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BY HIGH ENERGY HEAVY ION BOMBARDMENT

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INTRODUCTION

The use of high energy ion bombardment to simulate high fluence, high temperature neutron damage in metals has proven to be an unexpected and rewarding new scientific tool.⁽¹⁻⁷⁾ This relatively new approach to the study of radiation damage has generated considerable theoretical interest in the effects of extremely high defect production rates. The most notable achievement of this technique is the "preview" of some microstructural defects and dimensional problems⁽⁶⁻⁸⁾ we may expect to find in metals subjected to 20 years or more of intense radiation damage in future LMFBF's (Liquid Metal Fast Breeder Reactors) or CTR's (Controlled Thermonuclear Reactors). On the other hand, the very feature of this technique which makes it so attractive, namely the unusually high rate of defect production, can prove to be a pitfall to the unwary scientist. Careful analysis of the irradiation temperature and defect production rate is required before conclusive evidence can be obtained on kinetic processes in metals. The most notable example of this is the shift in "effective" irradiation temperature which can result from defect production rates of 10^{-4} or higher.⁽⁹⁾

The potential advantages of using an external beam of energetic ions to accelerate the radiation damage rate by several orders of magnitude were first recognized in 1969 by Nelson and Mazey at Harwell.⁽¹⁾ They found that they could produce in a matter of hours, a damage state in 316 stainless steel which

normally required more than a year of fast nuclear reactor irradiation to produce. The initial work was performed with low energy (100 KeV) heavy ions on stainless steel, but these same scientists later found that 20 MeV carbon ions could produce similar results in a much larger volume of sample.⁽²⁾ They have vigorously pursued this approach by examining the role of inert gases in the production of voids and extended the work to include high fluence damage in Ni.

Two other approaches were immediately taken by scientists at Battelle-Northwest and Atomic International Laboratories in the U.S. The BNW group concentrated on using higher energy (5 - 10 MeV) heavy ions, such as Cu,⁽⁹⁾ Ni,^(3,10) or Se^(7,10) to bombard stainless steel, Ni, Mo, Nb and Ta. These studies confirmed the work of Nelson and Mazey and revealed some rather intriguing three dimensional defect structures and saturation effects in Ni.⁽⁷⁾ The AI group chose to pursue the use of 1.4 MeV protons to produce damage in stainless steel and nickel and found equally interesting results.^(5,12) Other groups have now investigated the use of protons,⁽¹³⁾ deuterons,⁽¹⁴⁾ nitrogen ions⁽⁸⁾ and high intensity beams of electrons⁽¹⁵⁻¹⁷⁾ to simulate the high temperature damage produced by neutrons. The results of these latter experiments are currently appearing in the open literature and any extensive review of that work would be premature at this time.

It is the purpose of this paper to briefly review the mechanisms by which heavy ($Z > 28$) ions produce defects in metals and to point out some of the major differences in specific damage rates between electrons, neutrons, light ions, and heavy ions. Recent experimental information on the fluence dependence of the formation of voids in Ni and the temperature dependence of void formation

in Mo, TZM and Nb will be given. The effect of pre-injected helium on the formation of voids in nickel will also be discussed.

DISPLACEMENT OF ATOMS BY ENERGETIC HEAVY IONS

As a high energy heavy ion passes through a metal, it loses energy by two major processes; electronic and nuclear collisions with the metallic atoms. The electronic interactions result mainly in ionization of the atoms and does not significantly contribute to the forceable ejection of atoms from their equilibrium positions. On the other hand, a large fraction of the nuclear energy transferred in interactions between the incident nucleus and the struck nucleus results in displaced atoms. Lindhard, et al,^(18,19) and Schiott⁽²⁰⁾ have published rather comprehensive reviews of the factors which govern the rate at which energy is lost in both nuclear and electronic collisions and their theories have been modified to predict the number of displaced atoms produced by incident beams of energetic ions.⁽⁴⁾ Only a brief account of the calculation methods is given below.

There are, in reality, three separate problems that must be solved before we can arrive at the final answer of the displaced atom density; the range of the particle must be determined, the rate of nuclear energy loss must be calculated as a function of the distance into the solid, and finally, we must convert the nuclear energy loss into a displaced atom density. The Lindhard model assumes that the nuclear and electronic collisions can be treated independently, that the electronic energy loss is proportional to the velocity of the incident ion and that the atoms are randomly placed in the solid, (i.e., it ignores crystallographic effects).

The average range of an energetic ion can be calculated if we know the energy dependence of the nuclear and electronic stopping powers, $(dE/dX)_n$

and $(dE/dx)_e$, respectively. Calculation of these quantities involves a rather complex approximation of the interaction between incident and struck particles through a screened Thomas-Fermi type potential. The reader is referred to Lindhard, et al, ⁽¹⁸⁾ for a more detailed discussion. Assuming that the various stopping powers can be calculated, the average range of the incident particle is then

$$\bar{R} = \int_0^E \frac{dE}{\left(\frac{dE}{dx}\right)_n + \left(\frac{dE}{dx}\right)_e} \quad (1)$$

Equation 1 gives the total path length of an incident ion into the solid, but we are usually more interested in the average projected range of that particle into the solid. This latter quantity, $\bar{R}_p$, is the perpendicular distance from the incident surface to the final resting place. The projected range can be calculated by

$$\frac{\bar{R} - \bar{R}_p}{R_p} = \mu \Psi(E, k) \quad (2)$$

where μ is the mass ratio of the struck and incident particles.

$\Psi(E, k)$ is a parametric function of the incident ion energy and the atomic properties of the incident and struck ions through a constant k .

Equation 2 allows us to calculate the average projected range of the incident particle, but there is in reality a Gaussian distribution of ranges

around the average value. We can calculate the distribution of ranges in the normal fashion;

$$\frac{N}{C} = \frac{1}{\alpha\sqrt{2\pi}} \exp - \left(\frac{(R - \bar{R}_p)^2}{2\alpha^2} \right) \quad (3)$$

where N = concentration of stopped ions per cm^3 .

C = incident fluence of ions per cm^2 .

$\bar{R}_p$ = ave. projected range.

$$\alpha^2 \approx \gamma (\bar{R}_p)^2 F(k, E, V)$$

γ = four times the reduced mass ratio of the incident and struck atoms.

$F(k, E, V)$ is a function which depends on the degree of electronic scattering through the constant k , the energy E of the incident ion and the form of the scattering potential used; a screened Thomas-Fermi type for this study. (18)

We can now calculate the total amount of nuclear energy transferred to the metal atoms at any given distance into the solid by the formula

$$S_n(X) \approx \int_0^{R_p} f(R_p) S_n(R_p - X) dR_p \quad (4)$$

where $f(R_p)$ is the fraction of incident ions with projected ranges between R and $R + dR$

$S_n(R_p - X)$ is the nuclear energy transfer rate, evaluated at X for a particle with projected R_p .

The next step is to determine the displaced atom density resulting from the nuclear energy transfer rates calculated from equation 4. It has been recently noted that only 60% of the energy lost in nuclear collisions results in displaced atoms.⁽²¹⁾ This reduction comes about because some of the struck atoms lose energy in "nonproductive" electronic interactions with the surrounding atoms. Therefore, the "productive" energy used to displace atoms is really $0.6 \times \overline{S_n(X)}$.

The conversion from nuclear energy transfer to displaced atom density can be made by using a Kinchen and Pease⁽²²⁾ approximation which yields,

$$N(X) \approx 0.6 \cdot \overline{S_n(X)} \cdot \frac{1}{2 E_d} \cdot N_I \quad (5)$$

where $N(X)$ is the number of atoms displaced per cm^3 at a distance X into the solid.

E_d is the displacement energy

N_I is the incident ion fluence

The more universal term now being used is the number of times each atom is theoretically displaced during the irradiation. This unit, called dpa for displacements per atom, can be obtained from equation 5 by simply dividing by the atomic density, N .

The dpa value at any distance into the solid is then

$$\text{dpa}(X) = \frac{N(X)}{N_0} \quad (6)$$

COMPARISON OF DAMAGE RATES FROM HEAVY AND LIGHT ION BOMBARDMENT

The rate at which defects are produced in a metal is mainly a function of three things; the displacement energy, the specific efficiency for transferring energy in collisions between the incident ions, and the struck atoms, and the flux of particles which can be directed on the solid. In general, heavy ions, such as Ni or Ta, are several orders of magnitude more efficient in producing damage than are protons and carbon ions. On the other hand, much higher beam currents of the lighter ions are available. A few examples of these generalities will illustrate the point.

Figure 1 shows the relative effectiveness of the more common particles used to produce displacements in a metal like nickel. We see that each tantalum ion is five times more effective in displacing atoms than is a nickel ion, and 100 times more effective than a carbon ion and more than 5000 times more effective than a proton. This factor rises to 3×10^6 for 14 MeV neutrons and 10^7 for 1 MeV neutrons and to greater than 10^8 for 1 MeV electrons (the latter number is not shown in Figure 1).

The data in Figure 1 can be placed in more perspective by multiplying the damage efficiency by presently attainable beam currents listed in Table I. The data here is taken from the literature and must be considered to be temporary as advances in ion source technology will certainly increase some of the displacement rates in the future. The main limitation on beam currents of the lighter ions is the amount of heat input. For example, we have assumed that a few hundred watts per cm^2 is the upper energy input limit for reasonable temperature control of the samples. Above this limit, the temperature uncertainties would render quantitative work on nucleation and growth somewhat

TABLE I

CURRENTLY ATTAINABLE FLUXES OF HIGH ENERGY
PARTICLES USED TO PRODUCE VOIDS IN METALS

<u>Particles</u>	<u>Particles/cm²/sec</u>
Electrons (1 MeV)	4×10^{19}
Neutrons (>1 MeV) (EBR-II)	6×10^{14}
Neutrons (14 MeV) (Future CTR)	4×10^{14}
Protons (1 - 2 MeV)	6×10^{14}
Carbon ions (20 MeV)	1.2×10^{14}
Nickel ions (5 - 10 MeV)	6×10^{13}
Tantalum Ions (5 - 10 MeV)	6×10^{12}

suspect. Figure 2 shows the range of relative displacement rates currently attainable with electrons, neutrons, protons, carbon ions, nickel ions and tantalum ions. The larger beam currents presently attainable for high energy nickel ions gives it a slight edge over the tantalum ions even though tantalum is more efficient in imparting "useful" energy to the lattice. The maximum displacement rates of 1 MeV electrons, 1 MeV protons and 20 MeV carbon ions are roughly 2 orders of magnitude lower than the heavier ions although they are still some 3 orders of magnitude higher than displacement rates in present fast reactors and proposed CTR's. It should be pointed out that all of these techniques are not confined to operate at the maximum damage rates. They could, and most often do, vary the damage rate by several orders of magnitude below the maximum possible.

Figure 1 also illustrates another important distinction between the various ions used for the simulation work, namely, the volume of material in which the displacements occur. In contrast to high energy neutron bombardment which produces displacements uniformly throughout the solid, the energetic ions produce damage in a non-homogeneous fashion. Typical damage zones of high energy bombarding particles vary from 5000 Å for 7.5 MeV Ta, 1 micron for 5 MeV Ni, 7 microns for 20 MeV carbon, 10 microns for 1.3 MeV protons and ~50 microns for 1 MeV electrons. The increased range of the lighter ions greatly alleviates the specimen preparation problems although techniques are now available^(10,23) to thin even samples bombarded with Ta with a fair degree of accuracy.

The major disagreement in this field now centers around whether the voids are homogeneously⁽²⁴⁻²⁷⁾ or heterogeneously^(9,16,27-31) nucleated. The homogeneous theories are based on the assumption that voids are formed by the statistical agglomeration of vacancies or in the center of randomly distributed displacement spikes. The heterogeneous nucleation theories assume that gas atoms (either inert elements produced by transmutation or residual elements such as oxygen, nitrogen or hydrogen) are required to stabilize the void embryos no matter how the latter are formed.

Ion bombardment experiments can be tailored to give some insight into the void nucleation mechanisms. For example, unlike neutron irradiation studies, the presence or absence of inert gases in the metal is strictly up to the experimenter. The high defect production rate and the possibility of varying it over several orders of magnitude should prove or disprove theories that are inherently defect production rate sensitive. Finally, by choosing the proper incident particle, such as an electron, one can eliminate displacement spike effects and thereby determine their importance in void nucleation. The present experiments concentrate on the inert gas and rate sensitivity questions.

PRECIPITATION OF VACANCIES INTO VOIDS

Thus far we have only considered how the individual vacancies and interstitial atoms are produced. How do these defects, especially the vacancies, end up in clusters? The answer to this question is the subject of considerable controversy at the present time and a complete assessment of the situation is not the object of this paper. We will only point out here a few features that most scientists agree on and some of the major points of disagreement as a background for future discussion.

The first point of general agreement is that there must be a supersaturation of vacancies in the metal before voids can be nucleated and grown. Secondly, the supersaturation of vacancies can only produce voids if the vacancies can move to nucleation sites and reduce the amount of recombination. Hence, there is a minimum temperature required during irradiation to form voids. This minimum temperature is approximately 30% of the absolute melting point and is assumed to be associated with the vacancy migration temperature. There is also a maximum temperature above which the thermal production of vacancies reduces the supersaturation level below that required for void formation and growth. This upper temperature limit is approximately 50% of the melting point in most metals.

The third point of agreement is that because vacancies and interstitials are produced in equal numbers during irradiation, there must be some sinks which preferentially remove interstitial atoms during irradiation leaving an excess of vacancies in the lattice. The biased sinks are commonly assumed to be dislocations which are either present before irradiation or formed by the precipitation of interstitial atoms into dislocation loops.

EXPERIMENTAL

Material

The chemical analysis of metal foil used for this study is shown in Table II. Three millimeter diameter samples were punched from the foil and annealed to the conditions also listed in Table II. After annealing, the samples were electropolished to obtain as smooth a surface finish as possible.

Irradiation

A detailed description of the experimental arrangement used to bombard the samples is given in Reference 10. Briefly, the 3 mm samples were held on a heated stainless steel or tantalum furnace while being bombarded. Each sample was bombarded individually with a maximum of ten samples irradiated per run. The bombarding fluxes are slightly different for each species, but, in general, varied from 1 - 10 microamperes/cm² (6×10^{12} to 6×10^{13} particles/cm²/sec).

The Ni, Cu and Ta ions were produced from a sputtering source similar to that described by Mueller and Hartig⁽³²⁾ (see also Reference 10). The selenium ions were produced by a diode source.⁽³³⁾ Ideally, one would like to use only Ni ions to bombard Ni foil and refractory metal ions, i.e., Ta to bombard Nb and Mo. However, the low concentrations of heavy ions required to produce reasonable damage ($\sim 10 - 50$ dpa) resulted in less than 0.1% impurities at the position of examination. No second phase particles were observed at these levels when metallic ions different than the targets were used.

Some of the well annealed nickel samples were pre-injected with approximately 3 atomic parts per million of helium atoms from the University of Washington Cyclotron.⁽³⁴⁾ The helium atoms were uniformly distributed in a 25 micron thick layer by a technique described elsewhere.⁽³⁵⁾

TABLE II .

PRE-IRRADIATION PROPERTIES
OF MATERIALS FOR ION BOMBARDMENT STUDIES

Impurity	PPM (wt)			
	Ni	Mo	TZM	Nb
Al	0.5	<5	<300	100
C	90	200	100-300	30
Cd		<10		
Co	1	<5		
Cr	0.5	<5		60
Cu	5	<2		
Fe	10	100	<300	60
H	<0.1	0.8	1-10	2
Mg	<0.1	<1	<100	0.8
Mn		<2		
Mo		Bal.	Bal.	
N	<2	1	4-15	90
Ni	Bal.	<5		9
O	50	4.5	10-20	145
Pb		<10		
Si	<1	<10	<300	20
Sn	<10	<5		
Ta				200
Ti		10	4200-4700	60
V		5		5
W		150		80
Zr	3	<20	800-1100	60
Pre-irradiation Anneal				
Temp °C	700	1800	1800	750
Time T _m	2	0.5	0.5	0.7
Vacuum-Torr	2 x 10 ⁻⁶	1 x 10 ⁻⁵	1 x 10 ⁻⁵	1 x 10 ⁻⁷

Examination

The procedure for thinning the Ni samples has been described earlier.^(7,23) The same general technique was used for the Mo and Nb samples except for different jetting and electropolishing solutions.

Electron microscopy studies were conducted with a Hitachi 200F electron microscope. The average void size was determined from 160,000X photographs while the number density of voids was obtained by noting the thickness of the foil from stereo analysis or by the interference fringe technique. All volume changes are calculated from the experimentally determined void size and number density.

Determination of Displacement Density

The displacement density was calculated by a method described earlier⁽⁴⁾ and Figures 3 and 4 show typical calibration curves for Ni and Nb, respectively. The calibration curve for Mo is similar to Figure 4 and is not included here. Note that although the dpa values per incident particle are much higher for Ta than Ni or Se, the damage for Ta ions occurs over a much shorter range. This shorter range makes the determination of the penetration distance more critical and results in a much higher error band for dpa estimates.

RESULTS

Nickel

Both pure and helium doped samples were irradiated at 525 °C with 5 - 6 MeV Ni ions and 8 - 11 MeV Se ions. The displacement densities ranged from 0.4 to 480 dpa. Voids were found in all of the samples and Table III lists the average void size, number density and calculated volume change for each sample.

Figure 5 graphically displays the effect of increasing displacement damage on the average void size. The average diameter rises from approximately 100 Å at 0.4 dpa to approximately 300 Å at 67 dpa. Above 100 dpa there appears to be a slight reduction in the average void size. It is also worth noting that there was little, if any, significant difference between samples that were pre-injected with helium and those which were irradiated without helium. There also is no significant difference between samples which were irradiated with Ni ions and those bombarded with Se ions. The morphology of the voids in all samples is consistent with {100} truncated {111} octahedra similar to that determined by other studies^(36,37) except at the highest damage states where they appear to be more like {100} cubes.

Figure 6 shows that the average void density rises from $\sim 3 \times 10^{14}/\text{cm}^3$ at 0.4 dpa to a constant value of $\sim 3 - 4 \times 10^{15}/\text{cm}^3$ over the entire 2 - 480 dpa range except for the two highest dpa points of the Se bombarded samples. There is no noticeable difference between pure and helium doped samples or samples bombarded with Ni or Se ions over the majority of the damage range. This similarity is quite evident in Figure 7 where we compare the microstructure of doped and undoped nickel bombarded samples and an undoped selenium bombarded

TABLE III

VOID DATA ON NICKEL BOMBARDED AT 525 °C

<u>Ion Energy</u> <u>MeV</u>	<u>Calculated</u> <u>dpa</u>	<u>Ave.</u> <u>Size</u> <u>Å</u>	<u>Ave. Void Density</u> <u>x 10¹⁵/cc</u>	<u>Calculated</u> <u>Swelling</u> <u>%</u>
<u>Ni → Ni, 3 appm Helium</u>				
5	1	90	1.1	0.07
5	4.4	150	2.0	0.19
5	6.5	145	2.9	0.46
5	10	155	3.2	0.61
5	25	210	3.5	1.7
5	58	250	3.3	2.7
6	67	305	2.7	4.0
5	360	250	4.2	3.4
5	480	260	4.0	3.7
<u>Ni → Ni, No Pre-injected Helium</u>				
6	0.43	135	0.38	0.048
6	1.3	140	0.99	0.14
6	6	140	3.4	0.49
6	44	265	4.1	3.95
<u>Se → Ni, No Pre-injected Helium</u>				
11	0.47	90	0.30	0.012
11	2	70	1.7	0.05
11	2.3	120	2.7	0.24
8	12	210	3.6	1.7
8.8	47	270	4.0	4.1
8.8	95	220	7.6	4.2
6	400	180	14*	4.4

*Calculated from superlattice of fcc voids with 660 Å lattice constant.

sample. The average void size is about the same in all three samples as is the number density (taking into account the different thicknesses of foil that were examined).

The calculated volume change is shown in Figure 8. This figure reveals that the swelling increases from $\sim 0.02\%$ at 0.4 dpa to $\sim 4\%$ at 40 dpa roughly as the $3/2$ power of the dpa values. Above 40 dpa the volume change seems to have saturated at 4 - 5% up to 480 dpa.

At 360 - 480 dpa the voids developed into a rather interesting microstructure in both helium doped and undoped samples. Figure 9 shows the voids viewed in a $\{111\}$ and a $\{110\}$ foil orientation after Se bombardment, and Figure 10 shows the voids from a $[100]$ direction in Ni ion bombarded, helium doped nickel. These figures show that the voids are not randomly placed, but rather tend to line up in rows parallel to the $\langle 100 \rangle$ directions. Further analysis of this structure reveals that the voids are actually aligned in a fcc superlattice with a lattice spacing of $660 \text{ \AA}$. Figure 11 shows the comparison of a $\{110\}$ view to an artist's drawing of what the corresponding fcc structure would look like. The voids in the ion bombarded sample are actually $\{100\}$ truncated $\{111\}$ octahedra, so they do not have the exact appearance characteristic of perfect octahedra viewed in a $\{110\}$ foil orientation.

Molybdenum and Niobium

Pure Mo, TZM and Nb samples were bombarded with 5 MeV Ni ions over the temperature range of 650 - 1000 °C and niobium was irradiated with 7.5 MeV Ta ions at 900 °C. In the nickel experiment, the displacement density was held constant at approximately 5 dpa while the temperature was varied. The results of the microstructural examination are listed in Table IV. Voids were found in all samples after 800, 900 and 1000 °C irradiations, but only dislocation loops

TABLE IV

VOID DATA ON ION BOMBARDED Mo, TZM AND Nb (a)

<u>Irradiation Temp. °C</u>	<u>Ave. Void Size Å</u>	<u>Ave. Void Density x 10¹⁶/cc</u>	<u>Calc. Swelling %</u>
<u>Molybdenum</u>			
650 (b)	ND (c)	ND	--
800	50	5.2	0.34
900	75	4.7	1.0
1000	120	0.53	0.48
<u>Niobium</u>			
650 (b)	ND	ND	--
700	ND	ND	--
800	45	6	0.29
900	220	0.15	0.83
900 (d)	200	0.24	1.0
1000	350	0.018	0.34
<u>TZM</u>			
800	60	3.2	0.36
900	80	1.6	0.43
1000	105	0.36	0.22

(a) Damage level ~5 dpa produced by 5 MeV Ni ions except where indicated.

(b) 6 MeV Ni ions.

(c) ND - None detected.

(d) 7.5 MeV Ta ions, ~8 dpa

were found in Mo after the 650 °C irradiation and in Nb irradiated at 650 and 700 °C. Examples of the voids are shown in Figures 12 and 13.

The general effect of increasing irradiation temperature was to increase the average void size and reduce the average void density in both samples. There was little difference between Nb, TZM and Mo after the 800 °C irradiation, but the average void size in Nb was approximately 3 times that in Mo and TZM samples after the 900 and 1000 °C studies. The increased void sizes in Nb are accompanied by reduced number densities so that the total number of vacancies in the voids (i.e., the swelling) is not significantly different at the three temperatures. Figure 14 shows that the swelling for all three materials follows the characteristic bell shaped curve found in other neutron irradiated metals and alloys.

The morphology of the voids is difficult to determine in the Mo and TZM samples because of the small average size. The voids in niobium, especially after the 1000 °C irradiation, appear to take on the morphology of a truncated {100} cube. This shape is evident in Figure 15 which shows the voids viewed in {111} and {110} foil orientations. It appears that there is a slight amount of truncation on the {110} faces of the cubes.

Finally, a non-random alignment of voids was also found in Nb irradiated at 800 °C. Figure 16 shows this alignment when viewed in a {111} foil orientation. The rows of voids, parallel to $\langle 112 \rangle$ directions, suggest a bcc superlattice of voids in contrast to the fcc superlattice in Ni. The "lattice" constant of this array is determined to be 350 Å which would predict a void density (2 voids per bcc unit cell) of $4.7 \times 10^{16}/\text{cm}^3$. This agrees quite well with the value of $6 \times 10^{16}/\text{cm}^3$ determined by measuring the number of voids in a random orientation. The volume calculations in the latter case were made by noting the thickness

indicated from stereo measurements in an area of photograph which contained the voids. No aligned voids were found in Nb at higher temperatures nor was there any conclusive evidence for aligned voids in Mo or TZM at 800 °C.

DISCUSSION

It is fairly obvious from the present study that inert gas atoms such as helium are not necessary for the formation of voids in heavy ion bombarded Ni, Mo, TZM, or Nb. This point is reinforced by the fact that pre-injection of part of the nickel samples with 3 appm of helium atoms did not significantly alter the size, number density or volume change when compared to the undoped samples. These results are in agreement with those of Nelson and Mazey⁽¹⁾ on stainless steel although the latter investigators did find a significant effect when the pre-injected helium levels exceeded 10 appm. The higher helium concentrations increased the number density, but reduced the average size of the voids. Bloom and Steigler⁽⁸⁾ found much the same result from neutron irradiated stainless steel that contained pre-injected helium levels of 20 appm. The latter two experiments suggest that the helium level in our tests may have been too low to show a significant effect on the nucleation of voids.

The present results, and those of Nelson and Mazey,⁽¹⁾ do not agree with the work of Norris.⁽¹⁵⁾ He found that no voids could be produced in "pure" nickel during 1 MeV electron bombardment, but voids did appear when identical samples were irradiated after pre-injection with approximately 70 appm of argon atoms. He concluded from these experiments that 1) displacement spikes are not required for void nucleation because only mono- or divacancies are produced by 1 MeV electrons, and 2) that gas atoms are required for nucleation of voids. The inference from this⁽¹⁵⁾ and later studies⁽¹⁶⁾ is that inert gas atoms are essential for void nucleation, but Urban⁽¹⁷⁾ has recently shown that oxygen may play an important role. Urban's experiment was also conducted with high energy electrons so as to eliminate the displacement spike effects. He found

that voids could be formed in "pure" (non-inert gas injected) nickel if the samples were allowed to oxidize before bombardment. It is logical to conclude from this study that residual gases, such as oxygen, could act as the nucleating site for a void or in some manner stabilize void embryo. Urban's experiment also rules out the requirement that inert gas atoms are essential for nucleation although it is entirely possible that inert gas atoms along with other impurities could nucleate voids.

There are ample number of gas atoms in the present samples to act as nuclei for voids even though relatively "pure" starting materials were used. For example, the residual gas concentration (O + N + H) ranges from 100 appm in Mo to 200 appm in Ni and to as high as 1000 appm in Nb and TZM. If all of the gas atoms were divided evenly among the highest number density of voids in each sample, we would still have approximately 100 per void in Mo, and up to 1000 per void in Ni, Nb and TZM.

It is apparent that more attention must now be paid to the amount of impurity gases in metals. Future studies with extremely high purity, degassed samples will help in establishing the true role of gas atoms in the production of voids.

It is worthwhile at this point to compare the swelling observed in the heavy ion bombarded nickel samples to that obtained from neutron irradiation. Figure 17 shows results from ANL,⁽⁴⁰⁾ PNL,^(37,40) WADCO,^(41,42) and ORNL⁽⁴³⁾ studies in a rather wide range of temperatures (370 - 500 °C). It can be seen that the neutron induced swelling is in good agreement with the heavy ion work even though the helium varies by more than a factor of 200 in the neutron irradiated samples. No particular effort was made to control the gaseous impurity levels of neutron

irradiated samples, so it is quite possible that they contained as much or more residual gas atoms than the present high purity nickel which could provide ample nucleation sites.

The agreement in Figure 16 is also quite significant considering that the displacement rates were approximately 4 orders of magnitude different. Bullough and Perrin⁽⁹⁾ predict that the major effect of the higher displacement rates associated with the heavy ion work is to lower the "effective" Irradiation temperature. They predict that a high damage rate experiment will produce swelling comparable to a lower temperature neutron experiment. The amount of temperature shift is:

$$\Delta T = T_i^2 \frac{k}{E_v} \ln \frac{K_i}{K_n} \left[\frac{1}{1 + \frac{T_i k}{G} \ln \frac{K_i}{K_n}} \right]$$

where T_i = temperature of the ion bombardment

k = Boltzmann's constant

E_v = diffusion energy for vacancies

K_i = defect production rate during ion bombardment

K_n = defect production rate during neutron irradiation

For example, a 525 °C irradiation of Ni with $K_n = 10^{-6}$ gives $\Delta T = 148$ °C for $K_i = 10^{-2}$ or $\Delta T = 117$ °C for $K_i = 10^{-3}$. This means that the present work should be comparable to neutron irradiation studies in the 380 - 410 °C range, not too far from where most of the data in Figure 14 is obtained. Brimhall, et al,⁽⁴⁰⁾ also show that the swelling in neutron irradiated nickel is not too sensitive to the irradiation temperature in the 400 - 500 °C range so that it is reasonable that the shift in effective temperature will not be too serious. Such comparisons

are not expected to be valid near the temperature threshold for swelling in metals because Bullough's⁽⁹⁾ model neglects recombination effects. One must be very careful about drawing conclusions from ion bombardment experiments conducted in the temperature region where recombination is important.

The tendency for voids to form three dimensional lattice structures in Nb and He doped nickel during nickel ion bombardment is consistent with previous work on selenium bombarded nickel,⁽⁷⁾ nitrogen bombarded Mo and TZM,^(8,44) and neutron irradiated Mo and Nb.⁽⁴⁵⁾ The superlattices in all of these studies are identical to the metal crystal lattice, i.e., fcc in Ni, bcc in Nb, Mo and TZM.

There is no obvious reason for this behavior at the present time except the possibility that the voids are attempting to minimize the total strain energy in the solid induced by such large swelling. Kissinger⁽⁴⁶⁾ has found that there is a strain field associated with voids which can be detected by measuring the x-ray line broadening. It is possible that the long range interaction between these strain fields will determine whether or not voids shrink or grow on certain periodic positions in the samples.

It has also been suggested⁽⁴⁴⁾ that the anisotropy of the crystal lattice could initiate such an effect. This is in agreement with the fact that Ni, Nb, and Mo have rather high anisotropy factors.⁽⁴⁷⁾ One would expect on this basis that voids in more isotropic metals, like Al or W, would not form superlattices. This is consistent with observations by Packan⁽⁴⁸⁾ who has reported swelling in Al of 7.5% with no evidences of void alignment. However, the evidence for the exact mechanism of alignment is too meager to draw any definite conclusions at the present time.

The effect of bombarding temperature on swelling in pure Mo is in good agreement with neutron irradiation of identical stock material⁽⁴⁰⁾ except for the lowest temperature sample. The fact that no voids were found at 650 °C in Mo, a temperature at which voids are found in neutron irradiated Mo,⁽⁴⁰⁾ is expected because of the previously mentioned effective temperature shift.⁽⁹⁾ The calculated shift is approximately 140 °C for the 650 °C ion bombardment. Thus far, no voids have been found in neutron irradiation of Mo at 510 °C.

The similarity of swelling in the Mo and Nb samples was expected because the irradiations were conducted at roughly the same homologous temperatures. The rather large void size in Nb after the 900 and 1000 °C irradiations was rather unexpected but there is little high temperature neutron data with which to compare these results. It is significant that the total swelling (i.e., vacancies captured by voids) is roughly the same in the Mo and Nb samples.

The slightly reduced swelling in the TZM samples compared to the pure Mo appears to be mainly due to the factor of 2 - 3 lower void density in the TZM. This implies that the nucleation sites are not as numerous. If the total residual gas content is the controlling factor for nucleation, then one would expect more voids in TZM because it contains approximately 10 times more gas (Table II). However, the addition of Ti and Zr to the Mo could effectively getter the excess gas in solution and reduce the amount available for nucleation, thereby reducing the swelling.

The fact that approximately the same results (in terms of voids) were obtained from Ni and Ta bombardment of Nb at 900 °C is important because it shows that a few hundred appm of nickel impurity atoms are not significantly affecting the nucleation process. It is expected that there will be essentially no impurity effects of Ta in Nb because of their complete mutual solubility and similar

chemical properties. (49) Even though it appears that we could use Ni or Ta ions for bombardment of refractory metals, all future work will probably be conducted with the Ta ions.

CONCLUSIONS

1. Helium gas is not required for the formation of voids in Ni, Mo, Nb, and TZM.
2. An increase in the displacement rate in Ni by 4 orders of magnitude over neutron irradiation does not significantly change the void induced swelling when the shift of the effective temperature is taken into account.
3. Void induced swelling saturated at approximately 4 - 5% in Ni which is bombarded with heavy ions at 525 °C to more than approximately 50 dpa.
4. Voids form a three dimensional superlattice in Ni and Nb which is consistent with the crystal structure of the lattice. Doping Ni with helium atoms does not alter the tendency for alignment.
5. There is little difference between void induced swelling in Mo or Nb over the 800 - 1000 °C range at approximately 5 dpa. The swelling in TZM over the same temperature range is slightly less than Mo and Nb.

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FIGURE CAPTIONS

1. Displacement Damage Effectiveness for Various Energetic Particles in Nickel
2. Displacement Rates Currently Available by Energetic Particle Bombardment of Nickel
3. Displaced Atom Density for Ni and Se Ions in Nickel
4. Displaced Atom Density for Ta and Ni ions in Niobium
5. Effect of Displacement Damage at 525 °C on the Average Void Size in Nickel
6. Effect of Displacement Damage at 525 °C on the Number Density of Voids in Nickel.
7. Voids in Nickel After 525 °C Bombardment
8. Swelling in Nickel After 525 °C Heavy Ion Bombardment
9. Void Alignment in Nickel After Se Ion Bombardment
10. Void Alignment in Helium Doped Nickel After Ni Ion Bombardment
11. Face Centered Cubic Superlattice of Voids in Nickel
12. Voids in Nb and Mo After Heavy Ion Bombardment at 900 °C and 1000 °C
13. Effect of Irradiation Temperature on the Microstructure of TZM
14. Effect of Irradiation Temperature on Swelling in Heavy Ion Bombarded Mo, TZM and Nb
15. Morphology Determination of Voids in Nb After 1000 °C
16. Aligned Voids in Nb After 800 °C Irradiation
17. Comparison of Neutron Induced Swelling in Nickel to that Found in the Present Study

DISPLACEMENT EFFECTIVENESS FOR VARIOUS PARTICLES IN NICKEL

RANGE OF DISPLACEMENT RATES DURING IRRADIATION OF NICKEL

DISPLACED ATOM DENSITY FOR Se AND Ni IONS IN NICKEL METAL

DISPLACED ATOM DENSITY FOR Ta AND Ni IONS IN Mo METAL

AVERAGE VOID SIZE IN NICKEL BOMBARDED AT 525°C

AVERAGE VOID DENSITY IN NICKEL BOMBARDED AT 525°C

VOIDS IN NICKEL AFTER 525 °C BOMBARDMENT

INCIDENT ION	CALC dpa	HELIUM appm
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Ni	44	0
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Ni	58	3
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Se	47	0
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SWELLING IN NICKEL AFTER BOMBARDMENT AT 525°C

VOIDS IN Se BOMBARDED NICKEL ~ 400 DISPLACEMENTS/ATOM AT 525°C

(a)

(b) SAME AS a) EXCEPT FOR ORIENTATION

1000Å

ALIGNED VOIDS IN HELIUM DOPED NICKEL
360 dpa AT 525 °C

ALIGNED VOIDS IN HELIUM DOPED NICKEL
360 dpa AT 525 °C

FACE CENTERED CUBIC SUPERLATTICE
OF VOIDS IN NICKEL

VOIDS IN Mo & Nb

Mo

Nb

900°C

1000°C

EFFECT OF BOMBARDMENT TEMPERATURE ON VOIDS IN TZM

800 °C

900 °C

1000 °C

DAMAGE ~5 dpa

VOID INDUCED SWELLING

VOIDS IN NIOBIUM AFTER 1000 °C IRRADIATION

0.1 μ

VOID ALIGNMENT IN NIOBIUM - 800 °C IRRADIATION

SWELLING IN NEUTRON IRRADIATED Ni