The Effect of Oxygen on Void Stability in Nickel and Austenitic Steel

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April 1986

UWFDM-681

, Presented at the 2nd International Conference on Fusion Reactor Materials, 14-17 April 1986, Chicago, IL.

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Abstract

Surface energy values lower than those determined experimentally are often utilized in theories of void nucleation and growth in metals. Utilization of established surface energy values generally predicts no swelling in the absence of helium. However, swelling occurs in many metals even in the absence of helium. Surface active impurities, such as oxygen, can readily account for this discrepancy by reducing the surface energy of metals. This investigation shows that very low concentrations of oxygen in nickel and austenitic stainless steel can achieve the necessary decrease in surface energy.

A model has been developed to calculate the requisite quantity of oxygen in solution to stabilize voids. The criterion for void stability is that the void be the most energetically stable vacancy cluster in the metal. Knowing the fraction of oxygen which chemisorbs and the surface coverage required permits the determination of initial oxygen concentration needed to promote void stability. Calculations have been performed for austenitic stainless steel and nickel.

The model has been tested by irradiating nickel with 14-MeV Ni ions at 500°C. Oxygen was preinjected into one sample to a concentration of 75 appm. The irradiation reached a fluence of 3×10^{20} Ni-ion/m^2 (28 dpa at the damage peak). The irradiated foils were examined in cross section in the electron microscope.

1. Introduction

Void nucleation and growth have been extensively studied for the last two decades. Several authors have attempted to model the physics of void formation in metals. Unfortunately, most of these theories assume a metal surface energy of 1.0 J/m^2, which is lower than the experimental values for most metals. Two notable exceptions to this are Mayer and co-workers [1] and Wehner and Wolfer [2]. Using the appropriate surface energy, Mayer concludes that gas is required for void formation. Wehner and Wolfer predict that small void embryos will nucleate at very low doses without gas assistance; however, they suggest that gas may be necessary to prevent the collapse of these unstable embryos to dislocation loops. Si-Ahmed and Wolfer [3] point out that in the absence of gas, exceedingly low concentrations of stable voids result from utilizing established surface energies.

Some experimental evidence also lends support to the notion that gas is necessary for void stability in some metals [4-8]. For neutron irradiated materials, the (n,α) nuclear reaction produces helium to aid void formation. However, in electron- and ion-irradiated metals, helium is absent unless introduced by implantation; yet voids exist in helium-free metals bombarded by charged particles [5,9-11]. Therefore, the possibility of void stability promoted by residual gas atoms must be considered. Oxygen, a common impurity in metals, is a likely candidate because of its reactive nature.

This paper focuses on the role of oxygen in void stabilization in nickel and austenitic steel. A model introduced to calculate the required levels of oxygen needed for void formation in copper [12] after ion irradiation is extended to these two metals. This model is then tested experimentally for nickel.

2. Theory

Elastic continuum theory applied to vacancy clusters in metals allows the determination of the most stable vacancy cluster type. In nickel and austenitic steel, four defect clusters are found: the stacking fault tetrahedron (SFT), the faulted dislocation loop, the perfect dislocation loop, and the void. Recent calculations, using the best known values of the relevant materials parameters, indicate that the void is thermodynamically unstable at all sizes in both metals [13]. However, the void can be stabilized by surface energy reductions. The effect of a reduction in the surface energy of nickel from 2.1 to 1.5 J/m^2 on void stability is depicted in Fig. 1. The void becomes the energetically favorable vacancy cluster type. The situation is similar for steel when the surface energy is lowered from 2.2 to 1.0 J/m^2. These reductions can be achieved by chemisorption of oxygen onto the metal surface.

Bernard and Lupis [14] discussed the reduction in metal surface energy by surface reactive species. The Bernard-Lupis isotherm can be expressed as:

$$\Gamma(\theta) = \Gamma - \frac{RT}{mA} \ln \left(\frac{1}{1 - m\theta}\right) + mg\theta^2, \tag{1}$$

where $\Gamma(\theta)$ is the surface energy at a coverage of θ, Γ is the clean surface energy, θ is the fractional degree of surface covered by the impurity, m is an integer that depends on the stoichiometry of the impurity surface lattice, A is the metal molar surface area, and g is the magnitude of the interaction between impurity atoms.

For oxygen, metal surface contamination is a complex process. At relevant temperatures, free matrix oxygen is in atomic form on surfaces and in the bulk. Oxygen is distributed on the surfaces in a lattice configuration such as MO or M_3O. A comprehensive review of oxygen-metal interactions can be found in the literature [15]. The value of m in Eq. (1) is determined by the oxygen-saturated lattice type, $M_{m-1}O$. Once this lattice is fully formed, the lattice is saturated in oxygen. The introduction of additional oxygen results in the penetration of oxygen into the bulk and, ultimately, the formation of an oxide. This oxide can lead to an increase in the surface energy [16,17].

A disagreement exists in the literature regarding the saturation coverage, θ_{sat}, of nickel by oxygen. Some researchers believe $\theta_{sat} = 0.25$ [18,19] and others support $\theta_{sat} = 0.5$ [20,21]. This paper uses a value of $\theta_{sat} = 0.5$ ($m = 2$) for nickel. No information exists on the saturation coverage of austenitic steel. Some evidence exists that $\theta_{sat} = 0.25$ for iron [22,23] but increases as chromium is added [23,24]. A value of $m = 2$ is assumed for steel in this paper.

In view of the uncertainty in m and because the interaction energy between oxygen atoms is unknown, but often small [25], the last term in Eq. (1) is assumed to be zero. The resultant equation for nickel and steel is

$$\Gamma(\theta) = \Gamma - \frac{RT}{2A} \ln \left(\frac{1}{1 - 2\theta}\right) . \qquad (2)$$

Knowledge of the surface energy needed for void stabilization permits the calculation of the corresponding surface coverage by Eq. (2). To relate this coverage to the mole fraction, X, of oxygen in solution, the Langmuir-McLean isotherm [26] may be used:

$$\frac{\theta}{1-\theta} = X \exp \left[\frac{G_B - G_S(\theta)}{RT}\right], \qquad (3)$$

where G_B is the Gibbs free energy of atomic oxygen in the bulk and $G_S(\theta)$ is the Gibbs free energy of atomic oxygen on the covered surface. Assuming no change in G_S as a function of coverage up to $\theta = 0.5$, $G_S(\theta)$ is $G_S(0)$, the initial free energy of chemisorption. Brennan and Graham [27] find that the heat of adsorption of oxygen on nickel remains unchanged up to a coverage of one monolayer at 273°K.

Finally, to determine the fraction of oxygen in solution and on surfaces, a simple gas atom balance is employed. Before irradiation, some concentration of free oxygen exists in solution in the metal. When the irradiation commences, a terminal void density is rapidly reached [2]. The existing oxygen may now remain in solution, partition to the newly formed void surfaces, or re-associate in the interior of the embryos. The sum of the gas atoms at these three locations must balance with the number of gas atoms originally in solution. Thus,

$$nX\Omega + N_0\left(\frac{4\pi R_v^2}{A}\right) n_v\theta\Omega + 2\, N_0 n_v X g_2 \Omega = nX_0\Omega, \tag{4}$$

where n is the matrix atom number density, Ω is the atomic volume, N_0 is Avogadro's number, R_v is the average void embryo radius, n_v is the terminal void density, Xg_2 is the molar fraction of diatomic gas molecules inside the void, and X_0 is the initial free oxygen mole fraction. Calculations using Eq. (4) reveal that the last term on the left-hand side of Eq. (4) is negligible compared to the other terms. Thus Eq. (4) can be reduced to

$$X_0 - X = \frac{4\pi R_v^2 N_0 \theta n_v}{A n} . \tag{5}$$

Equation (5) in conjunction with Eqs. (2) and (3) determines the initial free matrix oxygen concentration that will stabilize void formation by sufficient surface energy reduction.

3. Calculations

The Gibbs free energies of oxygen in the bulk, G_B, and on the surface, G_S, are not well known. These terms can be approximated by $G_B = -(H_u + E_D)/2$ and $G_S = -(H_{cs} + E_D)/2$, where H_u and H_{cs} are the heats of solution and adsorption of molecular oxygen and E_D is the dissociation energy of molecular oxygen [26]. This approximation assumes entropy terms cancel. The values used in this calculation are $E_D = 498.4$ kJ/mol [28], $H_u^{Ni} = 195$ kJ/mol [29], and $H_{cs}^{Ni} = 420$ kJ/mol [30].

The void densities and radii used are taken from Wehner and Wolfer's data for a damage rate of 10^{-3} dpa/s [2]. These data are used for both the nickel and steel cases. The molar surface area is calculated according to Tyson [31] using his "average" population density factor. Table 1 lists all the parameters used in the calculations.

The calculated minimum free oxygen concentration needed for void stability is plotted versus temperature in Fig. 2. At low temperatures a greater oxygen concentration is needed due to the higher void density. At 650 to 700°C a minimum of about 1 appm is reached. Calculations, not shown in Fig. 2, reveal that the required oxygen levels increase above 700°C because of increasing oxygen solubility. Calculations for steel reveal similar trends, although a minimum of 3 appm oxygen occurs between 600 and 650°C.

4. Experimental Procedure

A Marz-grade nickel (99.995% pure) was used in this experiment. The initial oxygen concentration, determined by inert-gas fusion analysis, was 180 appm. Samples were cut into 1 cm x 0.5 cm foils and mechanically polished to a thickness of approximately 0.25 mm. The foils were then treated in flowing dry hydrogen at 1000°C for 4.3×10^4 s hours to reduce the oxygen levels from 180 to 75 appm. The deoxidation step was followed by a 1.8×10^3 s anneal at 150°C in a vacuum of 6.6×10^{-7} Pa to remove any hydrogen that may have diffused into the metal.

The degassed foils were mechanically polished with 0.3 μm alumina abrasive in order to clean the surfaces. Electrochemical polishing was avoided because this procedure can introduce gas [9]. One degassed nickel sample was pre-injected with 75 appm of 5-MeV O^{2+} ions at room temperature to give a total of 150 appm oxygen at the peak depth of 2 μm using the University of Wisconsin Heavy-Ion Irradiation facility. The first micrometer of the surface of this specimen was removed by sputtering with 3.5-kV Ar^+ ions. Profilometer measurements indicate a surface removal of 0.8 to 1.0 μm. This procedure resulted in a specimen with 150 appm oxygen at the 1 μm depth and 75 appm oxygen at the peak nickel-ion damage depth (2 μm).

A total of three foils were irradiated with 14 MeV Ni^{3+} ions: the oxygen preinjected foil, a degassed foil, and an as-received foil. The specimens were irradiated at 500°C with 14-MeV Ni^{3+} ions at a flux of 3×10^{16} ions/m^2/s to a fluence of 3×10^{20} ions/m^2. These values correspond to a peak dose rate and dose of 3×10^{-3} dpa/s and 28 dpa, respectively. The damage at 1 μm is approximately one-fourth that of the peak damage. The oxygen-implanted foil received half this dose. After irradiation, the foils were prepared for analysis using a cross-section technique described elsewhere [32]. The microscopy was performed on a JEOL TEMSCAN-200CX electron microscope.

5. Results and Discussion

Figure 3 shows the irradiation damage throughout the damage region for the three foils. Each of the foils showed evidence of some void formation. This was expected because all samples contained oxygen concentrations exceeding the minimum for void stability. Table 2 lists the average void densities and diameters at the 1-μm depth and at the damage peak. In all cases the swelling at the damage peak resulted from a relatively low density of voids with diameter of 40-60 nm. The void density at the peak damage depth in the as-received nickel is approximately an order of magnitude greater than in the degassed or oxygen-implanted foils. In the first micrometer of the as-received and degassed nickel, a sparse, heterogeneous population of large voids exists. The void size at the 1-μm depth is smaller and the void density is two orders of magnitude high in the oxygen implanted foil in comparison to the as-received or degassed nickel foils.

This last result is important in the following respect. It should be noted that the oxygen level at the 1-μm depth in the oxygen implanted nickel is twice the oxygen level in the peak damage region, but there is a hundred-fold increase in void density at the 1-μm depth for approximately one-fourth the damage level. The void density at the 1-μm depth in the oxygen implanted nickel was also substantially higher than in the as-received and degassed samples. This difference can be explained by assuming that the implanted oxygen is bound differently from the initial matrix oxygen. At room temperature, the injected oxygen is immobile and probably remains in solution. Once the irradiation starts, this free oxygen is able to partition to embryo surfaces. The heterogeneous nature of the voids in the peak damage zone indicates that most of the oxygen originally in the bulk is tied up at grain boundaries, dislocations, internal oxides, or other binding sites. Bombarding or knock-on atoms may free some of these bound oxygen atoms but it is not expected that the density of these liberated oxygen atoms will be high enough to stabilize many embryos. The chance of such an event is greater near large oxide particles or other oxygen-rich areas [33]. Thus, it seems likely that the injection of oxygen increases the free oxygen levels from a very low value to 75 appm.

It should also be noted that the void density of 2×10^{21} m^{-3} does not exceed the theoretical prediction of the terminal void density of 2×10^{22} m^{-3} [2]. A major uncertainty in the model is the heat of chemisorption of oxygen, H_{cs}, on nickel [30]. A 25% change in H_{cs} can alter X_o by two orders of magnitude. This carries an uncertainty in the calculation of the oxygen level for void stabilization. The model also assumes that all embryos obtain at least a minimum coverage. A free oxygen concentration below the calculated minimum can still stabilize some fraction of the void embryos. In fact nine oxygen atoms can stabilize a 1.3 nm diameter embryo.

The maximum void density also may not be reached due to the kinetics of the process. This model examines only thermodynamic potential. The physics of oxygen partitioning to sinks may prevent the stabilization of all void embryos. Finally, the model presented here considers void stabilization and not growth. Stabilized void embryos may grow and coalesce according to classical growth mechanisms. The difficulties mentioned above preclude unequivocable proof that gas is needed to stabilize voids in many metals. The trends, however, support this conclusion for nickel. Reduction of the starting oxygen levels and the re-injection of oxygen atoms should be a valuable technique in testing the limits of this model. Also, experiments are being conducted to test the conclusions regarding oxygen stabilization of void embryos in austenitic steel.

6. Conclusions

1. Voids are calculated to be thermodynamically unstable in extremely pure Ni.
2. In ion-irradiated nickel and austenitic steel, unbound residual oxygen can stabilize voids by reducing the metal surface energy.
3. Pre-injection of Ni with 75 appm oxygen dramatically increases the void nucleation rate at 500°C.
4. Oxygen implanted in the nickel prior to ion irradiation is mostly unbound and able to partition readily to void embryos.

Acknowledgments

The authors wish to thank Dr. P.T. Cunningham and Mr. D.E. Vance of Los Alamos National Laboratory for performing the gas analysis, Dr. W.G. Wolfer and Dr. S.J. Zinkle for their invaluable advice, and Pat Caliva for preparing the manuscript. This work was supported by the U.S. Department of Energy, Office of Fusion Energy.

References

[1] R.M. Mayer, L.M. Brown and U. Gösele, J. Nucl. Mat. 95 (1980) 44 (8 parts).

[2] M.F. Wehner and W.G. Wolfer, Phil. Mag. A. 52(2) (1985) 189.

[3] A. Si-Ahmed and W.G. Wolfer, in: Effects of Radiation on Materials: Eleventh Conference, ASTM STP 782, Scottsdale, Arizona, 1982, Eds. H.R. Brager and J.S. Perrin (ASTM, 1982) p. 1008.

[4] D.I.R. Norris, Rad. Eff. 14 (1972) 1.

[5] B.L. Eyre, J. Phys. F. 3 (1973) 422.

[6] J.M. Lanore, in: Fundamental Aspects of Radiation Damage in Metals, Vol. II, Gatlinburg, Tenn., 1975 (Conf. 75, 1006-P2, 1976) p. 1169.

[7] S.K. McLaurin, Ph.D. Thesis, University of Wisconsin (1984).

[8] S.J. Zinkle, Ph.D. Thesis, University of Wisconsin (1985).

[9] J.B. Whitley, Ph.D. Thesis, University of Wisconsin (1978).

[10] R.W. Knoll, Ph.D. Thesis, University of Wisconsin (1981).

[11] R.L. Sindelar, G.L. Kulcinski and R.A. Dodd, J. Nucl. Mat. 122 & 123 (1984) 246.

[12] S.J. Zinkle, W.G. Wolfer, G.L. Kulcinski and L.E. Seitzman, submitted to Phil. Mag.

[13] S.J. Zinkle, L.E. Seitzman and W.G. Wolfer, submitted to Phil. Mag.

[14] G. Bernard and C.H.P. Lupis, Surf. Sci. 42 (1974) 61.

[15] K. Wandelt, Surf. Sci. Repts. 2 (1982) 1.

[16] M. McLean and E.D. Hondros, J. Mat. Sci. 8 (1973) 349.

[17] E.D. Hondros, Pure & Appl. Chem. 56 (12) (1984) 1677.

[18] D.E. Taylor and R.L. Park, Surf. Sci. 125 (1983) L73.

[19] J.B. Benziger and R.E. Preston, Surf. Sci. 141 (1984) 567.

[20] C. Benndorf et al., Surf. Sci. 92 (1980) 636.

[21] H.J. Grable and H. Viefhaus, Surf. Sci. 112 (1981) L779.

[22] K. Molière and F. Portele, in: The Structure and Chemistry of Solid Surfaces, Ed. G.A. Somorjai (John Wiley and Sons, Inc., 1968) p. 69-1.

[23] B. Ozturk, Ph.D. Thesis, Pennsylvania State University (1981).

[24] T. Smith and L.W. Crane, Oxid. Met. 10(2) (1976) 135.

[25] G.A. Somorjai, in: Chemistry in Two Dimensions: Surfaces (Cornell Univ. Press, 1981) Chpts. 3, 6.

[26] R.H. Jones and W.G. Wolfer, J. Nucl. Mat. 122 & 123 (1984) 379.

[27] D. Brennan and M.J. Graham, Discuss. Faraday Soc. 41 (1966) 95.

[28] R.C. Weast, in: CRC Handbook of Chemistry and Physics, 59th Ed., (CRC Press, 1979) p. F-236.

[29] W.A. Fischer and W. Ackermann, Arch. Eisenhutt. 37 (1966) 43.

[30] I. Toyoshima and G.A. Somorjai, Catal. Rev. - Sci. Eng. 19 (1) (1979) 105.

[31] W.R. Tyson, Can. Met. Quart. 14(4) (1975) 307.

[32] S.J. Zinkle and R.L. Sindelar, Nucl. Instr. & Meth. in Phys. Res. B, in press.

[33] L. Wang, R.A. Dodd and G.L. Kulcinski, "Gas Effects on Void Formation in 14 MeV Nickel Ion Irradiated Pure Nickel", Proc. of 2nd Intl. Conf. on Fusion Reactor Materials, 14-17 April 1986, Chicago, IL.

Table 1.

Materials Parameters

Parameter	METAL	
	Nickel	Stainless Steel
Γ (J/m^2)	2.1	2.2
$\Gamma(\theta)$ (J/m^2)	1.5	1.0
A (m^2/mol)	4.84×10^4	5.18×10^4
G_B (kJ/mol O)	- 347	- 417
G_S (kJ/mol O)	- 459	- 519
n (m^{-3})	9.1×10^{28}	8.6×10^{28}

Table 2.

Void Parameters

Sample	Irradiation Temperature	Location	Oxygen Level	Peak Dose (dpa)	Average Void Density ($10^{20}/m^3$)	Average Void Diameter (nm)
As-Received Nickel	500°C	1 µm	180 appm	7	0.3	50
		Peak	180 appm	28	1.0	50
Degassed Nickel	500°C	1 µm	75 appm	7	0.1	50
		Peak	75 appm	28	0.07	60
Oxygen Implanted Nickel	500°C	1 µm	150 appm	3.5	20.0	14
		Peak	75 appm	14	0.2	40

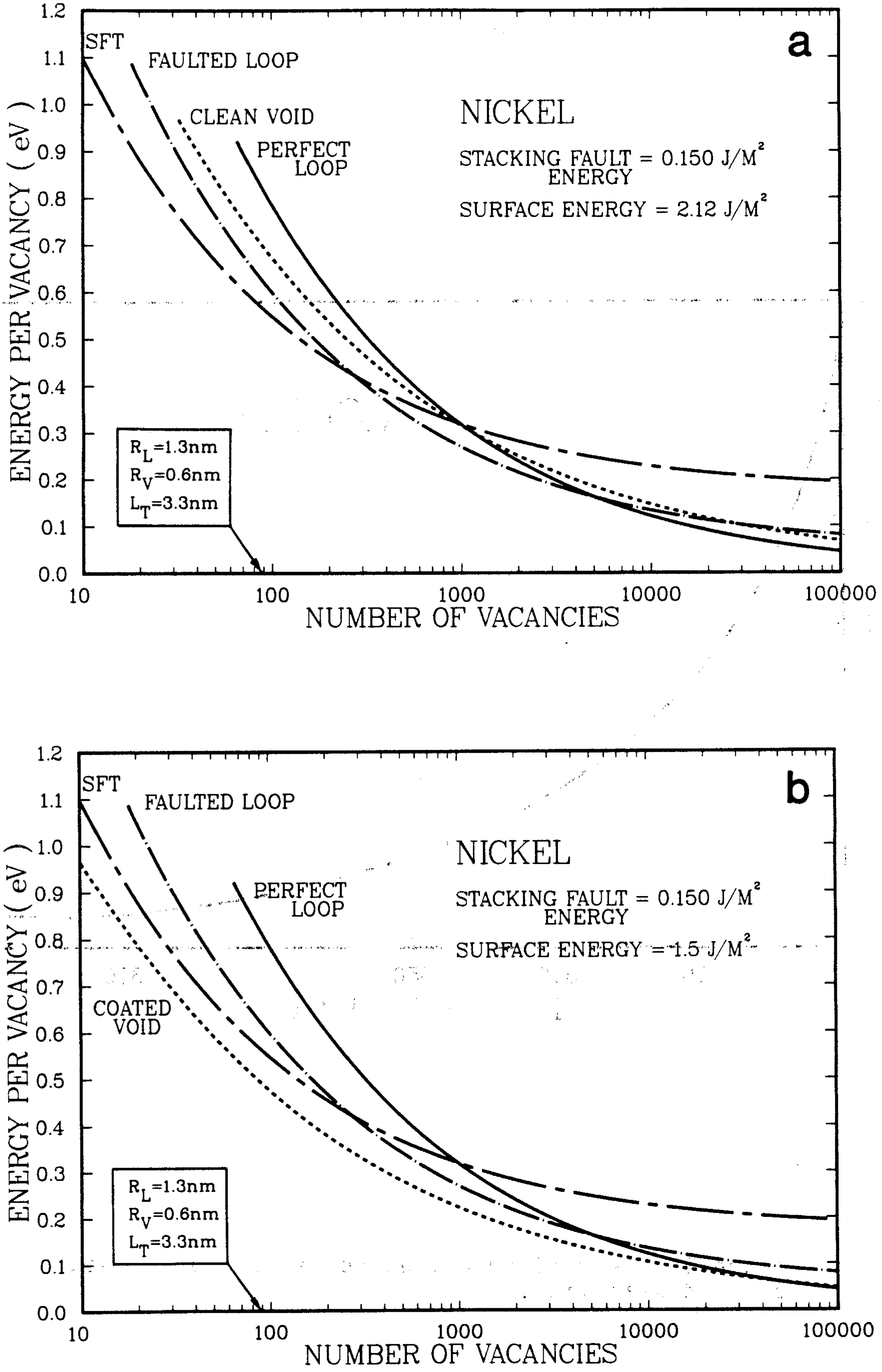

Figure 1. The effect of surface energy on void stability: (a) $\Gamma=2.1$ J/m^2 (b) $\Gamma=1.5$ J/m^2

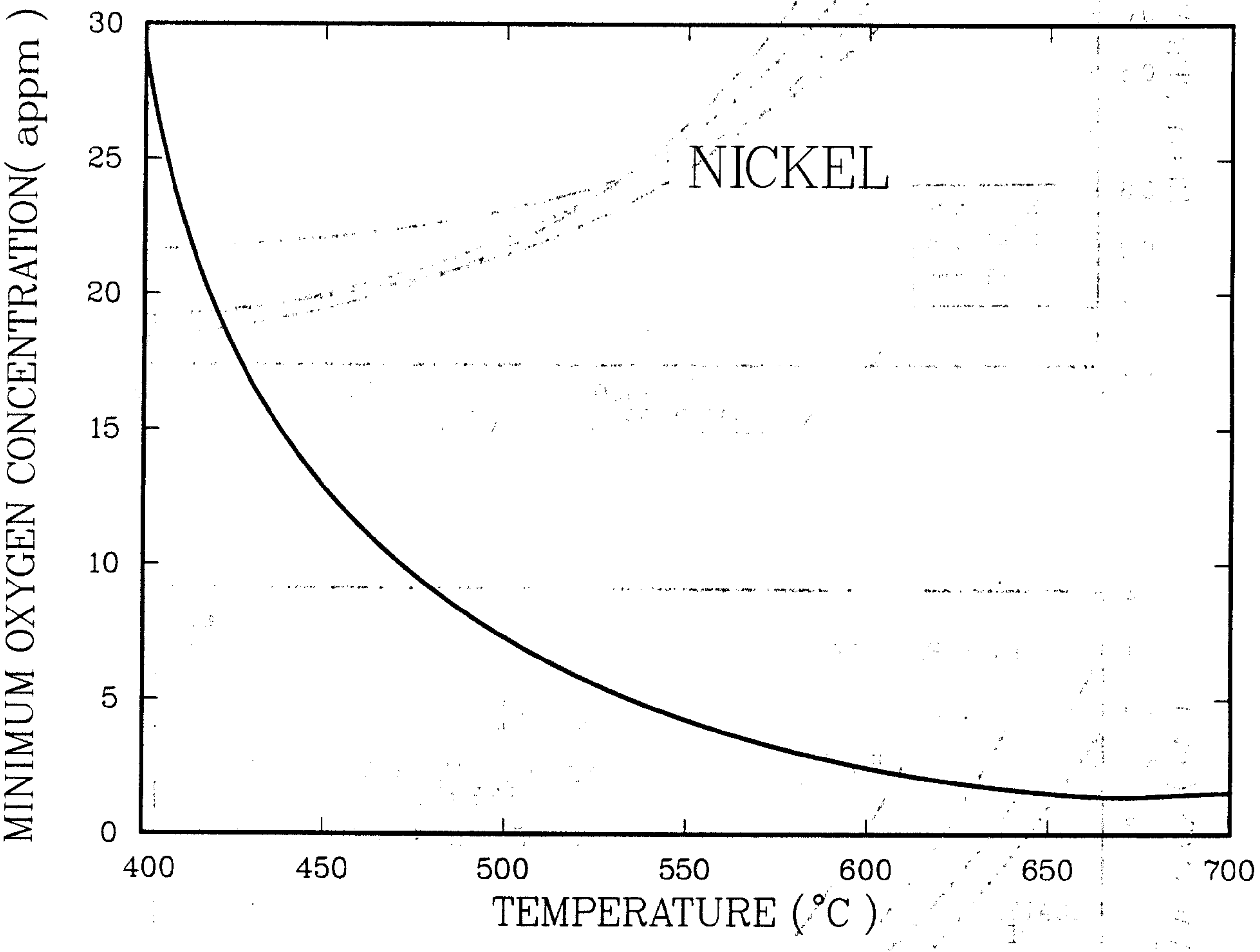

Figure 2. The minimum oxygen concentration needed for void stability.

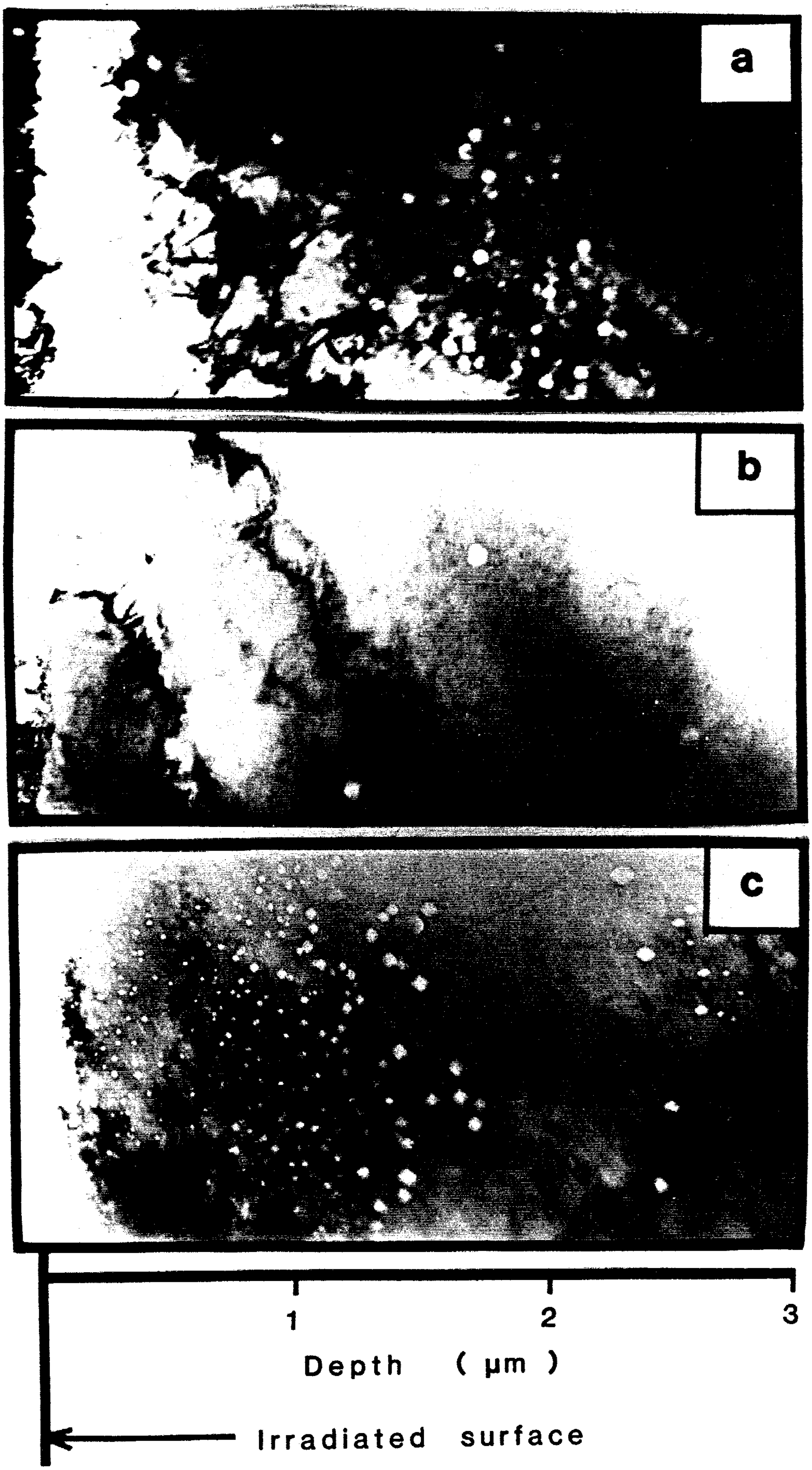

Figure 3. Void structure in nickel after 14 MeV Ni irradiation at 500°C. (a) as-received nickel, 180appm O (b) degassed nickel, 75 appm O (c) as (b) injected with additional 75 appm O to approximately 1-1.2 µm