Stability of Vacancy Clusters in Metals II: Effect of Oxygen and Helium on Void Formation in Metals

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EFFECT OF OXYGEN AND HELIUM ON VOID FORMATION IN METALS

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Abstract

A model is presented that determines the effect of oxygen and helium on the energies of the common vacancy cluster configurations, namely the void, dislocation loop and stacking fault tetrahedron. Representative calculations are given for the case of irradiated copper. The presence of oxygen tends to enhance the stability of the void during nucleation compared to the other vacancy cluster morphologies by decreasing the void surface energy through a chemisorption process. Helium also tends to stabilize void formation, because of the high binding energy of helium to a vacancy (or cluster of vacancies) compared to a dislocation. Gas concentrations as low as 0.01 appm He and 5 appm O are predicted to stabilize void formation in copper at certain temperatures. The predictions of the model are in good agreement with the available experimental results.

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1. Introduction

Macroscopic swelling due to void formation is a major issue in radiation damage studies. However, the physical mechanisms that comprise the void nucleation process are still not completely understood. In particular, the role of small amounts of gas in promoting void nucleation has not been quantitatively modeled. It has been recognized for some time that helium can have a strong effect on the void microstructure (Farrell 1980). Oxygen (Farrell 1980, Wolfer 1984) and hydrogen (Farrell 1980, Bullen et al. 1985) are also known to promote void swelling. Experimental studies (Shimomura and Yoshida 1967, Clarebrough et al. 1967, Norris 1972, Lanore et al. 1975, Knoll 1981, McLaurin 1984, Zinkle 1985) have indicated that gas may be required for void formation. In a preceding paper (Zinkle, Seitzman and Wolfer 1986; to be referred to as Part I) it was shown that void formation is not expected to occur in many metals in the absence of impurities on the basis of energy considerations.

It is well established that low levels of gaseous impurities can have a strong effect on the void microstructure (Farrell 1980). However, there has not been a satisfactory theoretical explanation for these observations to date. Russell (1978) presented a generalized void nucleation model which addressed the issue of gas-aided nucleation with modest success. Wehner and Wolfer (1985) have concluded that gaseous impurities do not affect the vacancy cluster nucleation process. Instead, they suggested that gases enhance observable void formation by simply preventing the collapse of these vacancy clusters into dislocation loops.

The present paper examines the effect of oxygen and helium on the relative stability of the various vacancy cluster morphologies. Oxygen is a common impurity in metals that occurs naturally or is introduced during industrial fabrication. Helium is introduced into metals during neutron irradiation as a result of (n,α) reactions. A new model is proposed which suggests that void formation may be stabilized by the process of oxygen chemisorption onto void embryo surfaces. A model is also presented for inert gases such as helium whereby void stability is enhanced due to helium-vacancy binding energy effects. These vacancy cluster stability models are complementary to void nucleation and growth models. Calculations are performed for the case of irradiated copper.

2. Role of Oxygen on Void Formation in Copper

It is well known that surface-active species such as oxygen or sulfur may chemisorb onto clean surfaces of metals and cause a reduction in the surface energy (Kozakevitch 1965, Hondros 1968, Bauer, Speiser and Hirth 1976, Eustathopoulos and Joud 1980, Somorjai 1981, Gallois and Lupis 1981). Chemisorption onto internal free surfaces, such as void embryos, may also cause similar effects (Felsen and Regnier 1977, Wolfer 1984). If the reduction in surface energy (Γ) is sufficiently large, then void formation may become energetically favorable. (Note: Experimental measurements of Γ in high-purity metals are generally not affected by the matrix oxygen impurities since the measurements are performed at elevated temperatures ($> 0.8\ T_M$) where the oxygen solubility is sufficient to prevent chemisorption on external free surfaces. However, at lower temperatures an oxygen supersaturation exists which can lead to chemisorption of the oxygen on internal free surfaces. The solubility limits of oxygen in copper are 60 appm and < 0.1 appm at 900 and 500°C, respectively.)

The change in surface energy due to the chemisorption of oxygen at a constant temperature is given by the Gibbs adsorption isotherm (Bauer et al. 1976, Gallois and Lupis 1981):

$$\frac{d\Gamma}{d \ln X} = - \frac{RT\ \theta_{sat}}{A_{Cu}} \tag{1}$$

where θ_{sat} is the saturated fractional surface coverage, X is the mole fraction of oxygen in solution and A_{Cu} is the molar surface area of copper. The value of A_{Cu} depends upon crystallographic orientation and is 3.41 x 10^4 m^2/g-mol for the (111) close packed plane. Experimental measurements of the surface energy have found that the surface of copper becomes saturated with oxygen at a coverage level of $\theta_{sat} \simeq 0.25$ (McLean and Hondros 1973, Bauer et al. 1976, Gallois and Lupis 1981). In the presence of higher oxygen partial pressures, oxygen is incorporated into the subsurface monolayers and an oxide layer forms (McLean and Hondros 1973, Bauer et al. 1976). These findings on the oxidation sequence are in good agreement with surface studies of chemisorption and oxidation in copper (Habraken, Mesters and Bootsma 1980). However, Habraken reported that $\theta_{sat} \simeq 0.5$ for oxygen chemisorption on copper.

The Langmuir-McLean isotherm may be used to determine the temperature-dependent relationship between oxygen in solution in the matrix and the degree of surface coverage (θ) on a void (Somorjai 1981, Jones and Wolfer 1984):

$$\frac{\theta}{1-\theta} = X \exp\left(\frac{G_B - G_S}{RT}\right) = (X_o - X_{cs}) \exp \frac{G_B - G_S}{RT} \tag{2}$$

where X_o is the mole fraction of oxygen initially present in the matrix, X_{cs} is the mole fraction of oxygen chemisorbed onto void surfaces, and G_B and G_S

are the Gibbs free energies for oxygen in the bulk and on the surface, respectively, relative to a single oxygen atom in vacuum. It is known that oxygen exhibits dissociative chemisorption on copper (Habraken and Bootsma 1979). If entropy terms are neglected, then $G_B \simeq -(H_u + E_D)/2$ and $G_s \simeq -(H_{cs} + E_D)/2$ where E_D is the dissociation energy of molecular oxygen and H_u and H_{cs} are the heat of solution and chemisorption for molecular oxygen (Somorjai 1981). Using E_D = 498.4 kJ/mol (Weast 1979), H_u = 84 kJ/mol (Pastorek and Rapp 1969) and H_{cs} = 209 kJ/mol (Somorjai 1981) yields the result for copper that $G_B \simeq$ -291 kJ/mol and $G_s \simeq$ -354 kJ/mol. The preceding approach implies that there is no effect of oxygen coverage on the heat of chemisorption. It is known that the magnitude of H_{cs} becomes appreciably smaller at high coverage levels (Tanaka and Tamaru 1963, Hayward 1971, Somorjai 1981). However, it appears that there is little change in H_{cs} for coverage levels up to $\theta = 0.25$, which corresponds to the range of interest in the present case.

The change in surface energy of copper due to oxygen chemisorption may be calculated using the method of Gallois and Lupis (1981)

$$\Gamma - \Gamma(\theta) = \frac{RT}{A_{Cu}} \left[\frac{\theta}{1-4\theta} + \frac{g\,\theta^2}{RT}\right] \tag{3}$$

where g corresponds to an interaction energy between neighboring adsorbed oxygen atoms. It has been empirically observed by Gallois and Lupis (1981) that g is negative and small, but its exact value is uncertain. Habraken and Bootsma (1979) have determined this interaction energy in copper to be $|g| \lesssim 17$ kJ/mol.

As shown in Figure 1, an evaluation of the energetics of vacancy cluster formation using the equations given in the accompanying paper (Part I) indicates that a surface energy of $\Gamma \lesssim 0.9$ J/m^2 is required in order for void formation to be stable in copper. Using Eq. (3), this corresponds to a surface coverage of $\theta \simeq 0.24$ for both $g = 0$ and $g = -17$ kJ/mol. This value may then be inserted into Eq. (2) in order to compute the requisite matrix oxygen concentration. The amount of oxygen that is chemisorbed onto void surfaces, X_{cs}, depends on the average void radius (R_v) and density (n_v):

$$X_{cs} = \frac{4\pi \, R_v^2 N_A \theta \, n_v}{A_{Cu} \quad n_{Cu}} \tag{4}$$

where N_A is Avogadro's number and n_{Cu} is the atom density of copper. Since we are interested in the stability of clusters at sizes where void nucleation occurs, it is appropriate to use values of n_v and R_v obtained from nucleation theory. Wehner and Wolfer (1985) have recently developed a dynamic void nucleation theory based on a Fokker-Planck description which enables the evaluation of the terminal void number density and which is in good agreement with experimental results. Table 1 lists the calculated temperature-dependent values of n_v and R_v obtained from their analysis of copper.

The calculated initial matrix oxygen content required to reduce the surface energy of voids in copper to 0.9 J/m^2 is plotted in Fig. 2. This oxygen concentration corresponds to the minimum amount of oxygen that is required to stabilize as voids all of the vacancy clusters that are nucleated during irradiation (Table 1). A lower oxygen concentration could result in partial stabilization of the void nuclei population. The critical oxygen concentration depends strongly on temperature, and exhibits a minimum value for intermediate temperatures. Relatively large amounts of oxygen are needed in order to stabilize void formation at low temperatures because of the high vacancy cluster density that is nucleated (Table 1). Large oxygen concentrations are also necessary at high temperatures because there is a lowered driving force for oxygen to come out of solution and chemisorb onto void embryo surfaces.

The interpretation of Fig. 2 is as follows: Charged particle irradiation at 1 x 10^{-3} dpa/s of pure copper containing less then 3 appm oxygen should not cause any substantial void formation at any temperature, as the nucleated vacancy clusters will evolve into SFT. On the other hand, irradiation of copper containing greater than 50 appm oxygen (~ 12 wt.ppm) should result in void formation throughout the entire swelling temperature regime (0.3-0.6 T_M). At intermediate oxygen concentrations, void formation should occur over a limited temperature regime centered around 325° (0.45 T_M). In particular, void swelling will not occur at high temperatures and the void swelling regime will be restricted to the lower temperature range for partially outgassed copper. Neutron irradiation of copper (1 x 10^{-6} dpa/s) is more complicated than indicated in Fig. 2 because helium generated during irradiation greatly enhances void stability in addition to the oxygen stability effects (see Section 3). It should be noted that electrolytic grade copper that has not been deoxidized typically contains 200 to 400 wt.ppm oxygen (Metals Handbook 1979). Copper is classified as "oxygen-free" if it contains less than 10 ppm oxygen by weight (~ 40 appm). In addition, electropolishing of metal foils prior to their irradiation may result in the introduction of oxygen into the foil (Sindelar, Dodd and Kulcinski 1985).

The predicted values of oxygen concentration required to stabilize void formation in copper at a given temperature are not expected to be exact due to the various approximations that were used to obtain the final result, such as the neglect of entropy terms and uncertainties in the oxygen heat of chemisorption on copper. Nevertheless, it is pleasing to note that the predictions are in good agreement with the limited amount of irradiation data that is available on copper containing known amounts of oxygen (Zinkle and Knoll 1984). A high dose 14-MeV Cu ion irradiation of high-purity copper containing < 5 ppm oxygen at a damage rate of 2×10^{-3} dpa/s did not result in any significant void formation over the temperature range of 100-500°C (Zinkle, Kulcinski and Knoll 1986). A very limited number of voids ($n_v \simeq 10^{17}/m^3$) were observed at one temperature, 400°C. There was no observable void formation at 300 or 450°C. Glowinski and coworkers found that copper containing 50 ppm oxygen (~ 200 appm O) formed voids easily following electron (Glowinski 1976) and ion (Glowinski et al. 1976, Glowinski and Fiche 1976a, 1976b) irradiation. Partial outgassing of the foils in a high-vacuum furnace prior to irradiation shifted the swelling peak to lower temperatures and completely eliminated high-temperature void swelling. As noted earlier, Fig. 2 predicts that partial deoxidation of copper will preferentially eliminate void formation at the high temperature end of the void swelling regime. Sindelar, Kulcinski and Dodd (1985) have recently observed a similar temperature shift in ion-irradiated stainless steels which they attributed to oxygen effects.

The effect of oxygen gas existing in the void interior was neglected in the preceding analysis of void stability. Application of Sievert's law data (Dürrschnabel and Vosskühler 1976) at 400°C shows that 10 appm oxygen in solution is in equilibrium with a partial pressure of 2.6×10^{-6} atm. The contribution to void stability for these pressures is negligible. We have also neglected to include the oxygen atoms residing in the void interior in the oxygen mass balance. This contribution can also be shown to be insignificant, i.e. $X \simeq X_0 - X_{cs}$. According to the present model, void stabilization in copper in the presence of oxygen is solely due to the chemical surface interaction between oxygen and copper.

3. Role of Helium in Void Formation in Copper

Unlike oxygen, inert gases such as helium have no effect on the macroscopic surface energy of copper (Felsen and Regnier 1977). There have been several investigations of the energetics of cavities in the presence of helium (Finnis et al. 1983, Trinkaus 1983). However, the derived energy equations contain several terms whose values are not well known. A simplistic estimate of the stability of vacancy clusters in the presence of helium may be obtained from the following relationships for the relative energies of a void, E_v, and of a dislocation loop or SFT, E_x, containing trapped helium:

$$E_v \simeq E_v^o - \left[\sum_{i=1}^{m} (E_{He}^B)_i - pV \right] \tag{5}$$

$$E_x \simeq E_x^o - m\, E_{He-D}^B \tag{6}$$

Here, E_v^o is the energy of a void in the absence of helium (Part I), E_x^o is the energy of a vacancy loop or SFT in the absence of helium (Part I), m is the number of helium atoms associated with the vacancy cluster, $(E_{He}^B)_i$ is the binding energy of the ith helium atom to the cavity, and E_{He-D}^B is the binding energy of interstitial helium to a dislocation. In a sufficiently dilute system (helium/vacancy << 1), the binding energies of helium atoms in a helium-vacancy cluster can be approximated by the formation energy of interstitial helium, E_{He}^F:

$$\sum_{i=1}^{m} (E^{B}_{He})_i \lesssim m\, E^{F}_{He}$$

This approximation breaks down for concentrated helium-vacancy clusters (see, e.g., Table 6.53 in Beeler 1983). The value of E^{B}_{He}/E^{F}_{He} decreases to about 0.5 as the helium to vacancy ratio approaches 1. The last term in Eq. (5) can be represented by the helium equation of state, $pV = zmkT$. The compressibility factor, z, is on the order of unity for all cases considered in this paper (Glasgow and Wolfer 1984). Therefore, $zkT \lesssim 0.1$ eV for temperatures in the void swelling regime. This factor is negligible compared to the uncertainties in E^{F}_{He}. From the above considerations, Eq. (5) may be approximated by

$$E_v \gtrsim E^{o}_{v} - m\, E^{F}_{He} \qquad (7)$$

The inequality sign serves as a reminder that the simplifications used to obtain Eq. (7) may result in an underestimation of the actual void energy, especially for high helium per vacancy ratios.

The values of E^{F}_{He} and E^{B}_{He-D} apparently have not yet been accurately determined for copper. Calculations of E^{F}_{He} for copper indicate that it should be ~ 3 to 4 eV (Baskes and Melius 1979). The binding energy of helium to a dislocation is taken to be $E^{B}_{He-D} \simeq 0.3$ eV, which is the calculated value for nickel (Baskes, Melius and Wilson 1980).

Figure 3 shows the calculated energy per vacancy of voids and stacking fault tetrahedra in copper in the presence of 3.5 and 35 He/vacancy cluster. This is equivalent to a helium concentration of 0.1 and 1 appm, respectively, for ion-irradiated copper at 400°C (Table 1) assuming that all of the helium initially present in the matrix is contained in the vacancy clusters. The presence of helium causes the void to be the most stable type of vacancy cluster for small cluster sizes. Previous atomistic calculations by Baskes (1977) led to a similar conclusion -- addition of helium to copper causes the void to be energetically favorable compared to planar defect clusters. Increasing concentrations of helium further enhance the stability of the void relative to the other vacancy cluster morphologies. The critical amount of helium required to make the void energetically stable compared to the stacking fault tetrahedron is given by

$$m_{crit} \simeq \frac{E_V - E_T}{E^F_{He} - E^B_{He-D}} \tag{8}$$

where E_V and E_T are given by Eqs. (3) and (4) in Part I and depend on the cluster size. Table 2 gives the values of m_{crit} for two different void sizes that are appropriate for void nucleation. Values are tabulated for E^F_{He} = 2 eV and 4 eV, which represents the lower and upper estimates for this quantity. The helium per vacancy ratio is << 1 for a critical sized void nucleus, indicating that Eq. (11) may be a reasonable approximation.

Figure 4 shows the minimum helium concentration required for void stability during irradiation as a function of temperature, assuming that all of the helium initially present in the matrix precipitates into the vacancy clusters. Values relevant for neutron (1×10^{-6} dpa/s) and ion or electron irradiation (1×10^{-3} dpa/s) of copper were obtained from the data in Tables 1 and 2. The minimum helium concentration for void stability decreases rapidly with increasing temperature. Figure 4 predicts that 0.1 appm He will cause the void to be the most stable vacancy cluster morphology during neutron irradiation at all void swelling temperatures (0.35 to 0.6 T_M). Irradiation at a higher displacement rate requires a higher helium concentration. Small amounts of helium should greatly enhance the stability of voids at high temperatures, and may "shift" the void swelling temperature regime to higher temperatures. Such a shift has been observed in irradiated copper (Glowinski and Fiche 1976), stainless steel (Farrell and Packan 1979, Packan and Farrell 1983) and nickel (Packan et al. 1978). Helium generation rates for copper in a fusion reactor first wall environment are ~ 10 appm/dpa. Therefore, void nucleation in pure copper would be stabilized after irradiation in a fusion reactor to a damage level of only ~ 10^{-3} dpa according to Fig. 4.

Figure 4 is in good agreement with the limited amount of experimental data on helium effects in copper. No voids were observed by Glowinski and Fishe (1976b) in degassed copper following ion irradiation at 450°C, whereas implantation of 1 to 100 appm He prior to irradiation resulted in void formation at 450 to 500°C. A recent 14-MeV neutron irradiation study of copper to a fluence of 10^{22} n/m^2 at a damage rate $\lesssim 10^{-7}$ dpa/s has been reported by Yoshida and co-workers (1985). The irradiation, which produced about 0.04 appm He as a result of transmutation reactions, resulted in void formation at 400°C and SFT formation at 25 and 200°C. These observations are in agreement with the void/SFT stability predictions given in Fig. 4. McLaurin (1983, 1984) observed that high-purity aluminum irradiated with 9-MeV Al ions at 50°C (0.35 T_M) did not form voids, whereas preimplantation of as little as 0.1 appm He resulted in significant void swelling with a void concentration of 1 x $10^{21}/m^3$. The corresponding He concentration per void in this case is $m_{He} \simeq 6$, assuming that all of the implanted helium is contained in the voids. Application of Eq. (8) to the vacancy cluster energetics data for aluminum (Fig. 1 in Part I) results in a calculated void stability criterion of

$m_{crit} \lesssim 5$ He atoms per void. For this calculation it was assumed that $E_{He}^{F} - E_{He-D}^{B} = 3.7$ eV and that the average void nucleus size was 200 vacancies ($R_V = 0.7$ nm). Therefore, void formation is predicted to be stable in aluminum for implanted helium concentrations $\lesssim 0.1$ appm He, in agreement with the observations of McLaurin (1983, 1984).

The model developed to describe helium effects in metals contains several assumptions that may limit its applicability. First, it is assumed that all of the helium that was initially in the matrix migrates to the void embryos where it is equally partitioned. Helium has a relatively high mobility in most metals and tends to cluster at vacancies or other high-order vacancy clusters (Baskes and Wilson 1976, Wilson, Bisson and Baskes 1981). Therefore, the above assumption should be valid in the experimental cases where helium initially exists as isolated atoms in a metal containing vacancy clusters (neutron irradiation or subthreshold coimplantation studies). The case of helium preimplantation by ion bombardment prior to irradiation is not accurately modeled here -- the implanted helium tends to spontaneously cluster at the implantation-produced vacancies, forming He_6V clusters in copper (Baskes and Wilson 1976), and becomes relatively immobile. Also, the nucleation code used in the present treatment does not account for heterogeneous nucleation at helium clusters. The results, therefore, may be inappropriate for most preimplantation studies. However, Makin (1982) found that the observed void density in irradiated stainless steel was not strongly affected by a 10 ppm He preinjection at room temperature. It is possible that the results obtained in this paper concerning helium effects may be valid for preinjection studies if low helium concentrations are involved (< 10 appm He).

4. Discussion

It was shown in the preceding paper (Part I) that continuum calculations predict void formation to be energetically unstable in many pure metals. The models introduced in the present paper show that both oxygen and helium may promote the stability of void formation in metals, although by different mechanisms. The surface energy of vacancy clusters in metals may be lowered by a factor of two or more in the presence of small oxygen concentrations if internal free surfaces behave similarly to external free surfaces (Hondros 1968, Bauer et al. 1976, Felsen and Regnier 1977). This process lowers the void energy but does not affect the loop or SFT energies, and thereby stabilizes void formation. The concept that adsorbed impurities may lower the void formation energy has also been noted by Russell (1973, 1978). The enhancement of void stability in the presence of helium is due to the very low solubility of this gas in metals. Helium is bound much more strongly to a vacancy or a cluster of vacancies than it is to a dislocation line. The lattice free energy can therefore be minimized if He is contained in voids as opposed to being bound to the dislocations associated with SFT or loops.

Gas pressure arguments, along with postulated surface energy reductions, have commonly been invoked in the past to explain the observed enhancement of void swelling in the presence of gas (Bullough and Perrin 1969, Russell 1978, Farrell 1980). The present results show that the oxygen or helium gas pressure that is needed to stabilize a void embryo is very small in magnitude (i.e. p is insignificant compared to $\frac{2\gamma}{R_v}$). Of course gas pressure can be an important factor in subsequent cavity growth. The models introduced in this paper determine the minimum amount of oxygen or helium that is necessary to cause the void to be stable compared to the alternative vacancy cluster morphologies and they are, therefore, appropriate for cavity *nucleation* studies such as Wehner and Wolfer (1985). The model does not address the subsequent issue of dynamic cavity *growth* (or shrinkage) in the presence of helium. This latter effect is already well described by gas-aided cavity growth models (Mansur and Coghlan 1983).

The gas effects models presented in this paper appear to be in good agreement with the limited experimental data that is available on oxygen and helium. Small amounts of oxygen in copper tend to stabilize voids at low irradiation temperatures; whereas, small helium concentrations preferentially stabilize voids at high temperatures. The combination of small quantities of oxygen and helium can stabilize void formation in copper at all temperatures relevant to void swelling. Figure 5 shows the minimum combined gas content that is needed to stabilize void formation in copper irradiated at a damage rate of 10^{-3} dpa/s. The combination of 10 appm oxygen and 0.01 appm helium in the matrix is predicted to result in void stabilization at all temperatures in the void swelling regime. Even lower gas levels are sufficient for void stability in copper during neutron irradiation (1×10^{-6} dpa/s). These gas concentrations are commonly found even in "high-purity" metals as a result of natural occurrence and fabrication procedures (oxygen) or are generated during a low-dose neutron irradiation (helium).

Kinetic effects (Brimhall 1974) have not been included in the present model, but simple diffusion calculations indicate that there is sufficient mobility of the gas atoms at all temperatures to supply the gas amounts needed to stabilize the void during vacancy cluster nucleation. The dose required to reach the terminal void density in copper during irradiation at 100°C is calculated to vary from 5 dpa at 1×10^{-3} dpa/s to 0.2 dpa at 1×10^{-6} dpa/s

(Wehner 1985). The corresponding mean thermal diffusion distance of oxygen or helium in the lattice during this nucleation period is at least two orders of magnitude larger than the mean spacing between void nuclei (Table 1).

The quantitative accuracy of the void stability predictions given in Figs. 2 and 4 has not yet been determined. However, the results should be accurate to better than an order of magnitude with the possible exception of the high temperature portion of the oxygen results due to uncertainties in the heat of chemisorption (H_{cs}) data. Some researchers have reported larger values of H_{cs} than used in the present case (Ostrovskii 1974), which would decrease the minimum oxygen concentration needed to stabilize void formation in copper at high temperatures (> 400°C) by as much as several orders of magnitude. However, the main purpose of this paper is simply to point out the general trends regarding the relationships between oxygen or helium concentration and void stability.

The continuum calculations presented in the preceding paper predict that void formation should not occur in most metals unless suitable impurities (such as gas atoms) are present. Previous researchers have similarly concluded that gas is necessary for void formation (Bullough and Perrin 1969, Lanore et al. 1975, Farrell 1980), although the physical mechanisms responsible for void stabilization by gas impurities were not quantitatively modelled. Recent experimental studies on high-purity aluminum (McLaurin 1984) and copper (Zinkle, Kulcinski and Knoll 1986) have shown that these two metals do not exhibit any significant void formation following self-ion irradiation to high doses over a wide temperature range. In addition, ion irradiation of a "low-oxygen" (200 appm O) austenitic stainless steel resulted in greatly reduced swelling (and no observable void formation at high temperatures) compared to a "high-oxygen" (1000 appm O) alloy (Sindelar, Kulcinski and Dodd 1985). It is not known whether stainless steel has ever been irradiated in a very low oxygen form (< 10 appm).

There have been many reported observations of void formation in high-purity aluminum and copper following irradiation with charged particles. For example there are more than twenty known reports of void formation in copper following electron or ion irradiation (Zinkle and Knoll 1984). From the preceding discussion, it appears that some type of gas must have been present in the foil during the irradiation. Significant oxygen levels can be found in high-purity copper unless special deoxidation steps are taken (Metals Handbook 1979). As mentioned previously, even "oxygen-free" copper may contain as much as 10 ppm oxygen by weight (~ 40 appm). Figure 2 predicts that this oxygen concentration should stabilize void formation over the entire void swelling temperature regime in copper (0.3 to 0.6 T_M). Unfortunately, irradiation studies to date on copper have not kept close control of their oxygen content -- oxygen concentrations are not even listed in most of the papers in the literature. It appears that all of the preceding charged particle irradiation studies on aluminum and copper that reported void formation should be reevaluated with respect to gas effects. These gas effects may have masked or distorted the effects of other irradiation parameters that were being studied.

The conclusion that gas is necessary for void formation is currently known to be valid only for aluminum and copper. However, it seems likely that many other metals may also be resistant to void formation in the absence of impurities (gaseous and otherwise) as indicated by the continuum calculations in the preceding paper (Part I). Future irradiation studies should be performed only on foils with a well-characterized and preferably low gas concentration.

From a metallurgical point of view, the theoretical prediction (and experimental confirmation) that voids are not inherently stable in metals such as Al and Cu during irradiation raises hopes that alloy development research may be able to prevent deleterious levels of void swelling. At least two conditions are needed to minimize void swelling. First, the base metal should be oxygen-free ($\lesssim$ 1 appm O) and should not contain any other surface-active impurities such as sulfur, or else, such impurities should be gettered by appropriate alloy additions. A second consideration is that helium generated during neutron irradiation cannot be allowed to freely interact with the embryonic vacancy clusters. Significant advances in this latter area have recently been made using microstructural tailoring of precipitates that may direct helium into a rather benign role (Maziasz 1985).

5. Conclusions

Both oxygen and helium tend to stabilize the formation of voids in metals, although by different mechanisms. The amount of gas that is required to cause void formation depends on the temperature and the displacement damage rate. Gas concentrations as low as 0.01 appm He or 5 appm O are predicted to cause void formation over a limited temperature range in copper irradiated at 1×10^{-3} dpa/s. Void formation should not occur in many pure metals such as aluminum and copper in the absence of gas. The common observation of voids in these metals following charged particle irradiation suggests that the irradiated foils contained a significant amount of oxygen (> 10 appm). Future irradiation studies should be confined to metals which have a well-characterized and preferably low gas content.

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Table 1. Calculated Critical Void Size and Density in Copper as a Function of Irradiation Temperature

Temperature (°C)	Void Density (m^{-3})		Critical Void Radius (nm)
	10^{-3} dpa/s	10^{-6} dpa/s	
100	5×10^{23}	2×10^{22}	0.6
200	5×10^{22}	3×10^{21}	0.6
250	2.5×10^{22}	1.5×10^{21}	0.6
300	9×10^{21}	2.5×10^{20}	0.6
400	2.5×10^{21}	-	0.6
450	1×10^{20}	-	0.6

Table 2. Minimum Helium Concentration for Void Stability in Copper

	$R_v = 0.6$ nm		$R_v = 1.0$ nm	
	m_{crit}	He/vacancy	m_{crit}	He/vacancy
$E_{He}^{B} = 2$ eV	4	0.056	8	0.023
$E_{He}^{B} = 4$ eV	2	0.026	4	0.011

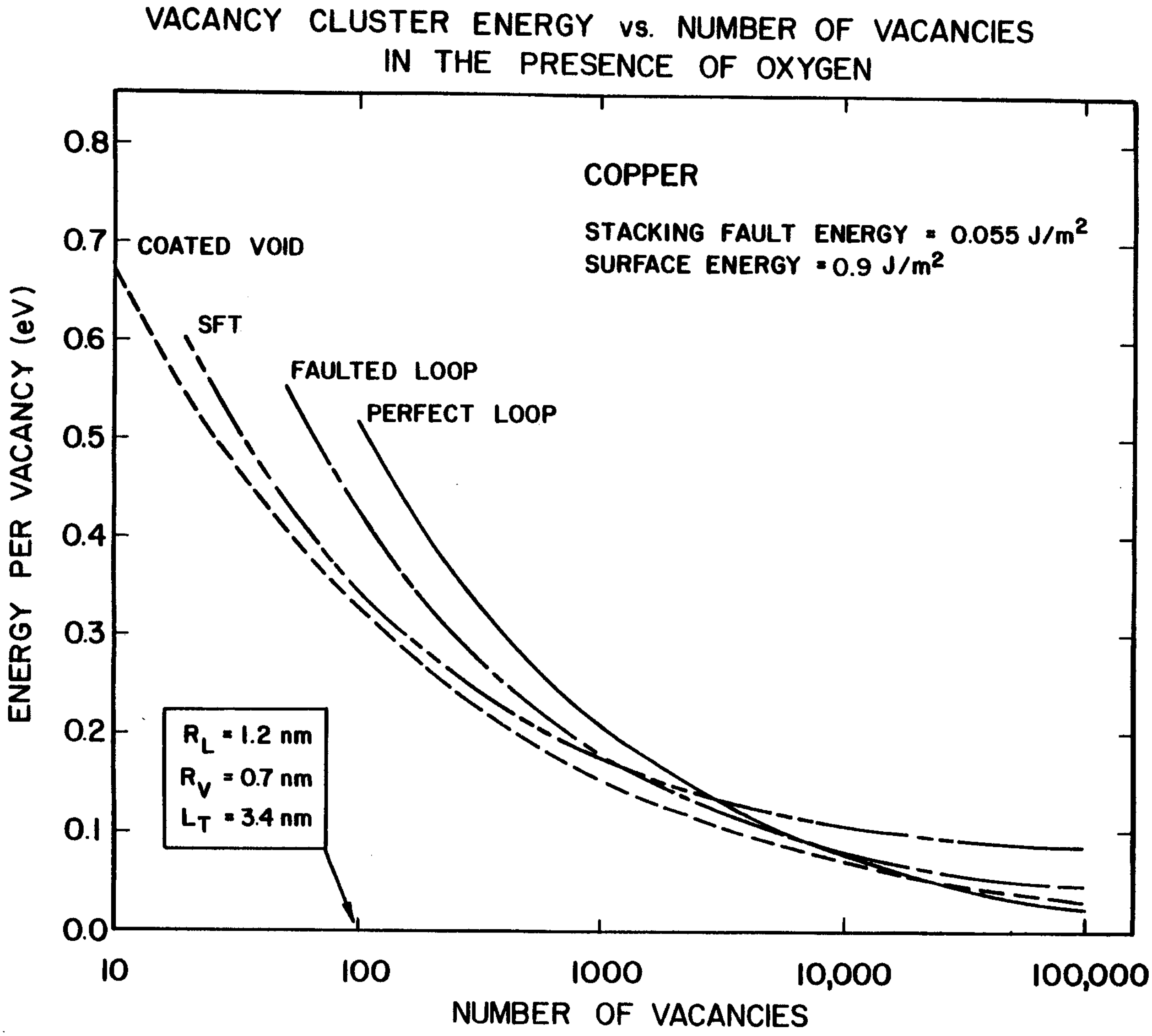

Figure 1. Specific energies of vacancy clusters in copper assuming a surface energy of 0.9 J/m^2.

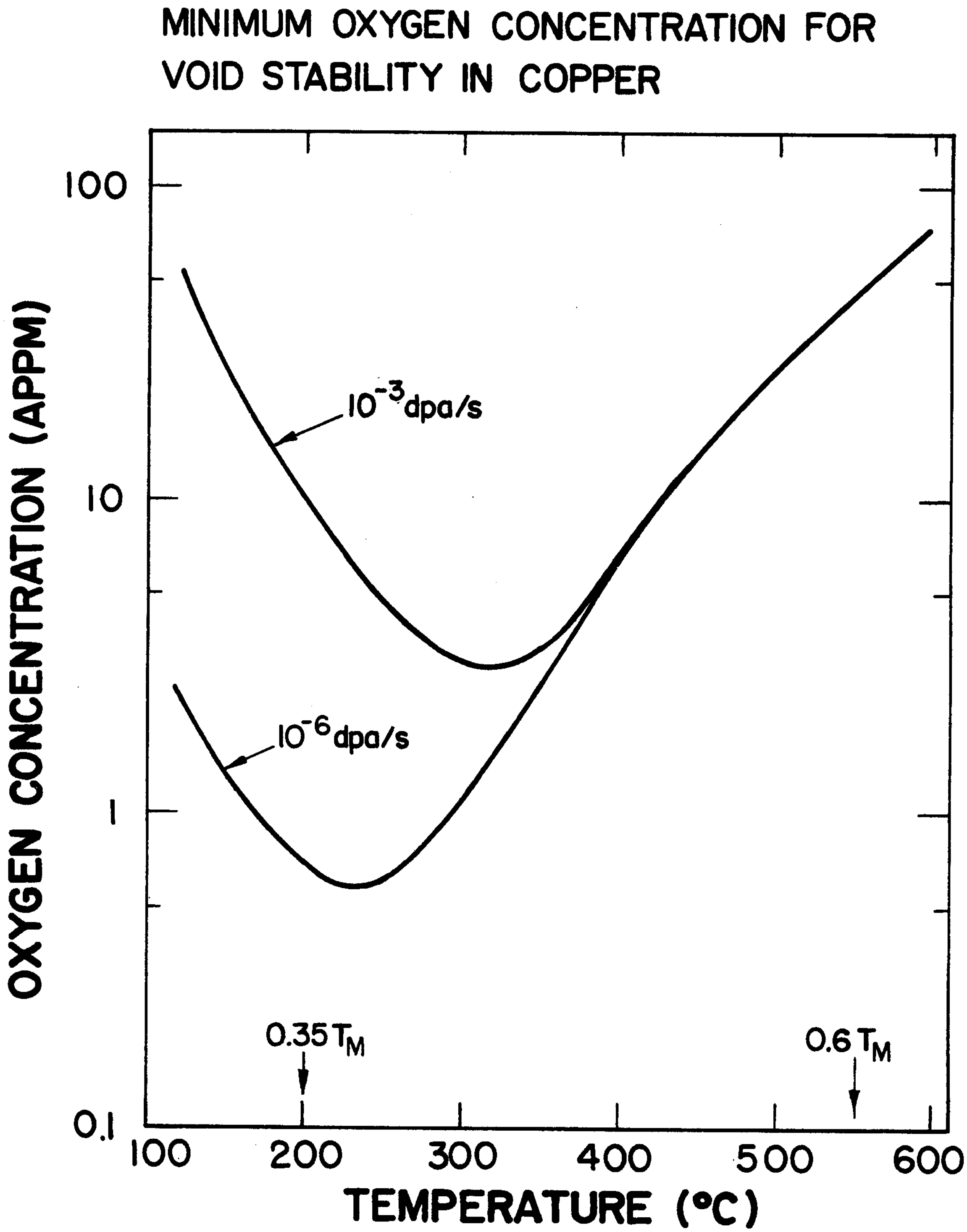

Figure 2. Minimum matrix oxygen concentration that is needed to make voids stable in pure copper during irradiation.

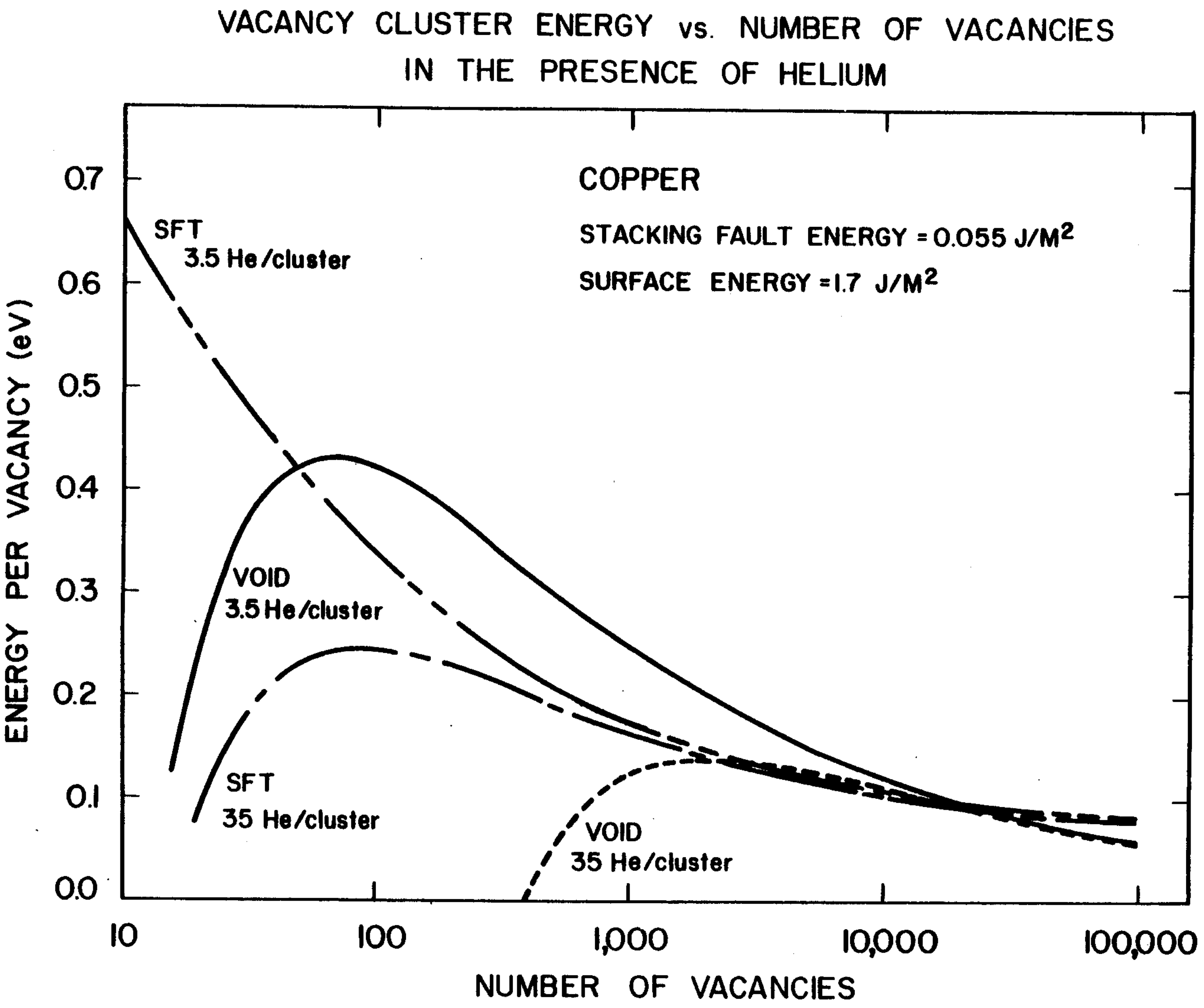

Figure 3. Void and stacking fault tetrahedron energies in pure copper in the presence of helium.

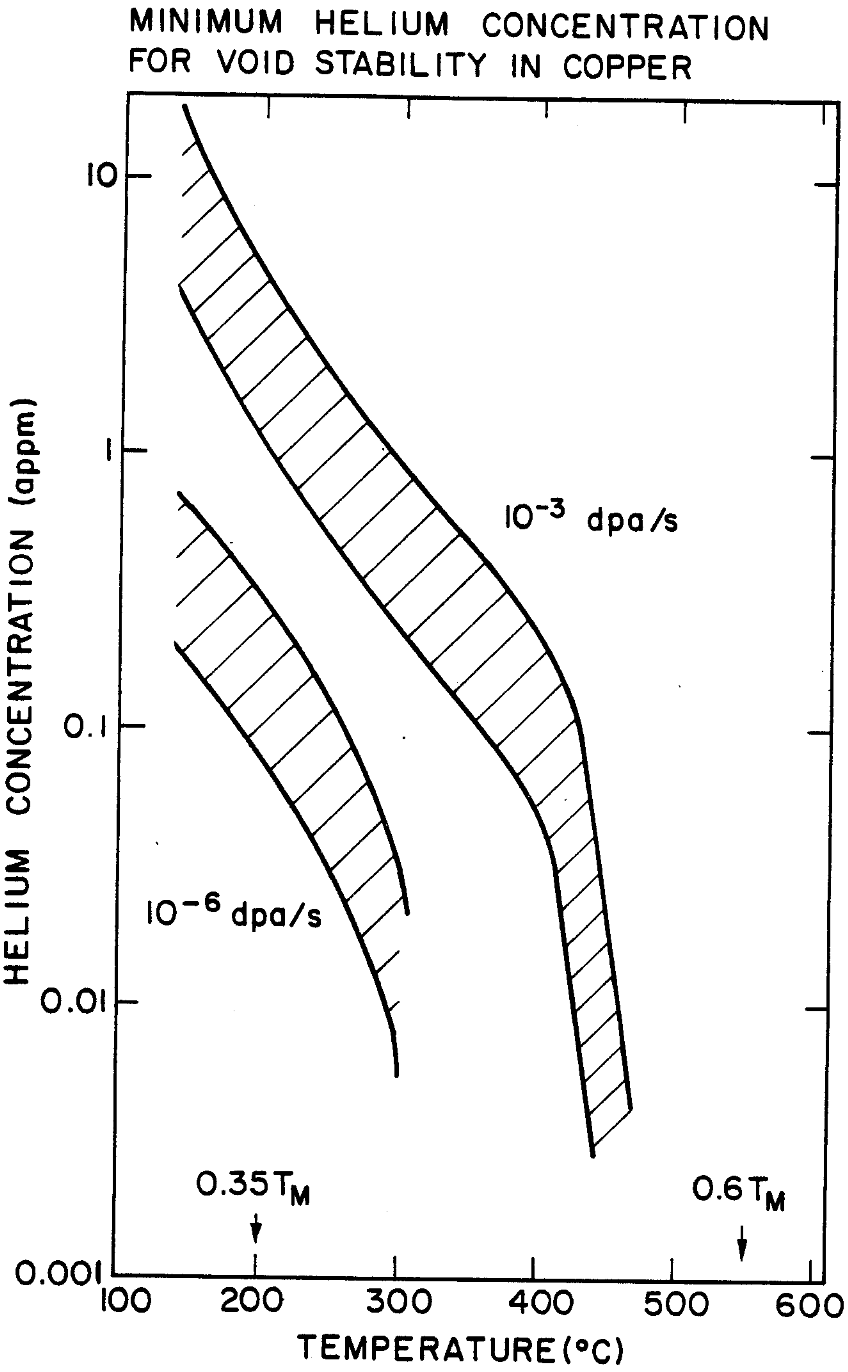

Figure 4. Minimum helium concentration that is needed to make voids stable in pure copper during irradiation.

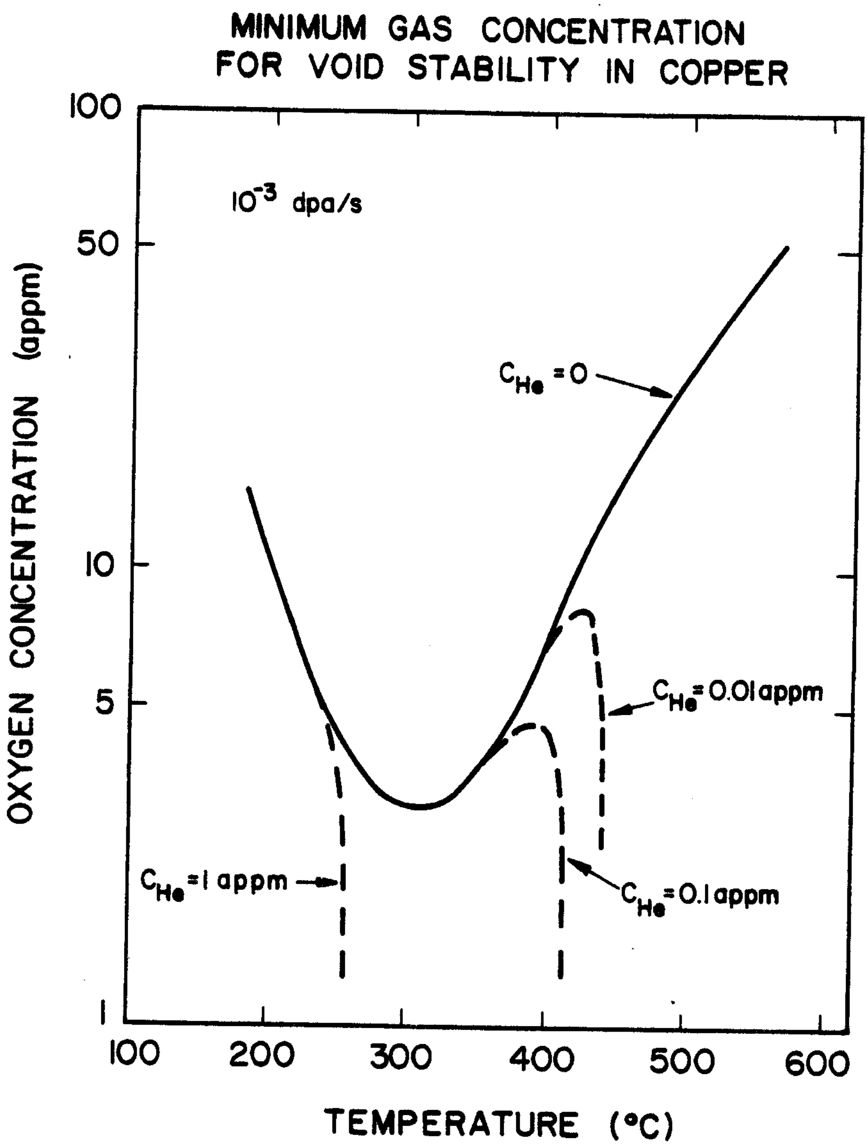

Figure 5. Minimum oxygen concentration that is needed to make voids stable in copper containing various amounts of helium for an irradiation condition of 1 x 10^{-3} dpa/s.