PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT III, 1963

X-Ray Diffraction Studies of Defect Structures in Irradiated Metals*

W. V. CUMMINGS

General Electric Company
Atomic Power Equipment Department
Vallecitos Atomic Laboratory
Pleasanton, California, U.S.A.

Lattice defects produced in molybdenum by neutron irradiation have been studied by x-ray diffraction. An analysis of the line profiles show that fragmentation effects saturate at an exposure of 5.0×10^{19} neutrons per cm^2 and a minimum crystallite size of 500 Å–600 Å is reached. The lattice parameter also reached a maximum at this point. The lattice microstrains, however, continue to increase with exposure in an isotropic manner.

1. Introduction

A. Nature of Radiation Damage

Various theories and models of radiation damage based primarily on considerations by Seitz[1),2)] have been proposed during the past few years. The simplest concept is based on the generation of interstitial-vacancy pairs by the bombarding radiation and their retention in the crystal lattice primarily as point defects. In an attempt to explain observed behavior and to cover all theoretical possibilites, this simple concept has been expanded quite extensively. In addition to point defects, the existence in irradiated solids of a number of other defects including dislocations, interstitial and vacancy agglomerates, and crowdions have been proposed. Small volumes of thermally agitated material, referred to as thermal spikes and displacement spikes[3)] also are postulated to be an originating source of defects. Several excellent reviews of these theories are available, such as those by Seitz and Koehler[4)], Dienes and Vineyard[5)], and Billington and Crawford[6)]. In all cases, experimental data verifying the nature of the defects produced and the damaging mechanism involved in their creation is limited and often contradictory.

A common characteristic of all proposed defects is that each will disrupt the periodicity of the crystal lattice. Since the diffraction of X-rays depends upon this periodicity, the study of irradiated materials by X-ray diffraction should disclose important information about the nature of these lattice defects. This technique has had limited use to date, primarily because of certain experimental difficulties involved in the detection of diffracted X-rays in the presence of a radioactive background. Techniques developed during the past few years have alleviated this problem to an extent that now this method of study can be used to supplement more established, but in many cases less definitive, analytical methods.

B. Material Selection

Crystal lattice defects produced in a heavy metal with a high melting point have been investigated. Displacement spike effects should be maximized[3)] and defect annealing during irradiation should be minimized in a material with these characteristics. Since previous studies of lattice parameter changes in irradiated molybdenum[7)] has provided background information, additional investigations of radiation effects in this metal were continued. This choice was also influenced by the fact that a large amount of line broadening was apparent in the diffraction patterns from this material but a quantitative analysis of this effect was not reported. Molybdenum that had been exposed to fast neutrons up to maximum integrated fluxes of 1.2×10^{20} neutrons per cm^2 (nvt) at temperatures less than 50°C were chosen for this study.

* This work was supported in part by the U. S. Atomic Energy Commission Contract No. W-31-109-Eng-52.

2. Experimental Results

A. Lattice Parameter Measurements

The results of lattice parameter measurements in irradiated molybdenum as reported previously[7] are shown in Fig. 1. In review, the lattice parameter increased with exposure until a maximum expansion of .048 per cent was reached at approximately 5.0×10^{19} nvt. For exposures greater than 5.0×10^{19} nvt, a reversion in a_0 occurred and a value 0.004 per cent less than that for the unirradiated state was measured for the highest exposure of 1.2×10^{20} nvt. A measurement of a number of interplanar spacings showed that this contraction was isotropic throughout the crystal. This shrinkage of the unit cell after relatively high exposures to fast neutrons following an initial expansion is not readily explained by the usual interpretation of radiation damage theories.

B. Line Broadening Analysis

Even though a reversal in Δa_0 occurs at higher exposure levels it can be seen in Fig. 1 that the breadth as measured at half-height increases almost linearly with exposure. This indicates that structure damage is increasing with integrated flux and that this damage is more complex than that caused by point defects alone. A quantitative analysis of the broadening was obtained by use of the method of line profile analysis as described by Warren and Averbach[8),9)], and Stokes[10)]. Lattice defects that produce broadening of X-ray diffraction lines should affect the structure in one of two characteristic manners. The defects either interrupt the coherency of the diffracting domains such as would result from fragmentation and decrease in the size of the crystallites or they should exist in the lattice in a manner that introduces microstrains or dis-

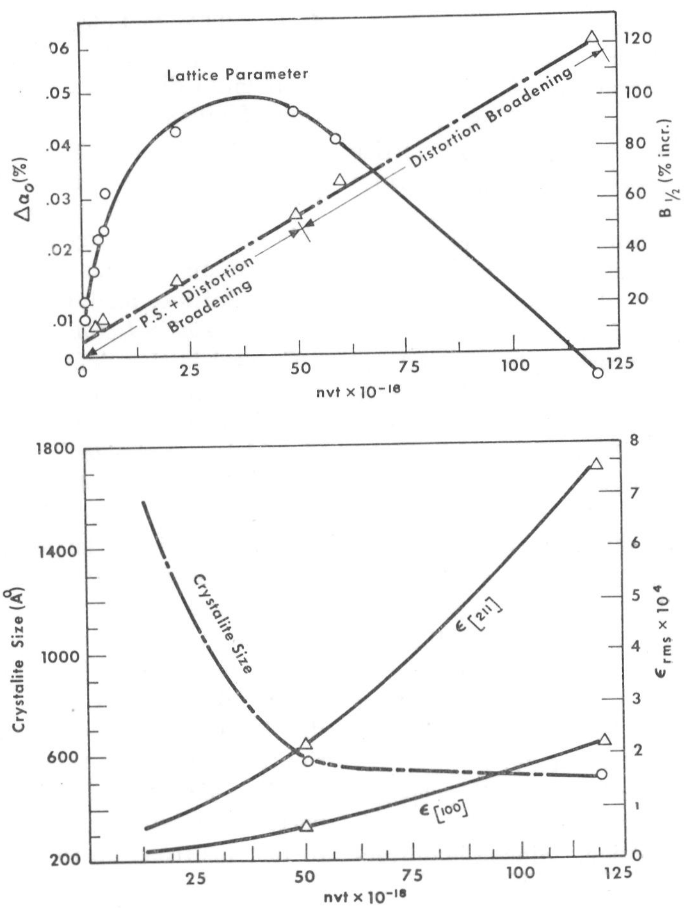


Fig. 1

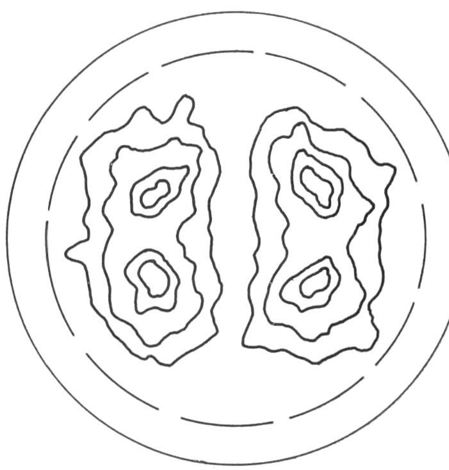
tortion. A classification of damage into either of these two categories should provide an indication of the nature of the defects that exist in the lattice. Both fragmentation and distortion result in broadened diffraction lines but under certain experimental conditions the broadened peak shapes can be analyzed. The two broadening peak effects can be quantitatively separated[9] allowing the size of the diffracting domains, or crystallite dimensions, and the magnitude of the distortion to be determined. This information, complemented with that obtained from a study of other diffraction effects such as lattice parameter changes, can be analyzed to determine possible types of structure defects and the mechanisms of damage involved in their production.

Profiles of the (200), (400), (211), (422), (110), and (220) reflections from five irradiated specimens and one annealed specimen were obtained. The specimens represented two exposure levels. Two specimens received an integrated exposure of 5.0×10^{19} nvt and the remaining three received 1.2×10^{20} nvt. $K\alpha$ X-rays from chromium, iron, copper and molybdenum targets were used. The type of X-radiation was chosen so that each reflection would be recorded at a high 2θ angle.

The analytical methods described in references (8), (9) and (10) above were used to separate and obtain the crystallite size and distortion functions and to determine the magnitude of these effects. Since the orders of reflections (200), (400), and (211), (422) were used, the crystallite size and distortion was determined for two crystallographic directions. This analysis for all five irradiated specimens, representing two exposure levels of 5.0×10^{19} and 1.2×10^{20} nvt and the two crystallographic directions [100] and [211] gave average crystallite sizes between 520 Å and 600 Å in all cases. Since the crystallite size did not decrease appreciably for exposures above 5.0×10^{19} nvt, this means that the large amount of additional broadening above this exposure level is essentially all caused by distortion or lattice microstrains. At each exposure level the r.m.s. strains ε_{rms}, were determined to be three to four times greater in the [211] direction than in the [100] direction. However, the strains in both directions increase by an approximate factor of 3.5 as the exposure level increases from 5.0×10^{19} to 1.2×10^{20} nvt. These plots of strain and crystallite size versus exposure also are shown in Fig. 1.

The value of Young's modulus in molybdenum differs slightly in the two crystallographic directions, but this difference is small ($E_{[211]} = 1.18\ E_{[100]}$) when compared to the difference in strains and can be assumed to have a negligible effect. Another relationship that is of possible significance is that at the temperatures involved in this experiment, the (211) plane is the major deformation plane in the body-centered cubic structure. This is also the crystallographic direction in which the largest strains occur.

Unirradiated



Irradiated

Fig. 2. Partial pole figures typical of highly oriented molybdenum.

C. Preferred Orientation Effects

Some of the material used in this test possessed a high degree of preferred orientation. Before irradiation, this texture was very sharply defined as shown by the (200) partial pole figure in Fig. 2 (top). The pole figure for the same plane is shown after an exposure of 1.2×10^{20} nvt in Fig. 2 (bottom). It is obvious from this breakup of symmetry and decrease in pole density maxima that a relatively large volume of metal has been re-oriented during irradiation. It also follows that the fragmentation that was observed and which apparently approaches saturation at an exposure of 5.0×10^{19} nvt is not solely a matter of low angle boundaries or dislocations, but that a substantial amount of relatively large angle re-orientation has occurred such as might be expected if portions or "spikes" of the material were resolidifying from a melted condition. The percent volume of re-oriented metal is not readily determined, but it is obviously quite substantial and a tendency toward randomness is indicated.

D. Summary of Radiation Effects

The following crystallographic effects have been observed in molybdenum exposed to fast neutrons up to a maximum of 1.2×10^{20} nvt.

1. The lattice parameter increases with exposure until a maximum expansion of .048 per cent is reached at approximately 5.0×10^{19} nvt. As exposure increases further, the lattice parameter decreases until a value of -0.004 per cent is reached at the highest exposure of 1.2×10^{20} nvt.
2. The breadth of the diffraction lines increases almost linearly with exposure.
3. An analysis of the line profiles shows that fragmentation of the crystallites occur. The crystallite size or size of the coherent scattering domains are in the range of 520 Å to 600 Å in specimens irradiated to 5.0×10^{19} nvt and also in specimens irradiated to 1.2×10^{20} nvt. This size does not vary significantly with crystallographic direction. This observation shows that crystallite size reached some minimum value relatively early during irradiation. In addition, the increase in line broadening above the exposure of 5.0×10^{19} nvt is nearly all a result of lattice distortion. These effects are shown in Fig. 1.
4. Further analysis of the line profiles show that the microstresses developed are anisotropic in nature. At an exposure of 5.0×10^{19} nvt, the strains in the [211] crystallographic direction are approximately four times greater than those in the [100] direction. At an exposure of 1.2×10^{20} nvt, these strains are in the same ratio but both have increased in magnitude by a factor of approximately 3.5. This is also shown in Fig. 1.
5. Texture studies on preferentially oriented specimens show that a relatively large volume of metal has been re-oriented as a result of the irradiation. An observed breakup of symmetry and decreased pole density maxima indicate the generation of relatively large angle re-orientations during irradiation. Partial pole figures of the (200) plane obtained before and after irradiation are shown in Fig. 2.

3. Discussion

As stated previously, present interpretations of existing theories on radiation damage do not readily explain the various results obtained in this experiment. The shrinkage of the lattice at higher exposures following an initial expansion, the anisotropic nature of the strains, and the maximum amount of fragmentation or lower limit in crystallite size that is reached at relatively low exposures are effects that have not been explicitly predicted.

A simple interstitial-vacancy pair generation within a crystal predicts that a net expansion of the lattice should occur[11]. Although the interstitial causes an expansion and the vacancy a contraction, the absolute magnitude of the interstitial effects is about five times that for the vacancy. The result should be a net expansion. Because of vacancy-interstitial recombinations during irradiation this expansion should approach some equilibrium value as exposure increases. This simple recombination mechanism by itself will not produce a lattice contraction. A lattice shrinkage during irradiation, after an initial expansion, must be explained either by a preferential increase in the concentration of vacancies over interstitials in some manner or by a substitutional solid solution of transmuted atoms which are smaller than the molybdenum atom. This second effect is found to be negligible. This means that some mechanism must be acting that will result in an increase in the ratio of vacancies to interstitials at the higher exposure levels.

From theoretical considerations and experimental studies, investigators agree in general that 1) the energy of formation for an interstitial is greater than that for a vacancy by a factor of about 5, and 2) the energy of migration for an interstitial is less than that for a vacancy by a factor of one-fifth to one-tenth[5]. At the irradiaton temperature of this experiment it is feasible that interstitials will be mobile and vacancies relatively immobile. Trapping sites for the mobile interstitials are originally present in the metal at defects caused by dislocations and at impurity atoms. In addition, other traps are constantly being formed if plastic deformation is occurring as might be interpreted from the values obtained for the magnitude of the distortion and from the preferred orientation analysis. As the interstitials move to these trapping sites, agglomeration should occur predominately along the (211) deformation plane. As the interstitials are spent in forming clusters the vacancies remain relatively unchanged. The result is an effective increase in vacancy-to-interstitial ratio within the lattice. The region around and within these clusters should be highly strained, and these strains should increase with irradiation.

Brinkman predicts a maximum effect from the kinetics of the displacement spike will occur in the heavier metals such as molybdenum[3]. The number of atoms affected by this spike is estimated by dividing the energy available for production of the spike by the average energy per atom when the metal is in the melted condition. This average energy is normally 0.1 to 0.2 ev for metals, but is adjusted upward to 1.0 ev because of the existence of unrelieved high pressure within the spike. If these very high pressures are relieved by plastic deformation, then two effects are probable and should be noted. First, the number of atoms associated with the displacement spike must be increased, since the average energy per atom is decreased when deformation occurs. If a value of 0.2 ev per atom and the other values pertinent to molybdenum are used, a spike size of about 180 Å is obtained and approximately 10^5 atoms are affected. Although this size for the displacement spike is greater than that previously predicted, it is still considerably smaller than the minimum crystallite size measured in this experiment. The second effect that is almost certain if irreversible yielding occurs in the material bordering the spiked zone, is the formation of quenched-in vacancies. These are vacancies in addition to those associated with Frenkel defect formation and may be present either as Shottky defects or as small clusters in the form of dislocation loops. The heating of the displacement spike volume to a very high temperature, a retention of this temperature for an appreciable length of time, than a rapid quench to the temperature of the surrounding media are all predicted in the original dissertation on the displacement spike model. The only additional effect necessary for a prediction of vacancy generation is evidence of associated plastic deformation. In relation to this action it should be noted that as the size of the crystallites decrease the probability of a spike zone intersecting a crystallite boundary becomes very great. The boundaries can best be visualized as regions where a high density of dislocations provide excellent trapping sites for migrating interstitials. The mean free path of an interstitial to a site that effectively removes it from the lattice therefore decreases with crystallite size, but the quenching action of the displacement spike continues to generate vacancies that are relatively immobile. The length of this mean free path becomes constant at the exposure of 5.0×10^{19} nvt; the point where crystallite size becomes a minimum and where the lattice parameter is maximum.

References

1 F. Seitz: Disc. Faraday Soc. **5** (1949) 271.

2 F. Seitz: Phys. Today **5** (1952) 6.

3 J. A. Brinkman: J. Appl. Phys. **25** (1954) 961.

4 F. Seitz and J. S. Koehler: *Solid State Physics*, ed. F. Seitz and D. Turnbull, Academic Press, Inc., New York **2** (1956) pp. 307-442.

5 G. J. Dienes and G. H. Vineyard: *Radiation Effects in Solids*, Interscience Publishers, Inc., New York (1957).
6 D. S. Billington and J. H. Crawford, Jr.: *Radiation Damage in Solids*, Princeton University Press, Princeton, New Jersey (1961).
7 D. L. Gray and W. V. Cummings: Acta Met. **8** (1960) No. 7, 446.
8 B. E. Warren and B. L. Averbach: J. Appl. Phys. **21** (1950) 595.
9 B. E. Warren and B. L. Averbach: J. Appl. Phys. **23** (1952) 497.
10 A. R. Stokes: Proc. Phys. Soc. **61** (1948) 382.
11 C. W. Tucker, Jr. and J. B. Sampson: *Interstitial Content of Radiation Damaged Metals from Precision X-Ray Lattice Parameter Measurements*, KAPL-1037, Jan. 26, 1954 (Unclassified).

DISCUSSION

Auleytner, J.: In connection with Dr. Cummings' lecture I should like to tell you about some effect observed by my collaborators Miss Szmid and Mr. Szaras from Institute of Nuclear Research of Polish Academy of Sciences. The mosaic structure of Al single crystals was investigated by means of X-rays before and after fast neutrons bombardment. An interesting change in the primary mean disorientation angle between mosaic blocks has been found. We can see (see Table I) that

Table I

	Disorientation angle before irradiation min.	Neutron dose n/cm^2	Disorientation angle after irradiation min.	Increase of the disorientation min.	Increase of the disorientation per cent
Al 9	19′	5.10^{18}	27′	8′	42
Al 11	23′	2.10^{18}	28.5′	5.5′	24
Al 12	30.5′	2.10^{18}	49′	18.5′	61

one specimen (Al 12) had a far worse structure than the other two. Its disorientation of mosaic blocks was *ca* 60% and 33% larger than that of Al 9 and Al 11 respectively. The specimen Al 12 has shown greater changes in the mosaic than Al 9 and Al 11 after irradiation. The increase of the disorientation was *ca* 61%, it is much more than in the case of crystals with better structure. Although you have investigated other type of crystal perhaps, have you observed such effect?

Cummings, W. V.: Yes, I think I have seen a similar effect, but in polycrystalline rather than single crystal material. Some of the material used in this experiment was highly oriented. Fig. 2 shows partial pole figure both before and after irradiation. It can be seen that the pole density maxima has not only decreased in maximum intensity, but a general reorientation has occurred. I believe that this is the same effect you are seeing in your aluminum crystals.

Bragg, R. H.: In view of the fact that the lattice parameter has changed you *should* expect a changed pole figure unless you took the trouble to move your X-ray detector to correspond to the correct Bragg angle for the new situation.

Cummings, W. V.: The counter was changed to the correct position and precautions were taken to include the full intensity of the broadened reflection.