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VOID FORMATION AND SOLUTE SEGREGATION IN ION-IRRADIATED NIOBIUM-BASE ALLOYS*

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Abstract

The void-volume fraction in unalloyed Nb and Nb-base binary alloys containing either ~2.4 a/o Mo, Ti, Zr, Hf, Ni, Fe, V or Ta has been determined following 3.0-MeV $^{58}Ni^+$ ion irradiation at 1225 K to ~50 dpa. Also, the thermal- and irradiation-induced segregation of these substitutional-atom solutes and the intrinsic, interstitial-O impurity (~0.06 a/o) to the specimen surface and within the irradiation-damaged layer have been determined. The void-volume fraction and the segregation of solutes have been shown to be correlated by the solute diffusivity and the relative chemical affinity of the substitutional solutes for O. The correlated diffusion of vacancy defects and O atoms is postulated to explain the experimental results.

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1. INTRODUCTION

Some design studies for fusion reactors have considered the use of a Nb alloy for material applications in the construction of the first-wall and limiter components [1]. The dimensional instability of a Nb alloy that can result from irradiation damage is an important factor to be considered for these applications. The effects of dilute (2.4 a/o) alloying additions of Mo, Ni, Fe or Ti on the dimensional instability due to void formation in Nb that results from 3.0-MeV^{58}Ni^{+} ion-irradiation at ~ 1225 K have been determined by Loomis and Gerber [2]. These experimental results show that the void-volume fraction is unexpectedly low in the Nb alloy containing the Mo addition whereas the void-volume fraction in Nb is nearly unaffected by the Ni and Fe additions. Experimental evidence exists which show that the spatial distribution of alloying solutes in metals can be altered during irradiation at elevated temperatures [3-7]. The interaction of solute atoms with the irradiation-produced defects that are diffusing in a defect gradient to defect sinks, e.g., specimen surface, void surface, grain boundaries and dislocations, provide strong driving forces for solute diffusion and redistribution. Since the properties of materials depend sensitively on alloy composition, this irradiation-induced segregation phenomenon can impact directly on void formation and, therefore, on the dimensional stability of the alloy in a fusion reactor environment.

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In this paper we present the results of an experimental investigation on the thermal-and irradiation-induced segregation of Mo, Ti, Zr, Hf, Ni, Fe, V and Ta solute in dilute (2.4 a/o) Nb-base binary alloys during 3.0-MeV$^{58}Ni^{+}$ ion irradiation at 1225 K. These solute-segregation results are correlated with the previously reported void-volume fraction results for ion-irradiated Nb alloys containing 2.4 a/o Mo, Ni or Fe [2] and void-volume fraction data that we have obtained in the present study for Ti, Zr, Hf, V and Ta solutes in Nb. The intent of this correlation between solute-segregation effects and the void-volume fraction in Nb is to determine the solid-state parameters for the Nb alloy and/or solute atoms in Nb that determine the dimensional stability or instability of Nb alloys in an irradiation-damaging environment. In this study we make the tacit assumption that the enrichment or depletion of solutes in the near-surface region (< 100 nm depth) of an irradiated specimen provides an accurate assessment of the tendency for segregation of the solute in the near-surface region of irradiation-produced voids. This assumption is justified on the basis of results obtained previously for other irradiated metals [3,8]. Future studies that utilize the Electron Energy Loss and Energy Dispersive X-ray techniques in combination with transmission electron microscopy observations of the irradiated specimens will test the validity of this assumption.

2. MATERIALS AND PROCEDURES

Niobium alloys containing either 2.4 ± 0.1 a/o Ta, Ni, Fe, Ti Zr, V, Hf or Mo and unalloyed Nb were prepared by arc-melting the constituents in a purified Ar atmosphere. The 2.4 a/o solute composition was chosen for this study to obtain a substitutional solid solution with the same solute concentration in each of the alloys at the beginning of the irradiations [9]. Sheet specimens of these alloys and unalloyed Nb with 0.13 mm thickness were annealed at 1470 K for 10^4s. Special attention was given to the surface preparation of the specimens for this study to insure a uniform alloy composition in the near-surface region (~ 1000 nm thickness). Determinations of the O and N concentration in the Nb alloys and unalloyed Nb by the vacuum-fusion technique showed that these materials contained 0.04 to 0.07 a/o O and 0.01 to 0.02 a/o N.

Specimens of the Nb and Nb alloys, each with a diameter of 3.05 mm, were mounted in a four-by-four array in a tungsten holder for simultaneous irradiation. The irradiations were performed in the ion-irradiation facility at Argonne National Laboratory using standardized procedures [10]. The specimens were irradiated with 3.0-MeV^{58}Ni$^+$ ions at a typical current density of 5 mA/m^2 giving a nominal atomic displacement rate of 5 x 10^{-3} dpa/s. The depth of the peak irradiation damage was 630 nm, and the depth of peak deposition of the bombarding ^{58}Ni$^+$ ions was 800 nm. Additional information on the damage computations is presented in Ref. [11].

The specimens were irradiated at 1225 ± 15 K to 50 ± 5 dpa in an all-metal system evacuated to a total pressure of ~ 3 x 10^{-6}Pa. The partial pressures of the residual gases in the ambient environment were monitored with a monopole residual gas analyzer (10^{-9}Pa sensitivity). The O partial pressure during the irradiation was ~ 2x10^{-8}Pa; the remainder of the ambient environment was mainly composed of N and CO. The dependence on irradiation temperature of the void-volume fraction in "pure" and O-doped Nb following 3.0-MeV^{58}Ni$^+$ ion-irradiation from Refs. [2] and [11] is shown in Fig. 1. Thus, the irradiation temperature chosen for the present experiments is on the low-temperature side of the temperature for maximum void-volume fraction in Nb. The diameter, number-density, and volume-fraction of voids in "pure" and O-doped Nb following irradiation at 1225 K with 3.0-MeV^{58}Ni$^+$ ions attain nearly unchanging values for damage levels $\gtrsim$ 30 dpa [12]. Hence, the void-volume fractions and solute-segregation effects that were determined in this study would not be expected to change on further irradiation. The procedures that were utilized in the specimen preparation for the TEM observations and in the subsequent data evaluation are outlined in Refs. [11] and [12].

The dependence on depth in the irradiation-damaged layer (~ 1500 nm thickness) of the thermal- and irradiation-induced segregation of solute atoms was determined by use of the Auger Electron Spectroscopy (AES) technique in combination with sputter-ion erosion of the surface. AES analyses at room temperature were performed using a primary electron beam at 5 KeV with a diameter of ~10 μm to excite the electron transitions. Depth profiling was accomplished by sputter-ion erosion with 1-KeV Ar ions in an Ar atmosphere of 6.5×10^{-3}Pa. The sputter-ion erosion rate was 3.5 nm per minute. The concentration of the elemental solute atoms in a thin surface layer (~1 nm) on the annealed or irradiated specimens was obtained from the peak-to-peak magnitude of the applicable peak in the Auger electron energy-distribution function and the AES elemental sensitivity factors that were determined for the as-prepared alloys. Since the O-concentration profile in the annealed and irradiated specimens was an important parameter for this study, the AES sensitivity factor for O was also determined for Nb specimens with known concentrations of O.

3. EXPERIMENTAL RESULTS

3.1. Void-Volume Fraction

The dependence on O concentration of the void-volume fraction ($\Delta V/V$) in Nb at 1200, 1225 and 1240 K following 3.0-MeV^{58}Ni$^+$ ion-irradiation to 50 ± 5 dpa from Ref. [11] is shown in Fig. 2. The ΔV/V data for the Nb-2.4 a/o Ni, Fe, and Mo alloys from Ref. [2] and the ΔV/V data for the Nb-2.4 a/o Ti, Zr, Hf, V or Ta alloys that were obtained in the present study are also shown in Fig. 2 at the appropriate O concentration. These ΔV/V data together with the average void diameter and void number density are listed in Table 1. These experimental results show that the addition of 2.4 a/o Ta to Nb containing ~0.06 a/o O results in a significant increase of the ΔV/V in Nb at 1225 ±15 K, whereas the addition of 2.4 a/o Mo to Nb results in a significant decrease of the ΔV/V in Nb. The addition of ~ 2.4 a/o Ni or Fe to Nb does not substantially change the ΔV/V in Nb. Although Ti, Zr, V, and Hf solutes significantly reduce the ΔV/V in Nb, these solutes are less effective than the Mo solute.

Table 1. Void Parameters for Nb and Nb Alloys Irradiated with 3.0-MeV ^{58}Ni^{+} Ions.

Alloy[a]	Temperature (K)	Damage (dpa)	d_v (nm)	c_v (m^{-3})	ΔV/V
Nb+2.3a/oNi	1225	45	32	1.4×10^{21}	0.024
Nb+2.3a/oFe	1225	48	29	1.7×10^{21}	0.022
Nb+2.3a/oMo	1225	46	4	1.1×10^{21}	$<$ 0.001
Nb+2.3a/oTi	1215	45	85	2.0×10^{19}	0.007
Nb+2.4a/oHf	1245	47	39	7.5×10^{19}	0.002
Nb+2.4a/oV	1245	49	56	3.9×10^{19}	0.004
Nb+2.4a/oTa	1240	53	160	5.4×10^{19}	0.116
Nb+2.4a/oZr	1235	57	62	4.2×10^{19}	0.005
Nb(0.06a/oO)	1225	51	37	1.4×10^{21}	0.037
Nb(0.001a/oO)[b]	1200	45	11	8.6×10^{19}	$<$0.001

[a] Alloys contain ~0.06 a/o O.
[b] Ref. [13].

3.2. Substitutional Atom Segregation

The segregation of the substitutional-atom solutes in the irradiation-damaged layer of the Nb alloy specimens following ion-irradiation at 1225 K is shown in Fig. 3. The solute-concentration profile for each of the alloys was determined from the AES spectrum that was acquired at room temperature for the surface layer (~1 nm thick) and ~3.5 nm depth and at intervals of 50-100 nm depth to a total depth of ~900 nm in the irradiation-damaged layer. The solute concentration-depth profiles in Fig. 3 are shown completely only for the Nb-Mo and Nb-Ni alloy specimens while profiles for the other alloy specimens are abbreviated for clarity in the figure. The solute concentration profiles for each of the irradiated alloys with the exception of the Nb-Mo alloy show an approximate exp(-depth) dependence on depth to ~ 50 nm. In the case of the Nb-Mo alloy, the experimental results show that the Mo concentration is substantially increased above C_0 (2.4 a/o) in the near-surface layers (< 50 nm) during ion-irradiation, but in the case of the Nb-Fe and Nb-Ti alloys the solute concentration is significantly reduced below C_0 in the near-surface layers. In the case of the Nb-Ta, -Ni, -V, -Zr, and -Hf alloys, the solute is moderately enriched above C_0 in the specimen near-surface layers. With the exception of the Nb-Ni alloy, the alloys tend to show an enrichment of solute at specimen depths in the region for peak irradiation damage. The Nb-Ni alloy was exceptional in that the solute concentration showed a maximum depletion in the peak damage region. It can be noted in Fig. 3 that even though the Fe and Ti solutes were depleted in the surface layers, the alloys showed substantial enrichment of these solutes in the peak damage region.

The relationship between the surface-solute concentration for each of the ion-irradiated alloy specimens (Fig. 3) and the diffusivity of the solute in Nb at 1225 K is shown in Fig. 4. The solute concentration in the surface layer (~ 1 nm thick) for alloy specimens that were simultaneously subjected to the same thermal and environmental conditions for the irradiated specimens, but were shielded from $^{58}Ni^{+}$ ions, are also shown in Fig. 4. The diffusivity of the solute atoms in Nb and other solid-state parameters that pertain to the alloys are listed in Table 2. It should be noted in Fig. 4 that the solute-concentration abscissa is shown to be positive on either side of the zero solute concentration. This unusual manner for the presentation of these data was selected because of the assumed change in the mechanism for the diffusion of the solutes in Nb, i.e., vacancy diffusion for Mo, Ta, V, Ti, Zr and Hf, interstitial-vacancy diffusion for Fe [14], and interstitial diffusion for Ni [14]. In support of a change in the diffusion mechanism for the solutes in the Nb alloys, we note in Fig. 3 that the concentration profiles for the Nb-Mo and Nb-Ni alloys show solute enrichment or depletion at specimen depths that are consistent with theoretical analyses by Okamoto, et. al. [15] on the solute redistribution processes in ion-bombarded alloys. The experimental results, when presented in this manner, show a linear relationship between the surface solute concentration and log D_s over the 10^{-24} to 10^{-16} m^2/s range of D_s. Furthermore, the enrichment of solute at the surface of the Nb alloys is highest for Nb alloys containing solutes with diffusivities that are relatively low in comparison with D^o_{Nb} and diffuse by a vacancy mechanism. On the other hand, the solute enrichment at the specimen surface attains significant levels if the diffusivity of the solute is 10^4 to $10^5 m^2/s$ greater than D^o_{Nb} and migrates by an interstitial mechanism, i.e., the Ni solute. In between these two extremes of solute diffusivity, i.e., 10^{-16} and 10^{-24} m^2/s, the extent of solute enrichment or depletion at the specimen surface was undoubtedly affected by interactions between the solute and O-impurity atoms. The significant levels of solute enrichment for the Nb-V, -Ti, -Zr and -Hf alloys that were annealed without irradiation (shielded, in Fig. 4) are indicative of such O-solute interactions. It can be noted in Fig. 4 that the irradiated Nb-Ti, -Zr and -Hf alloys show an unexpected difference in the segregation of the solutes; Ti is slightly depleted whereas Zr and Hf are slightly enriched in the surface layer. There appears to be no succinct relationship between the enrichment or depletion of solute in the surface layer of these alloy specimens and the change of the Nb lattice parameter (Table 2) by the solute addition.

Table 2. Diffusivity (D_s), Relative O Affinity (A_s) and Lattice Parameter (a_s) for Nb and Nb Alloys.

Alloy[a]	D_s^{Nb} $(m^2 \cdot s^{-1})$[b]	A_s^{Nb} $(\times 10^5$ Joule $\cdot$ Mole$^{-1})$[c,d]	a_s^{Nb} (nm)[e]
Nb+2.4a/oNi	4.2×10^{-17}	-1.6(NiO)	0.3293
Nb+2.3a/oFe	4.0×10^{-18}	-1.3(FeO)	0.3291
Nb+2.4a/oHf	3.4×10^{-20}	1.6(1/2 HfO_2)	0.3307
Mb+2.4a/oZr	1.4×10^{-20}	1.6(1/2 ZrO_2)	0.3309
Nb+2.3a/oTi	6.5×10^{-21}	1.5(TiO)	0.3295
Nb+2.3a/oV	4.0×10^{-21}	0.3(VO)	0.3298
Nb(0.06a/oO)	1.1×10^{-21}		0.3303
Nb+(0.001a/oO)	-	-	0.3000
Nb+2.4a/oTa	1.9×10^{-22}	0.1(1/5 Ta_2O_5)	0.3302
Nb+2.4a/oMo	1.6×10^{-24}	-1.1(1/2 MoO_2)	0.3298
Nb+2.4a/oW	1.0×10^{-27}	-1.1(1/2 WO_2)	~0.3298

[a] Alloys contain 0.04-0.07 a/o O.

[b] D_s at 1225 K, from Refs. [16-17].

[c] ΔH^o_{298} (Nb Oxide)-ΔH^o_{298} (Solute Oxide) from Ref. [18].

[d] Average of ΔH^o_{298}(NbO, NbO_2,Nb_2O_5) = 4×10^5 Joule/Mole.

[e] From Ref. [2] and this study.

3.3. Oxygen Segregation

The segregation of the O solute in the irradiation-damaged layer of the unalloyed Nb and Nb alloy specimens following ion-irradiation at 1225 K is shown in Fig. 5. The O-concentration profile for each of the alloys was determined from the AES spectrum that was acquired at room temperature for the substitutional-atom solute-concentration profile [Sec. 3.2]. As in the case of the substitutional-atom solutes, the O concentration profile for each of the irradiated alloys shows an approximate exp(-depth) dependence on depth to ~50 nm. The O-concentration profiles in Fig. 5 are shown completely only for the unalloyed Nb, Nb-Ti, Nb-Mo and Nb-Ni specimens while profiles for the other alloy specimens are abbreviated for clarity in the figure. It can be noted in Fig. 5 that the unalloyed Nb, Nb-Ni, and Nb-Fe specimens have nearly the same high O concentration (23-25 %) in the near-surface layer whereas the Nb-Mo alloy has the lowest O concentration (4.9 %). In the peak-damage region, the solute additions to Nb (with the exception of Ti) cause a reduction in the O concentration of irradiated Nb. The anomalous O enrichment in the peak damage region that was determined for the Nb-Ti alloy may be a consequence of the slightly higher initial O concentration (0.07%) in this alloy. Also, the Nb-Mo alloy shows an O concentration for specimen depths ranging from ~50 nm to ~300 nm that is slightly greater than the concentration for unalloyed Nb and significantly greater than the concentration for the other alloys (except Nb-Ti).

The relationship between the O concentration in the surface layer of the irradiated Nb and Nb alloy specimens (from Fig. 5) and the relative chemical affinity, A_s^{Nb}, of a solute for O (from Table 2) is shown in Fig. 6. The determination of the relative chemical affinity from the ΔH^o_{298} values for the different oxides should not be taken to mean that the solute oxides listed in Table 2 were present on the surface of the specimens. The oxides on the surface of the specimens were probably Nb oxides, i.e., NbO, NbO_2 and Nb_2O_5 [19], with solute atoms incorporated in the Nb oxide structure. In the case of solutes having a greater affinity for O than Nb, i.e., ΔH^0_{298} (Nb Oxide) $-\Delta H^0_{298}$ (solute oxide) > 0, the curve shows a general trend of decreasing near-surface O concentration with increasing solute affinity for O. However, in the case of the Ni and Fe solutes which have substantially less affinity for O than Nb, the O concentration on the surface of these irradiated alloys is approximately the same as the O concentration determined to be present on the surface of unalloyed Nb. The AES analysis for O in the surface region of the irradiated Nb-Mo alloy showed an exceptionally low O concentration, even though the Mo solute has substantially less affinity for O than Nb. The significance of these disparate surface-O concentration results and their correlation with the substitutional-atom solute segregation and the ΔV/V results for unalloyed Nb and Nb alloys will be discussed in Sec. 4.

The O concentration in the near-surface layer for Nb and the Nb alloy specimens that were simultaneously subjected to the same thermal and environmental conditions for the irradiated specimens, but were shielded from the $^{58}Ni^+$ ions, are also shown in Fig. 6. Comparison of the data for the irradiated and shielded specimens shows that a higher O concentration was present in the near-surface layers of the shielded specimens; the higher O concentration was particularly evident for the shielded Nb-Mo alloy.

The previous experimental results on void formation in ion-irradiated Nb [11] have shown that the O concentration (and to a lesser amount, the N and C content) determines the ΔV/V. By reference to Fig. 2, the O concentration in the Nb alloys that was effective in producing the observed ΔV/V can be easily deduced, i.e., reading in Fig. 2 the O concentration that produces an equivalent ΔV/V in the Nb-O system. The relationship between the effective O concentration and the surface O concentration on the alloys (from Figs. 5 or 6) is shown in Fig. 7. In the case of the Ni and Fe alloys, the effective O concentration was taken to be ~0.07 a/o rather ~0.01 a/o O because of the better correlation with the void diameter and number density in the more highly O-doped, unalloyed Nb specimen (Table 1). Thus from Fig. 7, the experimental results show that the addition of ~2.4 a/o Ni or Fe to Nb containing ~0.06 a/o O results essentially in no change in the O concentration in Nb that is effective in producing a ΔV/V. On the other hand, the addition of ~2.4 a/o Mo to Nb containing ~0.06 a/o O causes a reduction of nearly two orders magnitude in the O concentration that is effective in producing a ΔV/V. The other solutes have an influence on the O concentration that is intermediate to Mo and Ni or Fe.

4. DISCUSSION OF RESULTS

The void-volume fraction (ΔV/V) in unalloyed Nb and Nb-base binary alloys containing either ~2.4 a/o Mo, Ti, Zr, Hf, Ni, Fe, V or Ta has been determined following 3.0-MeV $^{58}Ni^+$ ion irradiation at ~1225 K to ~50 dpa. Also, the thermal- and irradiation-induced segregation of these substitutional-atom solutes and the intrinsic, interstitial-O impurity (~0.06 a/o) to the specimen surface and within the irradiation-damaged layer have been determined.

The experimental results show that the ΔV/V due to voids in ion-irradiated Nb containing ~0.06 a/o O is: (1) nearly unaffected by 2.4 a/o Ni or Fe additions, (2) increased substantially by a 2.4 a/o Ta addition, (3) decreased by 2.4 a/o alloying additions of Ti, Zr, V and Hf with increasing effectiveness in the same order and (4) decreased to the least ΔV/V by a 2.4 a/o Mo addition. The effectiveness of these solutes for reducing or increasing the ΔV/V in ion-irradiated Nb can be summarily explained if the relationship between the solute diffusivity, D_s^{Nb}, and the chemical affinity, A_s^{Nb}, of the solutes for O is considered together with the influence of D_s^{Nb} and A_s^{Nb} on the segregation of O to the specimen or void surface. Before presenting our current understanding of the processes that determine the effects of solutes on void growth in Nb, we will enumerate some of the experimental correlations between $\Delta V/V$, D_S^{Nb} and A_S^{Nb} determined in this study. These correlations will show the need to consider the relationship between D_S^{Nb} and A_S^{Nb} and their combined influence on the segregation of O.

The lowest $\Delta V/V$ (< 0.1%) in the alloys that were investigated in this study was determined for the 2.4 a/o Mo alloy. This lowest $\Delta V/V$ can be correlated with the lowest D_S^{Nb} that resulted in the highest amount (9.9%) of solute segregation to the specimen surface because of the vacancy inverse Kirkendall effect [3]. Also, the lowest $\Delta V/V$ for the Mo alloy can be correlated with the lowest O concentration on the specimen surface. The addition of 2.4 a/o Ta to Nb caused an unexpected large increase of the $\Delta V/V$ in Nb from 3.7 % to 11.6%. However, this large increase in $\Delta V/V$ by the Ta addition can be correlated with the slightly greater affinity for O by Ta. This slightly greater affinity is believed to result in an effective O concentration of ~0.03 a/o (Fig. 7) that causes a large $\Delta V/V$ (Fig. 2). Moreover, the slightly greater affinity causes a medium decrease in the surface O-concentration from that determined for unalloyed Nb containing ~0.06 a/o O. The small difference between D_{Ta}^{Nb} and D_{Nb}^{O} is an additional correlating factor that should be considered in connection with the slightly greater O affinity. The $\Delta V/V$ in Nb is not greatly changed by addition of the Ni and Fe solute, and this effect can be directly correlated with the absence of an affinity for O by these solutes which allows for a surface O concentration that is essentially the same as that observed for unalloyed Nb containing 0.06 a/o O. The lack of an effect of Ni and Fe on the $\Delta V/V$ in Nb can also be directly correlated with the extremely high D_S^{Nb} of these solutes. This correlation arises because these solutes diffuse by an interstitial (Ni) or interstitial-vacancy (Fe) mechanism. The Ni enrichment is observed because of the interstitial inverse Kirkendall effect [3]. Even though a significant enrichment of Ni and Mo in the specimen surface was determined, the different diffusion processes caused opposite effects for the ΔV/V in Nb and the surface O concentration. In the case of the V, Ti, Zr and Hf solutes, the significant reduction of the ΔV/V in Nb by these solutes is directly correlated with the strong chemical affinity of these solutes for O and the resulting low surface-O concentration. Also, the effects of these solutes on the ΔV/V in Nb are probably correlated with D_s^{Nb} values that are slightly higher than D_{Nb}^{O}, but this correlation is largely obscured in our data by the chemical affinity.

It can be noted in the previous discussion for each of the alloys, that there is de facto correlation between the specimen surface O concentration (also, by assumption, the void surface O concentration) and ΔV/V. On the basis of this correlation together with results from our previous research [11-13] and the experimental results of other investigators [20-23], we postulate that the diffusion of vacancy defects and O atoms in Nb are correlated in vacancy-nO complex with n values ranging from 0 to ~3. The diffusion of these complex (v-nO) to the intrinsic void nuclei [11] can account for the simultaneous increase of the diameter and number density of voids with increasing O concentration to ~0.04 a/o O in ion-irradiated Nb [11]. At ~0.04 a/o O concentration, the migration energy of the complex ($n \simeq 3$) may attain a high value such that mutual recombination of the irradiation-produced defects causes a precipitous decrease in the average void diameter giving a corresponding precipitous decline in ΔV/V (Fig. 2). The existence of these complex with high migration energy in Nb for $\gtrsim 0.04$ a/o O may account for the abrupt appearance of an ordered-void array in the irradiated Nb microstructure [24], especially at lower irradiation temperatures. Elastic interactions between void-O shell composites are believed to give rise to the ordering [24].

The postulated occurrence of correlated diffusion for O atoms and vacancy defects, i.e., v-nO complex diffusion, in Nb allows the desired connection of D_s^{Nb} and A_s^{Nb} to the segregation of O to the specimen or void surface. It is this connection which we seek to explain the effects of the solutes on $\Delta V/V$ in Nb. However, before discussing the implied relationship between the O segregation and $\Delta V/V$ in the Nb alloys, we briefly describe the kinematic processes for O that determine the magnitude of the O concentration in the near-surface layers. For the purpose of brevity and simplicity, we consider initially the situation for Nb in the ambient environment of this experiment. The time rate of change of O concentration on the surface of Nb, C_s, may be written [25]

$$\frac{dC_s}{dt} = k^+ P_{O_2} + D^1 \nabla C_B - k^- C_s , \qquad (1)$$

where P_{O_2} is the partial pressure of O in the ambient environment, k^+ is the rate constant for adsorption, k^- is the evaporation rate constant of O and/or Nb oxides, D^1 is the O diffusion coefficient between the surface and the bulk, and ∇C_B is the O concentration gradient between the bulk and the surface. The low vapor pressure of the undissociated Nb oxides and the low O dissociation pressure, e.g., $\sim 5 \times 10^{-14}$ Pa and $\sim 4 \times 10^{-16}$ Pa for NbO [26], respectively, show that the third term in Eq. (1) is negligible. Initially, when the surface is clean, the sticking coefficient, S, is close to unity and the O adsorption rate is $k^+ = 3.0 \times 10^3$ S·monolayers·Pa^{-1}·s^{-1} [25]. Thus, during the time of heating to the irradiation temperature (2×10^3 s) and during the time of the irradiation (10^4 s), ~0.75 monolayer of O was adsorbed on the surface. This adsorbed O diffused into the bulk of the Nb specimen at temperatures $\gtrsim$ 700 K. AES studies [25] have shown that the fractional occupation of available sites for O decreases sharply above 700 K. At 1225 K, the O would be uniformly and rapidly distributed in the bulk since the O diffusivity is $\sim 10^{-11}$ m^2/s [27]. The increase of the bulk O concentration would be << 0.01 a/o. During the time of cooling from the irradiation temperature (2×10^2 s), << 0.1 monolayer of O could have been adsorbed from the ambient environment. Thus the first term in Eq. (1) contributes a relatively small amount to the observed surface O concentration. We conclude from Eq. (1) that the increase in the O concentration in the surface layer of irradiated or shielded Nb (and Nb alloys) is due to segregation of O from the bulk to the surface layers either during irradiation or during cooling from 1225 K. Farrell, et al. [25] have shown from AES experiments that O-doped Nb specimens with negligible surface concentrations of O at elevated temperatures (~1875 K) show a high surface-O coverage (0.5 monolayer) immediately upon cooling below 775 K. Hofmann, et al. [28] have shown that O in Nb diffuses to the surface during constant sputter-ion erosion for specimen temperatures > 775 K. Loomis and Gerber [13] have shown that significant diffusion of O to the surface of Ti-coated Nb occurs at 1200 to 1280 K during ion-irradiation. Thus segregation of O to the surface of Nb occurs during irradiation at 1225 K as well as as during cooling from 1225 K. The segregation of O to the surface of Nb during irradiation is attributed to the diffusion of v-nO complex in the defect gradient between the surface and the bulk. The driving force for segregation of the O to the surface of Nb during cooling is the reduction of the surface energy by O enrichment [28]. The amount of O that segregates to the surface during irradiation or cooling is diminished by either substitutional-solute atom-vacancy-oxygen complex formation or processes that reduce the defect gradient. Kelly and Lam [29] have discussed the preferential loss of O from Nb_2O_5, MoO_3, TiO_2, and V_2O_5 to form lower oxides on sputtering with O ions. In the case of Nb_2O_5, the conversion to NbO is incomplete after bombardment with 35-keV O ions to a dose of 5×10^{16} ions/cm^2. The conversion of Nb_2O_5 to NbO is complete after a dose of 1×10^{17} ions/cm^2. We have estimated that the maximum dose of O ions impinging on the specimens in this experiment is $< 10^{13}$ ions/cm^2. The O ions result from forward scattering of the ambient O by the 3-MeV $^{58}Ni^+$ ions. Thus, the preferential loss of O from oxides on the surface of specimens by O ion sputtering is not considered significant in the present experiment.

From the preceding discussion, we believe the O segregation results obtained in this study provide an accurate assessment of the tendency for O segregation to void surfaces in the presence of substitutional-solute atoms in Nb. The growth of voids in ion-irradiated unalloyed Nb and Nb alloys, depends sensitively on the arrival of a small net flux of irradiation-produced vacancy defects at intrinsic void nuclei (in the case of Nb, these void nuclei are believed to be O-coated cavities [11]). Thus, we arrive at the desired connection of D_S^{Nb} and A_S^{Nb} with segregation of O to the void surface for an explanation of the effects of the solutes on $\Delta V/V$ and solute segregation effects in Nb. To make this connection we must make use of the diffusion of v-nO complex that have been postulated. It is implicit in this discussion that sinks, e.g., dislocation loops and dislocation network, are present in the irradiation-damaged layer which have a slight preference for irradiation-produced interstitial defects. In addition, we expect diffusion of the solutes to these dislocation sinks.

In the case of the Mo addition to Nb, the exceptionally low D_S^{Nb} for Mo atoms causes an enhanced flux of Nb atoms relative to Mo atoms away from the near-surface region of void nuclei (and specimen near-surface) giving an enrichment in the Mo concentration. The mean diffusivity of the atoms in the near-surface region is lowered which together with the reduced diffusivity of the v-nO complex allows increased defect recombination resulting in a low ΔV/V. Also, reduction of the mean atom diffusivity in the near-surface region causes a decrease in the gradient of the v-nO complex concentration near the void surface and the specimen surface. The low A_s^{Nb} of Mo atoms and the decreased defect concentration gradient allows increased, thermal-induced migration of O atoms away from surfaces (void and specimen). The segregated, slow diffusing Mo atoms in the irradiated alloy inhibit the diffusion of O atoms to the surface on rapid cooling from the irradiation temperature.

In the case of the V, Ti, Zr, and Hf solutes in Nb, the strong binding of these solute atoms to the v-nO complex effectively reduces the flux of the v-nO complex to the void and surface sinks with a corresponding reduction in ΔV/V and O concentration in the surface. In the case of the Ni and Fe solutes, the flux of v-nO complex to the void nuclei and voids are essentially unaltered because of the low A_s^{Nb} of these solutes for O and because these solutes diffuse by an interstitial or interstitial-vacancy mechanism. The diffusion of the Ni and Fe solutes by mechanisms that are not "pure" vacancy may account for the small reduction of ΔV/V in Nb from 3.7% to 2.4%. Thus, solutes with relatively low diffusivity in Nb or relatively high chemical affinity for O in Nb are substantially more effective than solutes with relatively high diffusivity in Nb for reducing the ΔV/V in Nb.

In this study, the effects of the substitutional-solute atoms on the ΔV/V in Nb resulted from the addition of ~2.4 a/o solute to Nb containing ~0.06 a/o O. If the O concentration in Nb is $\lesssim$ 0.04 a/o or $\gtrsim$ 0.10 a/o, the effect of a solute on the ΔV/V in Nb is expected to be different (from Fig. 2). Moreover, if the substitutional-solute concentration is increased or decreased from 2.4

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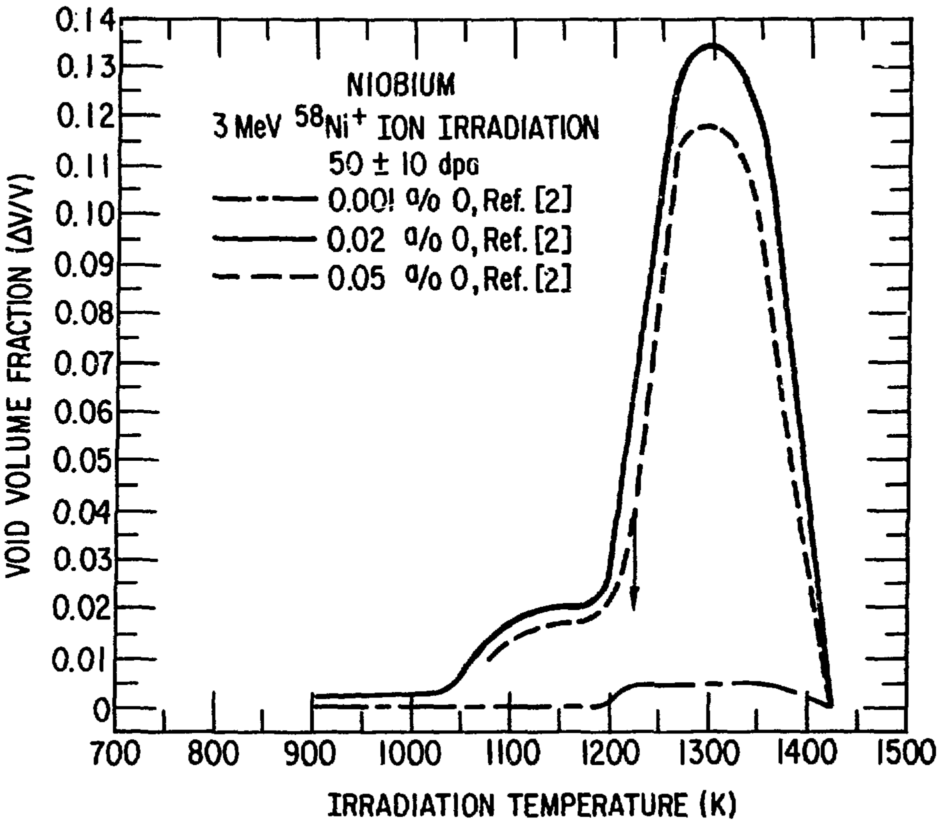

Fig. 1. Dependence of ΔV/V on Irradiation Temperature for Nb Containing O Impurity.

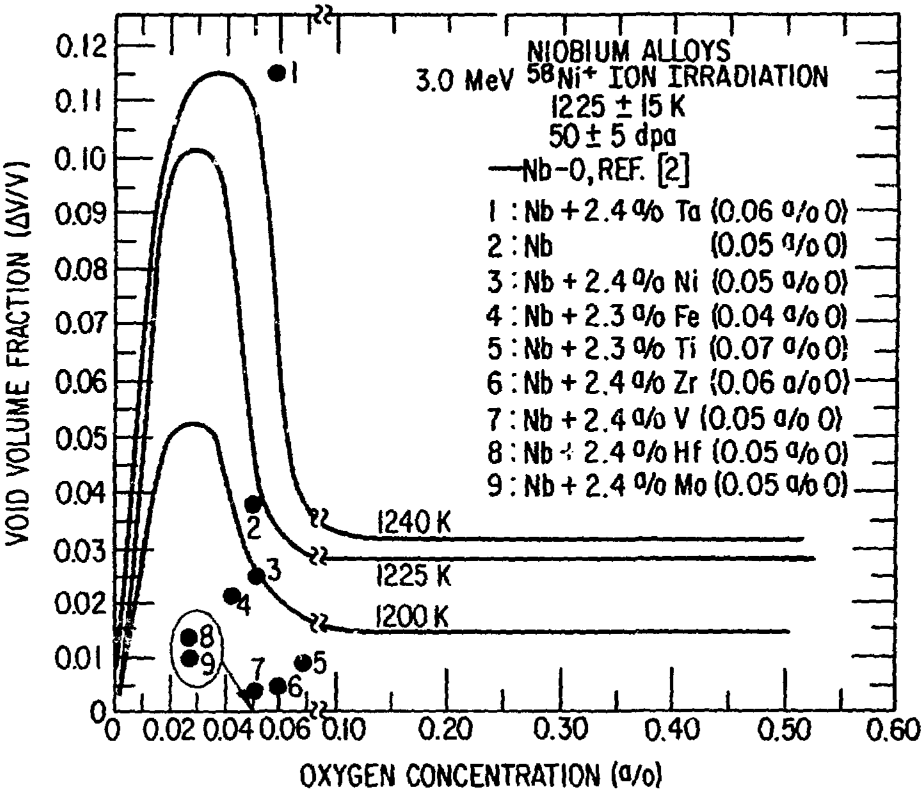

Fig. 2. Dependence of Void-Volume Fraction in Ion-Irradiated Nb on O Concentration and Substitutional-Atom Solute.

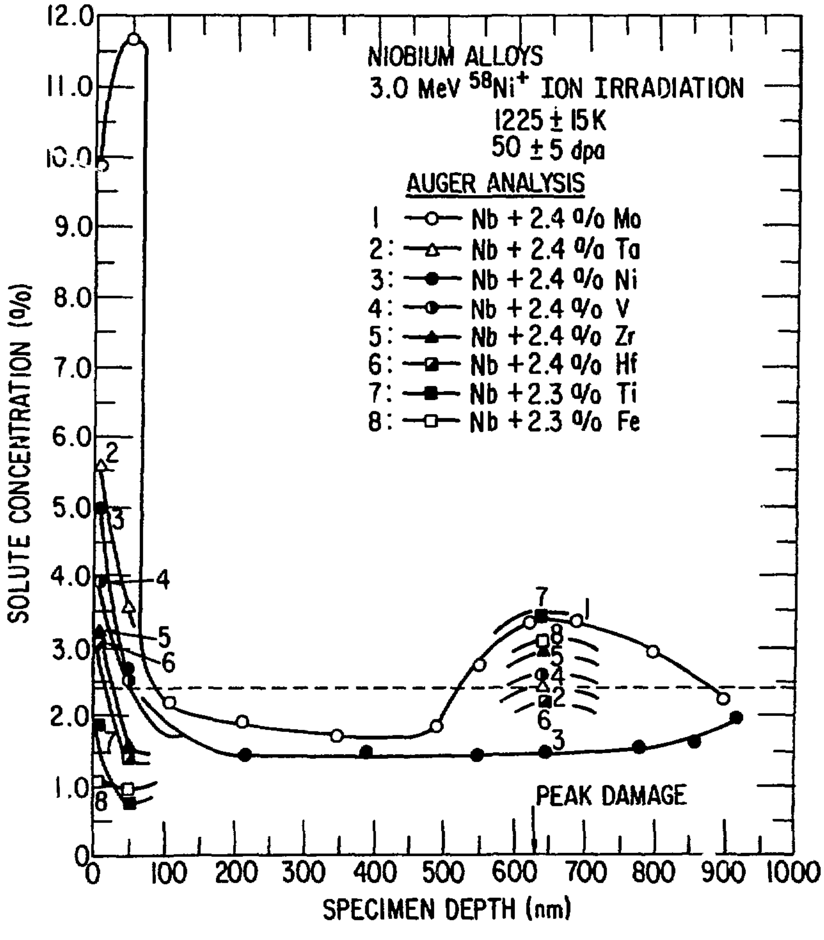

Fig. 3. Dependence of Substitutional-Solute Atom Segregation in Ion-Irradiated Nb on Depth in the Irradiation Damaged Layer.

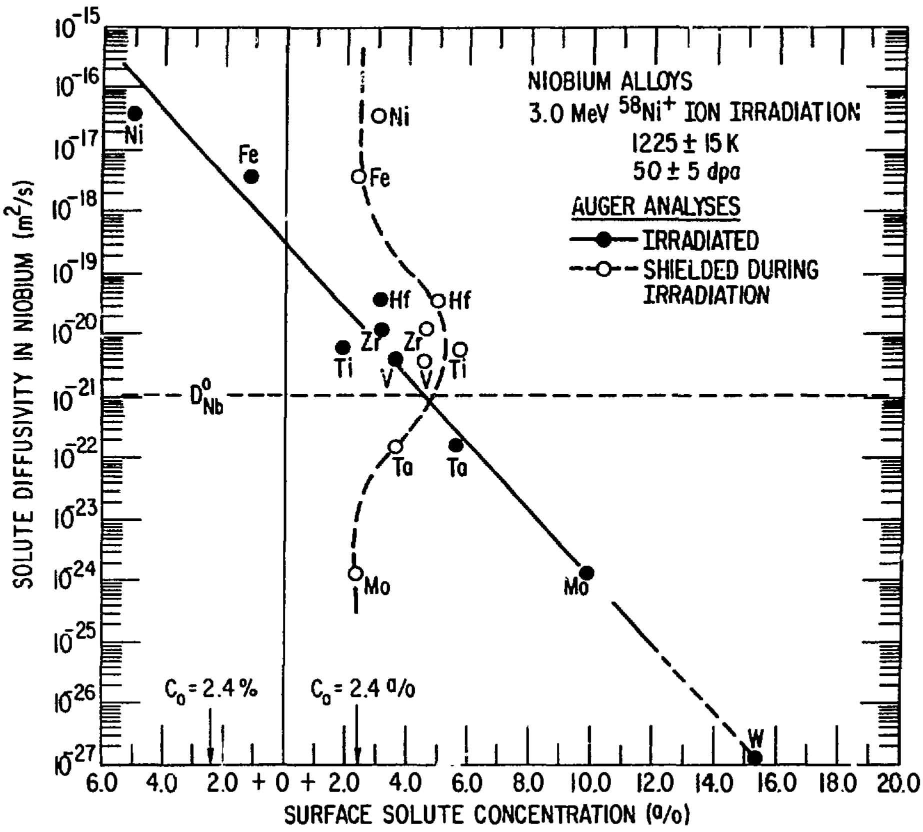

Fig. 4. Dependence of the Surface-Solute Concentration on Solute Diffusivity for Ion-Irradiated Alloys at 1225 K.

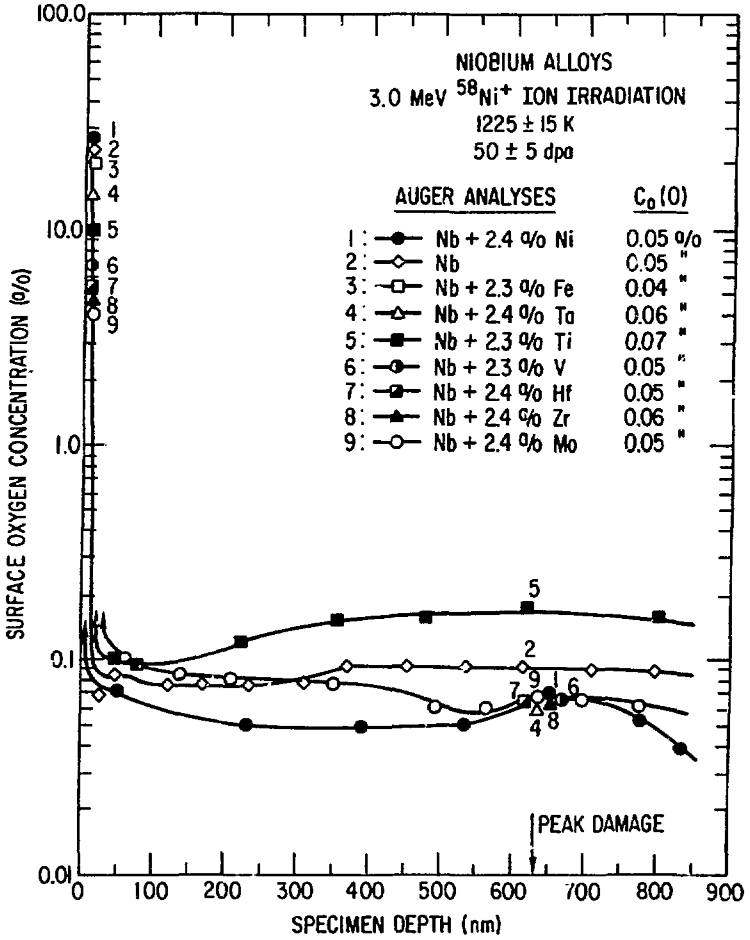

Fig. 5. Dependence of O Concentration in Ion-Irradiated Nb on Depth in the Irradiation-Damaged Layer.

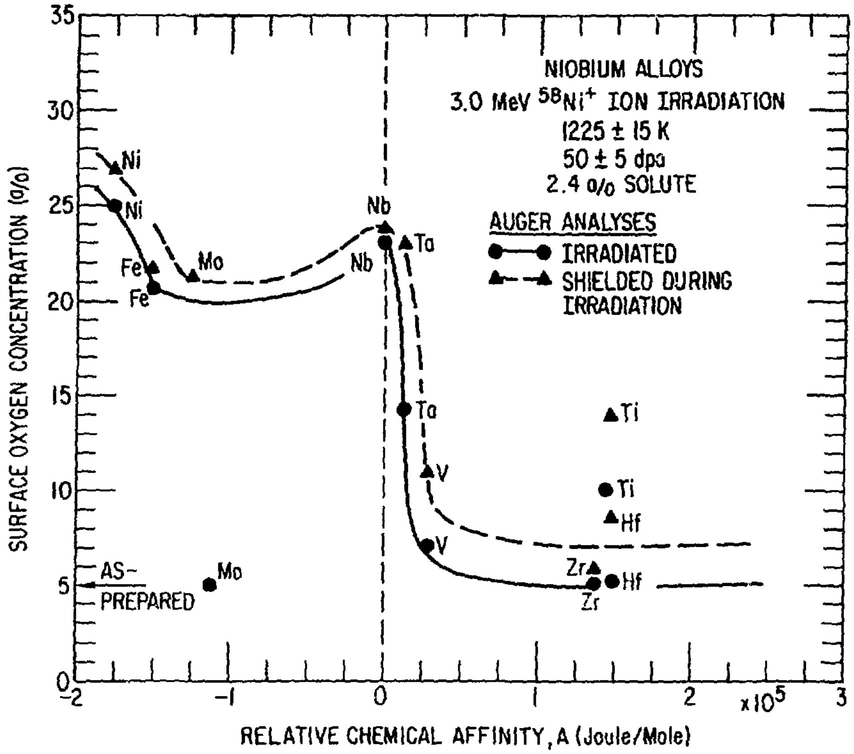

Fig. 6. Relationship Between the Surface O Concentration and Solute Affinity for O.

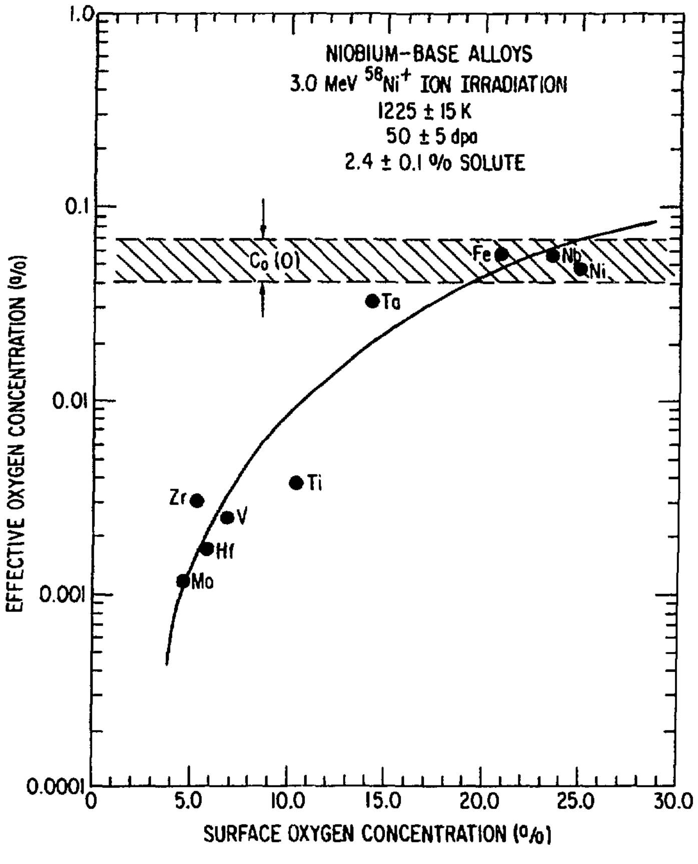

Fig. 7. Effective O Concentration in the Nb Alloys.