure which may be indexed in the hexagonal system. The a_o and c_o refer to the hexagonal axes.

to vacancies. Work is planned, to be discussed later, which may well reveal the cause of the anisotropy in the lattice parameter change on irradiation.

"Thermal" Effects

One of the very striking changes occurring in the X-ray diffraction patterns of single crystals of boron carbide in the two irradiations in the Brookhaven reactor was the large increase in the intensity of the thermal diffuse scattering by the lattice due to the irradiations. The MTR irradiation shows this effect in a very extreme fashion. The thermal diffuse reflections which usually have an intensity of only 10^{-3} the intensity of the Bragg reflections in an organic crystal, and probably much less than this in unirradiated boron carbide, were found in the MTR irradiated boron carbide to be at least as intense as the Bragg reflections. Previously these changes in the thermal diffuse reflections had been interpreted, due to their apparent decrease in intensity on cooling to liquid nitrogen temperatures, as being due to a loosening of the lattice thus degrading the lattice vibration spectrum to lower frequencies. Liquid nitrogen measurements on the MTR irradiated crystals, however, does not reveal a pronounced temperature sensitivity of the thermal diffuse reflections and the alternative explanation for the changes, realized at the outset, now is favored. This alternative explanation is that surrounding interstitial or substitutional foreign atoms and lattice vacancies there are permanent lattice distortions which lead to a thermal diffuse type of X-ray scattering [3,4]. This scattering of course does not arise from the thermal motion of the atoms in the lattice and so is essentially temperature insensitive.

The single crystal diffraction data of the MTR irradiated material also showed pronounced changes in the intensity of the Bragg reflections relative to unirradiated crystals. Many of the changes followed the pattern to be expected from an anisotropic temperature factor, indicating a large temperature effect for reflections of the type 00.ℓ and a much smaller effect for reflections of the type h0.0. Intermediate reflections showed effects varying continuously between the two extremes.

Thus the irradiated single crystals of boron carbide show very strong "thermal" effects, namely, intense thermal diffuse scattering and a large but anisotropic temperature factor, which apparently do not have a thermal origin. It now seems quite certain that the effects are due to local lattice distortions due to radiation produced imperfections. Indeed, the theoretical analysis of Huang [3] predicts effects of this type for the lattice distortions produced by the solute atoms in a substitutional solid solution. Experimental and theoretical work is in progress to study these effects.

Structural Changes

In addition to the systematic intensity changes of the Bragg reflections traceable to an apparent anisotropic temperature effect in the MTR irradiated material, there were other very pronounced changes in the Bragg intensities. Preliminary calculation of the structure factors of some of the affected reflections reveals that these changes are not simply due to depletion of the boron content of the crystals. Rather it seems possible that there are certain preferred positions for interstitials and the intensity changes are due to the displacement of the lattice atoms in particular directions because of this preference. Data are being collected for a Fourier "difference" synthesis using irradiated and unirradiated single crystals. This approach should reveal the magnitude and direction of the average atomic displacements of the lattice atoms due to the irradiation-produced interstitials and vacancies.

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References

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