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THE EFFECT OF TEMPERATURE ON VOID
FORMATION IN IRRADIATED PURE AND IMPURE METALS

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ABSTRACT

Void formation has been studied in a number of irradiated high purity metals at Battelle-Northwest and the results are given and discussed in this paper. Particular emphasis is devoted to the temperature dependence of swelling in molybdenum, nickel and rhenium. In general, voids occur in the temperature region approximately $0.3 T_m$ to $0.55 T_m$ where T_m is absolute melting temperature. This temperature regime is essentially determined by the relative stability of vacancy configurations at the low temperature end and the vacancy supersaturation at the high temperature end. The results are further discussed in terms of current theories of void formation. The effect of small variations in impurity level in molybdenum and nickel on void formation has also been studied. Large differences in the size and number density of voids occur in material of the same overall purity level but with relatively small variations in type and amount of impurity. However, the void swelling appears to depend only on the magnitude of the overall purity level. These results are compared to similar results of other investigators on other materials.

THE EFFECT OF TEMPERATURE ON VOID FORMATION IN IRRADIATED PURE AND IMPURE METALS

J. L. Brimhall, H. E. Kissinger, and G. L. Kulcinski

INTRODUCTION

The study of voids in irradiated metals has evoked considerable interest and study in recent years. The amount of literature on voids has increased correspondingly and no attempt will be made to review it here. Here at Pacific Northwest Laboratories, emphasis has been placed on studying void formation in high purity metals, particularly the metals molybdenum, nickel and rhenium. Analyses have been done principally by transmission electron microscopy, small angle x-ray scattering and microhardness.

It is recognized that irradiation temperature, fluence and material purity have profound influence on the irradiation produced microstructure and voids in particular. Studies on the nature of radiation damage produced over a wide range of temperature and the effect of small amounts of impurities on void formation in particular have been limited.

In this paper, void formation in a wide variety of pure metals is discussed. The effect on void parameters and volume changes over a wide spectrum of irradiation temperatures is shown for the metals molybdenum, nickel and rhenium. The results are discussed relative to current knowledge about microstructural defects and theories of void nucleation and growth. The limited data on other pure metals are discussed in terms of the general picture of void formation and possible reasons for apparent

anomalous behavior. Some results on the effect of purity on void formation in nickel and molybdenum are presented. Although alloys would be expected to behave differently than pure metals, even very slight differences in the amount and type of impurities can result in significant differences in void behavior. These results are discussed in light of similar results by other workers in the field.

EXPERIMENTAL TECHNIQUES

A brief mention of the experimental techniques and procedures is given here. A more detailed account can be found in previous articles. (1-3)

All material used in the experiments was in the form of foils approximately 0.1 mm in thickness except for the single crystals. Single crystals approximately 3 mm in diameter were grown by zone refining. Sections 0.5 mm thick were cut from the single crystals for electron microscopy. All specimens were given preliminary vacuum anneals at 0.6 to 0.65 T_m (T_m = absolute melting temperature). A number of different reactors have been used for the irradiations and all the fluence values refer to a neutron energy >1 MeV except for the EBR-II irradiation in which the neutron energy is >0.1 MeV. The irradiations at elevated temperature were monitored with a thermocouple except for experiments in the EBR-II for which the temperature was calculated. All irradiations at the ambient temperature of 50 °C were done in helium atmosphere. The elevated temperature irradiations in the EBR-II and Hanford reactors were done in liquid sodium or NaK. For irradiation in ETR, the samples were encapsulated in molybdenum or niobium and encased in a graphite block.

Analysis of the void parameters and resultant volume change were all done by transmission electron microscopy or small-angle x-ray scattering.

The volume change at low temperatures was determined by dimensional changes in single crystals.

PURE METALS - RESULTS

In this section the results from a variety of pure metals of the void size, density, distribution and volume fraction are presented. The metals are divided into bcc, fcc and hcp for ease of presentation. The results of one particular experiment in the EBR-II on which a wide spectrum of metals were irradiated under identical fluence and temperature conditions are also given.

Bcc Metals

The great bulk of the work at BNW on bcc metals has been done on molybdenum. The temperature regime for void formation in molybdenum extends from 575 to at least 1150 °C ($0.29 - 0.49 T_m$) as determined by direct observation in the electron microscope. Typical microstructure of voids in molybdenum is shown in Figure 1 together with those from nickel and rhenium. The total volume change after irradiation is plotted as a function of irradiation temperature in Figure 2. The region of void formation is indicated by the bell-shape part of the curve. Some of the high temperature values have been normalized to a fluence of $2.5 \times 10^{19} \text{ n/cm}^2$ using a linear extrapolation. Some data from other sources has also been included and the numbers on several of the data points refer to the reference from which that data was obtained. The curve shows significant swelling at lower temperatures as well as elevated temperatures with a minimum in the swelling in the temperature range 400 - 600 °C. The microstructure in this minimum swelling range reveals large interstitial dislocation loops and small vacancy loops. (2)

Vacancy loops have been identified by Eyre, et al, after irradiating at the low temperature of 200 °C.⁽⁶⁾ At 575 °C both vacancy loops and voids are present.⁽²⁾ A few vacancy loops persist at irradiation temperatures up to 750 °C, but voids are the only type of vacancy damage at temperatures above 750 °C. The void size increases and density decreases with temperature. The distribution of voids is very homogeneous both in size and number density.

Vanadium, niobium, tantalum and iron have been irradiated in the EBR-II at 450 °C. A summary of the data from this particular experiment in which a number of pure metals were irradiated is given in Table I. A high density of very small voids are observed in vanadium whereas a low density of large voids form in iron. The vanadium results agree well with that reported by Wiffin.⁽⁷⁾ As will be seen later, the results from iron are somewhat anomalous. No voids form in niobium, molybdenum or tantalum at this temperature which is $<0.3 T_m$ for these metals. Workers at Oak Ridge have reported seeing voids in niobium irradiated in the EBR-II at 450 °C.⁽⁸⁾ However the total fluence was a factor of ten higher than that given here and this could explain the presence of voids in their work. In addition, the temperatures are not known that accurately.

There does not appear to be a consistent morphology of void shape in the bcc structure. The voids are faceted by both $\{110\}$ planes and $\{100\}$ planes. Figure 3 illustrates the various shape of voids in molybdenum. For the foil orientation $\{110\}$, Void A is consistent with a cube with $\{100\}$ faces and Void B shows both $\{110\}$ and $\{100\}$ faceting. In iron, most of the voids appeared to have $\{110\}$ faces.⁽⁹⁾ Similar morphologies have been reported by others.⁽⁴⁾ Since voids of different

TABLE I

SUMMARY OF VOID DATA IN METALS
IRRADIATED TO 3×10^{21} n/cm² AT 450 °C

<u>Metal</u>	<u>Purity</u> %	<u>T/T_m</u>	<u>Diameter</u> <u>of Void</u> <u>Angstrom</u>	<u>Number</u> <u>Density.</u> <u>n/cm³</u>	<u>ΔV/V</u> %
Ag	99.999	0.59	--	--	0
Au	99.94	0.54	--	--	0
Cu	99.999	0.53	1600	2×10^{12}	0.5
Ni	99.997	0.42	400	1.8×10^{14}	0.68
Ti	99.96	0.42	--	--	--
Fe	99.98	0.40	280	1×10^{14}	0.12
Zr	99.9	0.39	--	--	--
Pt	99.97	0.35	500	8×10^{13}	0.7
V	99.9	0.33	50	3×10^{16}	0.20
Nb	99.9	0.27	--	--	0
Mo	99.98	0.25	--	--	0
Ta	99.99	0.22	--	--	0
Re	99.97	0.21	--	--	0

morphology exist in the same general area, the selection of the particular planar faces may be purely random.

Fcc Metals

The temperature regime for void formation in nickel extends from about 250 °C to 650 °C ($0.30 T_m$ to $0.55 T_m$). A few voids are present after 750 °C irradiation but it is suspected these are gas bubbles. Figure 4 shows the typical curve for the variation in volume fraction with temperature in which the swelling goes through a maximum. Results from nickel irradiated at low temperatures, ≤ 50 °C, indicate that vacancy loops or stacking fault tetrahedra form in this temperature range.⁽¹⁰⁻¹³⁾ Postirradiation annealing studies of nickel irradiated at 50 °C also show that stacking fault tetrahedra are the predominant vacancy defect.⁽¹⁾ The overall development of the defect structure is then very similar to molybdenum. Planar vacancy defects form at low temperatures, $\approx 0.3 T_m$, and three-dimensional vacancy clusters are stable and form at elevated temperatures $\gtrsim 0.3 T_m$.

The size of the voids in nickel increases continually with temperature at constant fluence, Figure 5, but a saturation in the size is indicated in the high temperature range. The void density must increase initially with temperature (dotted line in Figure 5) in the transition region from planar defects to three-dimensional voids. The number density then decreases continually with temperature as shown in Figure 5. This inverse relationship between size and density produces the rather constant volume fraction of voids over a wide temperature range, Figure 4. However, when the size reaches a saturation, the volume fraction decreases since the number density continues to decrease.

Preliminary work on pure nickel irradiated at very low fluence shows that the critical fluence level for void formation lies between 2 and 7×10^{18} n/cm² at 280 °C. The density increases rapidly with fluence. At the lowest fluence at which voids were observed, the size was still considerably above the resolution limit of the microscope. Analysis of the size distribution indicated that the size did not appear to extend down past the resolution limit. Once voids are nucleated, they must grow very rapidly. However, in the initial stages a small void will show a much higher growth rate merely because it is so small. No attempt was made to determine a fluence dependency of the void volume at these low fluences because of the limited data. Holmes, however, has shown a linear fluence dependence for pure nickel at a slightly higher temperature and higher fluence range.⁽¹⁴⁾

Copper, aluminum, gold, silver and platinum have also been irradiated and analyzed for void formation. Void formation in platinum, copper and aluminum is similar to that in nickel. The upper temperature limit for copper appears to be about $0.55 T_m$ (Table I). No voids have yet been found in silver or gold. A temperature of 450 °C may be just past the upper temperature limit for void formation ($0.59 T_m$ for Ag, $0.54 T_m$ for Au). However, voids also have not been observed in gold irradiated at 280 °C ($0.41 T_m$) to a fluence of 2.5×10^{19} n/cm². Voids formed both in copper and nickel under these latter irradiation conditions. These results suggest strongly that the low stacking fault energy of gold may be hindering void formation.

The morphology of voids in the fcc structure can best be described as a tetrakaidecahedron with {111} and {100} faces. There is some question

as to whether the basic or initial shape is the {100} cube with {111} truncation or the {111} octahedron with {100} truncation. A systematic study of the parameters affecting void morphology in fcc metals has not been made.

HCP Metals

The temperature regime for void formation in rhenium extends from about 635 °C to 1450 °C ($0.27 - 0.51 T_m$) Figure 6. In terms of the homologous temperature, the region of void formation appears to extend to a lower temperature range than that of molybdenum or nickel. It is now suspected, however, that the two lower temperatures, 635 and 720 °C, may be higher because of excess gamma heating so the behavior of rhenium is not necessarily anomalous. The data also represents a higher fluence than that given for either nickel or molybdenum and this could also account for the observation of voids at a lower temperature. The only distinguishing feature of the void formation in rhenium was the rather inhomogeneous distribution throughout the foil and the rather large size distribution as compared to either pure molybdenum or nickel. Compare the microstructure of rhenium in Figure 1 with nickel or molybdenum. Rhenium also shows the minimum in the swelling in the temperature range 400 - 600 °C which is quite similar to molybdenum. Interstitial loops have been identified after irradiation in this temperature range, but it was concluded that vacancy defects were too small to detect. (15)

No voids form in titanium and zirconium after irradiation at 450 °C to $3 \times 10^{21} \text{ n/cm}^2$ ($E > 0.1 \text{ MeV}$). (16) This temperature is $0.42 T_m$ for titanium and $0.39 T_m$ for zirconium if an extrapolated melting temperature for the α phase is used. The defect structure consists principally of vacancy dislocation loops and dislocation fragments, Figure 7. Investigation

of specimens irradiated both at lower temperatures and lower fluences reveal a lower density and smaller size of dislocation loops, but no basic change in microstructure. Workers at Chalk River have also failed to observe voids in zirconium alloys irradiated at 450 °C to a higher fluence.⁽¹⁷⁾ There have been no reports of studies using a higher irradiation temperature than 450 °C. It should be mentioned that voids have now been reported in magnesium,⁽¹⁸⁾ so it appears that titanium and zirconium are truly anomalous in their behavior.

Comparison of Void Formation in Several Pure Metals

To illustrate the temperature dependency of void formation in a wide variety of metals, the void volumes from Table I are plotted as a function of T/T_m , Figure 8. Only the data from this particular EBR-II experiment in which the fluence and temperature were constant are plotted. No attempt was made to extrapolate from other irradiations. With some major exceptions, the typical bell shape curve similar to Figures 2, 4 and 6 is evident. The homologous temperature for both the high melting point metals, molybdenum, rhenium, niobium, tantalum, and the low melting point metals, gold and silver, fall outside the range of the void formation curve. Titanium and zirconium are anomalous as mentioned previously. The void volume fraction for iron is also significantly too low. However, the trend toward void formation and swelling in the temperature interval of approximately 0.3 to 0.5 T_m is plainly evident from the figure.

DISCUSSION

Void formation in metals has been analyzed theoretically and phenomenologically by a number of investigators.⁽¹⁹⁻²²⁾ Harkness and Li⁽¹⁹⁾ using a classical nucleation and growth approach predict a bell shape curve for the temperature dependence of the volume fraction as is

observed. Their curves for the temperature variation of the nucleation rate and growth rate has the same form as the temperature variation of the number density and size as shown in Figure 5. In this approach, it was assumed that the displacement spikes serve as the nuclei for voids. Wiedersich has developed a completely homogeneous nucleation theory for void formation in which a random distribution of vacancies and interstitials are assumed.⁽²²⁾ Recently, Norris has produced voids in nickel by electron bombardment;^(23,24) a situation in which there are no displacement spikes.

— Spikes are, therefore, not essential. The temperature dependence of the void volume fraction in nickel calculated by Wiedersich agrees reasonably well with the results presented here. A lower temperature for maximum swelling is observed experimentally as would be predicted since the fluxes and, hence, defect generation rate are lower in our experiments than was used in the theoretical curves. Further, a decreasing sink density at higher temperatures would produce a lower temperature of maximum swelling and a sharper drop off in the swelling with temperature than shown by the theoretical curves. One of the important questions in explaining void formation is the apparent preferential drift of the interstitials to dislocation sinks, which results in an excess of vacancies available for void formation. Bullough, et al, have developed a model of the void growth rate which considers explicitly the preferential migration of the interstitials to dislocations and they predict a maximum in the growth rate as a function of temperature.⁽²¹⁾ Their prediction of the maximum for molybdenum agrees quite well with the temperature for maximum swelling in Figure 2. Void swelling in molybdenum extends to a higher temperature than they predict and this may be due to a higher value for the interstitial migration energy,

E_M^i , than was actually used. It was stated that the diffusion parameters for molybdenum are not well established.

It is generally agreed that the reduction in swelling at high temperatures is due to a reduction in the supersaturation of vacancies. Because of the increased mobility and thermal equilibrium concentration of vacancies at elevated temperatures, the irradiation cannot maintain a sufficient excess concentration of vacancies. At the low temperature end, it would appear intuitively that the much reduced vacancy mobility hinders void nucleation and growth. Bullough, et al,⁽²¹⁾ also show that an increase in the recombination of vacancies and interstitials reduces the growth rate at lower temperatures.

An equally important factor in determining the onset of void formation as the irradiation temperature increases, is the stability of the three dimensional vacancy cluster or void nuclei relative to other configurations. The energies of the various vacancy defect configurations in fcc metals as a function of their size has been analyzed by Sigler and Wilsdorf⁽²⁵⁾ and by Johnson.⁽²⁶⁾ Only in nickel and aluminum is the void the energetically favored defect principally because of the higher stacking fault energy in these metals. However, it has now been shown that voids form in copper and platinum as well. Therefore, the vacancy clusters can be stabilized as a three dimensional defect and prevented from transformation into the more stable planar defect. It has yet to be demonstrated that voids form in gold or silver during irradiation. The extremely low stacking fault energies in these metals may require the necessity of a very high fluence in order for voids to form. This is the situation in stainless steel in which much higher fluences are required for void formation than in a similar metal such as nickel. The results in gold show the effect of stacking fault energy alone, however, without the complicating effect of alloying in the

stainless steel.

Bullough and Perrin⁽²⁷⁾ have shown theoretically that gas atoms are necessary for the stabilization of a three dimensional vacancy cluster in iron against collapse into a lower energy planar configuration. These gas atoms may be helium generated by the irradiation or soluble gases, such as hydrogen or oxygen. Recent experimental evidence using electron bombardment has shown that either inert gases^(23,29) or dissolved gases such as oxygen⁽²⁹⁾ appear to be necessary for the nucleation of voids. The experimental results presented here support this view. The vacancies in molybdenum irradiated at temperatures $< 575^{\circ}\text{C}$ precipitate as vacancy loops and in nickel irradiated $< 280^{\circ}\text{C}$, they precipitate as vacancy loops or stacking fault tetrahedra. The critical lower temperature limit is then not solely dependent on vacancy mobility since, in molybdenum at least, both vacancy loops and voids form at temperatures above which vacancies are believed to be mobile. The vacancy loops also form at temperatures considerably below 575°C and it is expected that vacancies must have some mobility in order to form loops. The increase in swelling at the very low temperatures, $\sim 50^{\circ}\text{C}$ in Figure 2, is most likely due to isolated vacancies or small clusters since it is universally agreed that vacancies are not mobile in this range. The lower temperature limit is then not solely determined by vacancy mobility, but is also dependent on the mobility and stabilizing influence of the gas atoms as a function of temperature.

The assignment of a lower temperature limit for void formation must, of course, take into account the fluence. In these experiments, void observation was limited by the resolution of the microscope and at very low

fluences, the voids may be too small or too low density to observe. Also, in some materials it may be necessary to go to a higher fluence in order to attain sufficient vacancy supersaturation, because of an increased recombination rate. Regardless of the fluence, there is a critical temperature region which divides the stable three-dimensional clusters from the two-dimensional clusters. Increasing the fluence should not change this fact. Inability of gas atoms to stabilize the vacancy clusters in titanium and zirconium may explain the presence of vacancy loops in these metals rather than voids.⁽¹⁶⁾ Voids may form in these metals upon irradiation to a higher temperature, but this has not been done to date. The role of gas atoms and other impurities will be discussed further in the next section.

It is difficult to make definitive conclusions concerning the void morphology. In nickel, the {111} planes have the lowest energy, but only slightly less than {100} planes.⁽²⁶⁾ Only a slight amount of impurity could alter the energy relationships thus allowing {100} faceting of the voids. Stiegler, et al, observed {111} octahedral voids in high purity aluminum but {100} square voids in commercial purity aluminum.⁽²⁹⁾ Dissolved gases also affect the morphology of quenched-in voids in fcc metals.⁽³⁰⁾ In the bcc metals, there is no consistent morphology in molybdenum even within the same area of the sample (see Figure 3). It is difficult to explain how impurities could be the sole explanation in this case unless the differentiation in surface energies may be so slight that local impurity fluctuations throughout the matrix are affecting the surface energies. Full explanation of void morphology must await careful experiments using controlled amounts of impurities.

IMPURITY EFFECTS - RESULTS

In this section, the effects of small variations in impurity level on void formation is presented. Impurity effects have been studied in nickel and molybdenum.

Nickel

Four different grades of nickel were irradiated at three different temperatures, -350, 400, and 450 °C at a constant fluence of 2.5×10^{19} n/cm². The chemical analyses for each of the three grades of "high purity" nickel are given in Table II. The fourth grade of nickel is commercial purity or "A" nickel and is listed as about 99.4% nickel. On the basis of overall purity, the "A" nickel is about two orders of magnitude less pure.

The size, density and volume fraction of the voids as a function of the irradiation temperature are summarized in Table III. The micrographs in Figure 9 illustrate the differences in void size and number density among the various grades of nickel irradiated at 450 °C. Regardless of purity the average void size increases and the number density decreases with increase in temperature. The size distribution also varies considerably among the three materials as shown in Figure 9. This difference in the void parameters among the different grades of nickel extends to high fluences.⁽³¹⁾ The volume fraction, however, is approximately the same in the three high purity materials within the experimental error limits. The data from commercial purity "A" nickel is difficult to compare since voids were only positively identified in material irradiated at 450 °C. However, it is conceivable that the void size could be less than the resolution limit of the microscope at 350 °C if the size were extrapolated downward from a size of 90 Å at 450 °C. In general, the relationship between

TABLE II

CHEMICAL ANALYSES OF THE THREE GRADES OF HIGH PURITY NICKEL

Metallic Impurities	ppm by Weight			"A"
	I	II	III	
Mg	2	1	--	
Al	4	--	0.5	
Si	5	--	<1	
K	--	2	--	
Ca	2	--	1	
Fe	7	10	10	
Co	--	3	1	
Cu	5	20	<0.5	
Zn	--	40	<4	
Zr	--	--	3	
Ga	--	20	--	
Pb	--	8	--	
Purity (Metallic only)	99.997%	99.99%	>99.998%	99.4%
Interstitials				
C	50	70	90	
O ₂	57	<100	50	
N ₂	<5	<6	<2	
H ₂	6	6	1.5	

TABLE III

VOID PARAMETERS AS A FUNCTION OF
IRRADIATION TEMPERATURE FOR NICKEL

Nickel Grade	Diameter (Å) Temperature			Density ($\times 10^{-14} \text{ cm}^{-3}$) Temperature			Vol Fraction (%) Temperature		
	350 °C	400 °C	450 °C	350 °C	400 °C	450 °C	350 °C	400 °C	450 °C
I	97	120	132	16.0	9.0	5.0	0.06	0.07	0.06
II	155	192	254	3.6	1.2	0.9	0.06	0.04	0.06
III	210	280	340	1.2	0.5	0.4	0.06	0.05	0.07
"A"	Not Detected	<90	90	Inhomogeneous			--	--	<0.01

void size-density and temperature is also expected to hold for the commercial purity nickel.

If one considers only the three high purity nickels, there appears to be no consistent correlation between void parameters and overall purity. The differences in average size or density does not correlate with the differences in overall purity although these differences in purity are extremely small. The least pure nickel, Nickel II, shows a void size and density intermediate between the other two high purity nickels. If one, however, compares the high purity with the commercial purity, a significant difference is noted. Both the size and density are much smaller in the commercial purity and hence the volume fraction is much reduced. In this case, the amount of impurities are so great as to affect a decrease in the total void volume. There is then a clear difference between the "A" nickel and the other "high purity" nickels. Even though in the high purity nickels the void size and number density varied significantly among the three types, the volume fraction remained essentially constant.

The microstructure resulting from interstitial damage was also much different in the high purity as compared to the commercial purity nickel. Occasional dislocation loops within a complex dislocation network were observed in the high purity nickel, Figure 10. In the commercial purity, dislocation loops were the only manifestation of interstitial damage, Figure 11. The loops in Figure 11 lie on the $\{110\}$ planes with $\bar{b} = \frac{a}{2} \{110\}$ and are pure edge in character. Loops marked "A" lie nearly in the plane of the foil and show only residual contrast from the small displacements

perpendicular to $\bar{b}$. The shape appears to be square with sides parallel to $\langle 001 \rangle$ and $\langle 011 \rangle$. Very rarely a loop with a stacking fault was observed as shown by the fringes in loops "B" in Figure 11a. The fault contrast disappears in Figure 11b when the diffraction vector $\bar{g}$ is changed to $\langle 113 \rangle$. This contrast behavior is expected from Frank faulted loops with a loop Burgers vector of $\frac{a}{3} \langle 111 \rangle$. Measurements of several of the unfaulted loops showed them to be interstitial in nature. The nature of the faulted loop was not determined. The distribution of loops was rather inhomogeneous as there was a greater density in some areas than others. It was not possible to determine the relative concentration of voids in areas of high loop density since quite thick regions were observed in the analysis of the loops. It was not possible to observe the very small voids in these thick regions.

Molybdenum

Three different purities of molybdenum have been irradiated at elevated temperatures and the void characteristics compared. The three types are (a) triple-pass, zone refined single crystal (Z.R.), (b) a commercial high purity molybdenum (MRC), and (c) a commercial alloy (TZM). The chemical analysis for Z.R. and MRC are given in Table IV. The TZM molybdenum has approximately 0.5% Zr and 0.1% Ti. The samples were irradiated at estimated temperatures of 635 and 720 °C, and Figure 12 shows the voids in the molybdenum after irradiating at the higher temperature of 720 °C. As mentioned previously, the actual temperatures may have been somewhat higher. The voids are slightly larger and the density smaller for the Z.R. molybdenum as compared to the MRC molybdenum. Although voids did form

TABLE IV

CHEMICAL ANALYSIS OF ZONE REFINED AND MRC MOLYBDENUM

<u>Impurity</u>	<u>3 Pass Z.R.</u>	<u>MRC</u>
W	100	300
Ni	1	2
Cu	3	10
Fe	2	70
K	40	50
Si	12	20
Mn	--	2
Ca	--	3
C	3	500
D	4	5
N	1	1
H	1	1

in the TZM molybdenum irradiated at 635 °C, no voids were observed after irradiation at 720 °C. At 720 °C second phase precipitation occurred in the TZM molybdenum. The precipitates are shown as black-white contrast in Figure 12; no contrast attributed to voids was observed.

DISCUSSION OF IMPURITY EFFECTS

Previous work on quenching and irradiation has shown a relationship between purity and void formation.^(29,30,32) Quenching studies on aluminum⁽³²⁾ and copper, silver and gold⁽³⁰⁾ show that void formation is enhanced by the presence of gaseous impurities particularly hydrogen. Farrell found an increase in void formation in aluminum that had been pre-injected with hydrogen by proton bombardment.⁽³³⁾ Packan, however, on comparing as-received with degassed aluminum found little difference in the void structure,⁽³⁴⁾ so there is some question as to the effectiveness of hydrogen. Stiegler, et al⁽²⁹⁾ at Oak Ridge have studied the void formation in both commercial purity 99% and ultra high purity aluminum 99.9999% during irradiation. Voids formed at a much lower fluence in the high purity aluminum than in the commercial purity. They attributed this to a much higher concentration of dissolved gases which serve as stabilizing agents for the voids in the high purity aluminum. The impurities in the commercial purity aluminum getter the dissolved gases and remove them from solution.

Our results on high purity and commercial purity nickel essentially agree with those mentioned above. The same conclusions as to the role played by the impurities in the nickel could be reached. The impurities, however, affect the complete nature of the radiation damage, not only void formation. The presence of only a low density of loops and voids in the commercial

purity nickel represents a much less advanced state of microstructural damage than in the high purity material in which the dislocation loops had grown into a network with a high density of voids. Since the visible damage is due to those defects remaining after recombination, the recombination rate in the commercial purity nickel must be considerably greater than in the high purity nickel. Therefore, the vacancies neither precipitate as voids, nor precipitate as a two-dimensional type defect at these temperatures. The vacancies are then free to annihilate with interstitials or interstitial-type defects. Impurities can also trap the interstitials. The presence of the square loop and faulted loops indicates considerably different behavior of the interstitial defects. There is no evidence for the formation of these particular square loops and faulted loops in high purity nickel irradiated at a lower fluence. The impurities may be more important in hindering the development of high density of loops and a dislocation network. With fewer sinks for interstitials, a greater annihilation rate with vacancies will result. As mentioned before, it is generally agreed that dislocation act as preferential sinks for interstitials and this factor allows for the build up of an excess vacancy concentration.

It is not possible to draw too many conclusions from the results comparing the three high purity nickels. An overall chemical analysis does not truly indicate the extent of impurities in solution. The three materials had essentially the same overall purity and only differed as to the concentration of the different types of impurity. A significant difference in impurity distribution among the high purity nickels could

account for the rather significant differences in terms of size and number density. Since the diffusivities and binding energies of the different impurities varies considerably, an uneven distribution of impurity and clustering of impurities could be expected. The loss of interstitials to sinks and the recombination rate, however, were not affected significantly since the overall swelling did not vary.

An experiment involving the irradiation of deformed material illustrates the effect of this impurity distribution. Nickel I was irradiated at 350 °C — in the as-received condition in which the microstructure consisted of a dislocation cell structure. Microstructural observations showed that the material recrystallized during the irradiation. The resulting void distribution was very inhomogeneous as shown in Figure 13. During such a low temperature irradiation, any inhomogeneous impurity distribution would be retained because of the very low diffusion rates at these temperatures. Inhomogeneous impurity distribution could result from segregation of impurities to grain boundaries for instance. The resultant void distribution is then a reflection of this impurity distribution. Note the difference in the distribution between Figure 13 and Figure 9a. Very similar observations and conclusions have been made by Farrell from results of cold worked and irradiated iron.⁽³⁵⁾ Strings of voids in irradiated aluminum have also been attributed to inhomogeneous distribution of impurities remaining after boundary migration.⁽²⁹⁾ It is probably fair to say that the significant differences in the number density and size distribution of voids in the high purity nickels point to much heterogeneous nucleation of voids.

The above reasoning on the effect of impurities could be applied to the results for Z.R. and MRC molybdenum. The significant result in the molybdenum experiment is the lack of voids in the TZM molybdenum at the higher irradiation temperature. The formation of the precipitates can require vacancies which are amply supplied by the irradiation process. Further, once the precipitates are formed, the interfaces can serve as sites for interstitial-vacancy annihilation. Consequently, the vacancies are not available for void formation. The only indication of interstitial damage was some dislocation fragments. It would seem that concurrent precipitation may be an effective way to reduce swelling. Of course, obtaining the right precipitation reaction at the right temperature in the material of interest may be rather difficult.

CONCLUSIONS

The temperature regime for void formation in pure metals extends from approximately $0.3 T_m$ to $0.55 T_m$ (T_m = absolute melting temperature). The results on the temperature dependence of the swelling in nickel and molybdenum agree reasonably well with the theoretical predictions for these metals. The temperature region at which vacancy clusters can be stabilized against collapse into a planar configuration is an important criterion in defining a lower temperature limit for void formation. The upper temperature limit is due to a reduction in the supersaturation of radiation produced vacancies. The anomalous behavior of titanium and zirconium in which no voids have been observed is believed due to the inability of the gas atoms to stabilize the vacancy clusters in these metals. The lack of voids in gold is probably due to the very low stacking

fault energy and a higher fluence than was used in the present experiments will be necessary before voids are found.

The complete radiation induced microstructure must be considered in evaluating the effects of impurities. The dislocation microstructure due to interstitial atoms is considerably altered and much less developed in impure nickel compared to high purity nickel. Since there is a one to one correspondence between vacancies and interstitials, the vacancy concentration and hence void formation are much reduced in the impure nickel. Small differences in the type and amount of specific impurities can have a significant effect on the size, number density and distribution of voids but the resultant swelling depends primarily on the magnitude of the overall purity.

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FIGURE CAPTIONS

- Figure 1. Representative micrographs of voids in irradiated molybdenum, nickel and rhenium. The temperature corresponds to the low temperature end of the void formation range.
- Figure 2. Swelling in molybdenum as a function of irradiation temperature. Fluence normalized to $2.5 \times 10^{19} \text{ n/cm}^2$.
- Figure 3. Micrograph illustrating different void morphologies in molybdenum. Foil orientation is near $\{110\}$.
- Figure 4. Swelling in nickel as a function of irradiation temperature. Fluence normalized to $5 \times 10^{19} \text{ n/cm}^2$.
- Figure 5. Effect of irradiation temperature on void size and number density in nickel. Fluence = $5 \times 10^{19} \text{ n/cm}^2$.
- Figure 6. Swelling in rhenium as function of irradiation temperature. Fluence normalized to $4 \times 10^{20} \text{ n/cm}^2$.
- Figure 7. Micrograph of titanium irradiated to $3 \times 10^{21} \text{ n/cm}^2$ ($E > 0.1 \text{ MeV}$) at 450°C . Most dislocation loops are of vacancy type.
- Figure 8. Swelling in a variety of pure metals as a function of homologous temperature. All irradiations at 450°C to a fluence of $3 \times 10^{21} \text{ n/cm}^2$ ($E > 0.1 \text{ MeV}$).
- Figure 9. Micrographs illustrating void formation in various purities of nickel irradiated at 450°C to $2.5 \times 10^{19} \text{ n/cm}^2$.
- Figure 10. Micrograph of the dislocation structure in Nickel I irradiated at 350°C to $2.5 \times 10^{19} \text{ n/cm}^2$.
- Figure 11. Micrographs of the dislocation loops in "A" nickel irradiated at 450°C to $2.5 \times 10^{19} \text{ n/cm}^2$. Foil orientation near $\{110\}$. (a) and (b) are same area imaged under different diffraction vectors $\bar{g}$.

Figure 12. Micrographs of various purities of molybdenum irradiated at 720 °C to 5×10^{20} n/cm². The black spots in the TZM molybdenum are small precipitates.

Figure 13. Micrograph illustrating inhomogeneous void distribution in nickel irradiated at 350 °C in the as-received condition to a fluence of 2.5×10^{19} n/cm².

(a) Mo-650°C (.32 T_m),
 5×10^{19} n/cm²

(b) Ni-350°C (.36 T_m),
 2.5×10^{19} n/cm²

(c) Re-720 °C (.29 T_m),
 4×10^{20} n/cm²

Figure 1. Representative micrographs of voids in irradiated molybdenum, nickel and rhenium. The temperatures correspond to the low temperature end of the void region.

FIG. 2
BRIMHALL

Figure 3. Micrograph illustrating different void morphologies in molybdenum. Foil orientation is near (110) .

FIG. 61
BRIMHALL

FIG. 5
BRIMHALL

FIG. 6
BAMMAY

Figure 7. Micrograph of titanium irradiated to 3×10^{21} n/cm^2 $E > 0.1$ MeV at 450°C . Most dislocation loops are of vacancy type.

(a) Ni-I

(b) Ni-II

(c) Ni-III

(d) "A" Ni

Figure 9. Micrographs illustrating void formation in various purities of nickel, irradiated at 450°C to 2.5×10^{19} n/cm².

Figure 10. Micrograph of the dislocation structure in nickel-I irradiated at 350°C to 2.5×10^{19} n/cm².

(a) $\bar{g} = [002]$

(b) $\bar{g} = [\bar{1}13]$

Figure 11. Micrographs of the dislocation loops in "A" nickel irradiated at 450 °C to 2.5×10^{19} n/cm². Foil orientation is near (110). Micrographs (a) and (b) are same area imaged under different diffraction vectors $\bar{g}$.

(a) Zone Refined

(b) MRC

(c) TZM

Figure 12. Micrographs of various purities of molybdenum irradiated at 720 °C to 1.5×10^{20} n/cm². The black spots in the TZM molybdenum are small precipitates. Voids form only on the zone refined and MRC.

Figure 13. Micrograph illustrating inhomogeneous void distribution in nickel irradiated in the as-received condition. 2.5×10^{19} n/cm² at 350 °C.