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ORDERED DEFECT STRUCTURES IN IRRADIATED METALS*

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INTRODUCTION

It has been generally accepted that irradiation of high purity metals produces a completely random array of microscopic defect clusters. This observation was supported by transmission electron microscopy observations over the past 10 - 15 years^(1,2) and was especially true in the matrix far from internal surfaces such as grain boundaries or precipitates. However, scientists have recently discovered⁽³⁻⁵⁾ that the concept of a completely random array is no longer true under certain circumstances, namely, when metals are irradiated at approximately one-third of their melting point at a fluence which corresponds to every atom being displaced many times. Such irradiations produce high densities of defect clusters whose strain fields interact and cause the defects to seek an ordered array that will minimize the total energy of the system. It is the object of this paper to present some examples of ordered loop and void structures in pure metals observed at Battelle Northwest laboratories, and to briefly review the information on ordered void structures obtained at other facilities.

EXPERIMENTAL

Descriptions of the sample material⁽⁶⁾ used for the BNW studies, irradiation techniques,⁽⁷⁾ analysis procedures^(6,8) and methods for calculating the damage in the samples^(9,10) are given elsewhere. Briefly, 3 mm diameter samples were irradiated on a temperature controlled furnace with high energy heavy ions. The bombarding species were either 5 MeV Ni, 6 MeV Se ions or 7.5 MeV Ta ions. A specific amount of the damage layer was removed and the samples prepared for observation with a 200 KV electron microscope.

ORDERED LOOP STRUCTURE IN NICKEL

Irradiation of high purity nickel at temperatures of 370, 400 and 450 °C to approximately 15 dpa* with 5 MeV Ni ions produced microstructures similar to that in Figure 1. The defect structure is characterized by a high density of black spots and dislocation loops aligned in mutually perpendicular rows. The foils have a very strong {100} texture and the rows are aligned parallel to the <100> directions in the foil plane with an average spacing of 350 Å. The ordering

*dpa = displacements per atom.

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Figure 1. Alignment of the radiation damage in nickel produced by bombardment with 5 MeV Ni^{++} ions to 1×10^{16} ions/cm² at 370 °C.

extended over entire grains with very little denuding ($< 500 \text{ \AA}$) of the damage around grain boundaries as seen in Figure 1. The cluster density is difficult to measure because of overlapping, but it appears to be in excess of $4 \times 10^{16} \text{ cm}^{-3}$.

Examination of the microstructure at high magnification clearly showed the presence of dislocation loops which have no stacking fault contrast and are, therefore, prismatic in nature. The loops are also inclined to the foil plane, and the line of no contrast is parallel to the $\langle 110 \rangle$ direction. Based on the conditions outlined by Thomas

and Bell,⁽¹¹⁾ the loops most likely lie on $\{111\}$ planes with a $\frac{a}{2} \langle 110 \rangle$ Burgers vector.

The very small black spots could be resolved at high magnification to be squares with sides parallel to the $\langle 100 \rangle$ directions. Some examples are circled in Figure 2. Stacking fault tetrahedra should project as squares in this orientation. The existence of stacking faults is confirmed by the presence of streaks in the diffraction spots (insert, Figure 2). The streaks are a result of the reciprocal lattice points extending in a direction perpendicular to the fault which in this case is the $\langle 111 \rangle$ direction.⁽¹²⁾ The $\langle 111 \rangle$ direction projects as the $\langle 110 \rangle$ direction in the (100) plane and the insert in Figure 2 shows streaks in the $\langle 110 \rangle$ direction.

Figure 2. Evidence for stacking fault tetrahedra in ion bombarded Ni. Note square projection of tetrahedra (circled) in (100) orientation and streaking of diffraction spots in the $\langle 110 \rangle$ direction (insert).

Several conclusions can be drawn from these observations. It is known that interstitials are inherently more mobile than vacancies, and that after irradiation the interstitial type defects tend to be larger but fewer in number than the vacancy type defects. It is then reasonable to conclude that the dislocation loops originate from the interstitial atoms and the stacking fault tetrahedra from the vacancies. Stacking fault tetrahedra have been previously identified in nickel irradiated with neutrons at 50 °C and annealed at temperature <500 °C.^(13,14) Tetrahedra have also been observed in quenched and annealed nickel.⁽¹⁵⁾ Interstitial loops have been identified in nickel irradiated with neutrons at 50 °C and subsequently annealed,⁽¹³⁾ and have also recently been identified in nickel irradiated directly at 350 °C.⁽¹⁶⁾ Therefore, previous results would strongly support the concept that the dislocation loops are interstitial in nature and that the remaining vacancies form stacking fault tetrahedra.

The unique feature of the microstructure is the well delineated ordering of interstitial dislocation loops. Furthermore, since the loops align in $\langle 100 \rangle$ rows in the (100) plane, the arrangement in three dimensions must be a cubic type of array. This cubic ordering is felt to be a result of loop movement by self climb and/or prismatic glide into a position where the interaction energy between loops is a minimum. Foreman and Eshelby⁽¹⁷⁾ and Kroupa⁽¹⁸⁾ have derived the interaction energy for the particular case of loops lying on parallel planes with equivalent Burgers vectors. One can use their expressions to derive the spatial distribution of constant forces for climb of two parallel (111) loops with identical $\frac{a}{2} \langle 110 \rangle$ Burgers vectors. Figure 3 shows the results of such a calculation for Ni and reveals that loops moving only by self climb should come to rest at a position of 35° or 65° to the plane normal. If the rows of loops form only at 35° to the loop plane normal and repeat this ordering in three dimensions, then such a grouping would produce a fcc stacking. Rotation of a fcc lattice into a (100) orientation would consequently result in a cubic array such as that observed experimentally. A more quantitative analysis is difficult at this time because there are four {111} planes in Ni, each with three

Figure 3. Constant force curve for self-climb between two parallel loops.

possible $\frac{a}{2} \langle 110 \rangle$ Burgers vectors. Further work on these complex interactions is in progress.

It can be shown that a structure such as that observed in Figure 1 cannot be caused by prismatic glide alone. Hudson⁽¹⁹⁾ has developed the expressions for the force in the glide directions for two identical loops and his theory would predict that the rows of loops would form at 45° to the loop plane normal in nickel. This would not produce a cubic array when rotated into a (100) orientation such as that observed in Figure 1.

ORDERED VOID STRUCTURES IN METALS

There have been several independent and simultaneous observations in the past year of three dimensional ordered arrays of voids in metals.^(3-6,20) These observations have been made on a wide variety of materials in Ni, Mo, Mo - 0.5 Ti, TZM, Nb, and Ta which

were both ion bombarded and neutron irradiated, with and without inert gases such as helium present during the irradiation. One of the striking features of these observations is that the void superstructure has the same stacking as the parent atomic lattice (i.e., fcc in Ni and bcc in Mo, Nb, and Ta).

Figure 4a shows a typical fcc cubic array of voids in 6 MeV Se ion bombarded Ni. Identical results were obtained from 5 MeV Ni ion bombarded Ni foils which contained 3 atomic parts per million of pre-injected helium. Both of these studies were conducted at 525 °C and they reveal that the threshold for the super lattice formation is approximately 350 - 400 dpa in Ni.

Figure 4a. Face centered cubic superlattice of voids in nickel which has been ion bombarded to 400 dpa at 525 °C.

4b. Body centered cubic superlattice of voids in molybdenum which has been ion bombarded to 130 dpa at 900 °C.

Figure 4b exhibits a typical bcc cubic array of voids in 7.5 MeV Ta bombarded Mo. The damage level is approximately 130 dpa and the bcc structure has been confirmed by observations in the (111) and (110) orientations. Similar results were obtained with Nb bombarded with Ni ions at 800 °C. (3)

Figure 5 shows a typical bcc void array found by Evans⁽⁴⁾ in Mo bombarded with 2 MeV nitrogen ions at 870 °C to approximately 100 dpa. Projections of the void lattice in the (100), (110), and (111) orientations unambiguously confirms a bcc superlattice in that metal.

Figure 5. The projections of a bcc lattice along the [011], [010] and [111] directions together with micrographs showing the projections of the void lattice along the same directions. Courtesy of J. H. Evans.

Wiffen^(5,20) has found similar bcc ordered lattices in bcc metals which have been irradiated to the 30 - 40 dpa range. Figure 6 shows typical microstructures of pure Mo, Nb and Ta. An important feature of this study was that the formation of the superlattice must be

Figure 6. Ordered void lattices in neutron irradiated refractory metals. Courtesy of F. W. Wiffen.

relatively insensitive to displacement rates. For example, approximately the same results were obtained from Mo which was ion bombarded at 10^{-2} dpa/sec (see Table I) and that which was neutron irradiated at 10^{-6} dpa/sec.

The reasons for the void alignment have been explored by Malén and Bullough⁽²¹⁾ using the theory of anisotropic elasticity. They concluded that the interaction between the displacement fields of the voids was responsible for the ordered arrays. These displacement fields arise from the anisotropy of the elastic constants. Malén and Bullough⁽²¹⁾ calculated that the interaction between a faceted void at the origin and another of equal size at R is

$$E(R) = - \frac{8d (1 - \beta)^2 P''}{3r_v \pi C_{44}} \left\{ \left(\frac{r_v}{R} \right)^3 - \frac{28 C_{44}}{9d (1 - \beta)} \left(\frac{r_v}{R} \right)^5 \right\} [3 - 5 S(4)]$$

where P'' = a surface energy term required to maintain a faceted void with eight faces.

r_v = radius of the void

$$\beta = \frac{C_{12} + C_{44}}{C_{12} + 2C_{44}}$$

$$d = C_{11} - C_{12} - 2C_{44}$$

C_{11}, C_{12}, C_{44} = elastic constants

$S(4)$ is a geometrical structure factor accounting for the positions of the surrounding voids.

Malén and Bullough⁽²¹⁾ find that the ratio of the equilibrium spacing to the void radius should be $a/r_v \cong 8$ in Mo by requiring that the interaction be a minimum at the equilibrium lattice spacing, a , $dE_2(a)/da = 0$ and that $d^2E_2(a)/da^2 > 0$ for stability. A similar treatment predicts $a/r_v \cong 6$ for Nb.

Table I* lists the experimentally determined a/r_v ratios for all the materials in which void super structures have been found. It is seen that the experimentally determined a/r_v ratios of 7.7 - 11 for Mo, 6.1 - 8.8 for Mo-0.5 Ti and 7.3 for TZM agree well with that theoretically predicted⁽²¹⁾ for pure Mo. The agreement for the a/r_v ratio in neutron irradiated Nb(7.2) and that theoretically predicted (~ 6) is quite reasonable, but it is considerably less satisfactory

*Note that the ion bombardment temperatures have been corrected to equivalent neutron irradiation temperatures according to Bullough and Perrin.⁽²²⁾

TABLE I
SUMMARY OF DATA ON ORDERED VOID LATTICES

Material	Bombarding Species	Irradiation Temp. °C	Damage Level dpa	Super-lattice Structure	a, Void Lattice Constant A	2 r _v Ave. Void Size A	$\frac{a}{r_v}$	Reference
Ni ^(a)	5 MeV Ni	525 (390) ^(b)	360	fcc	620	250	5.0	3
Ni	6 MeV Se	525 (390)	400	fcc	660	180	7.3	3.6
Mo ^(a)	neutrons	585	36	bcc	265	64	8.3	5
Mo ^(a)	neutrons	790	36	bcc	328	72	9.1	5
Mo	2 MeV N	870 (660)	~100	bcc	220	~40	~11	4
Mo	7.5 MeV Ta	900 (680)	130	bcc	230	60	7.7	This study. 10
Mo-0.5 Ti ^(a)	neutrons	585	36	bcc	215	69	6.1	5
Mo-0.5 Ti ^(a)	neutrons	790	36	bcc	315	72	8.8	5
TZM ^(c)	2 MeV N	870 (660)	400	bcc	220	~60	~7.3	4
Nb	5 MeV Ni	800 (620)	5	bcc	350	45	15.6	3
Nb ^(a)	neutrons	790	34	bcc	665	186	7.2	5
Ta ^(a)	neutrons	585	20	bcc	205	61	6.7	20

(a) Contains He from pre-injection or produced neutronically.

(b) () Effective neutron irradiation temperature corresponding to 10⁻⁶ dpa/sec.

(c) Nominally 0.5 Ti - 0.1 Zr - 0.03 C - Bal. Mo.

in the ion bombarded Nb(15.6). The theory completely fails to predict ordering in Ta but as Malen and Bullough point out, certain approximations will have to be refined in order to present a more complete result of faceted voids. No theoretical attempt has been published treating the case of fcc Ni so little can be said about the ordering in that metal aside from the fact that Ni also has a considerable amount of elastic anisotropy. (23)

The physical significance of the ordered void structure is that it may limit the amount of void induced swelling in metals when the equilibrium a/r_v value is reached. At this point, the voids would be the predominant sinks for both vacancies and interstitials. There will be no net growth if equal amounts of both vacancies and interstitials add to the voids and saturation of the void induced swelling should occur.

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