Classical thermodynamic approach to void nucleation in irradiated materials

R. Kemp*[1], G. Cottrell[2] and K. D. H. Bhadeshia[1]

One of the major problems in building a future fusion power station is the development of suitable structural materials. These materials will be exposed to high energy neutron bombardment, with consequent changes in their mechanical properties – embrittlement, hardening and swelling, for example. A missing link in modelling these effects is an effective treatment of the nucleation of voids under irradiation. These voids are initially stabilised by transmutation helium but, once formed, grow by vacancy accumulation. In this paper, a quasi-chemical model is developed to calculate the entropy of a steel/helium system. Although a substantial contribution from quasi-chemical effects might be expected, the steady state concentrations of dissolved helium are found to be too low for such effects to manifest. The steady state concentration of dissolved helium is low in absolute terms, but the resulting supersaturation is very high, making it reasonable to assume that all available nucleation sites are instantaneously activated.

Keywords: Irradiation damage, Void nucleation, Thermodynamic modelling, Fusion power generation, Helium

Introduction

In a fusion power station, the materials facing the reaction plasma undergo continuous bombardment with high energy neutrons. These neutrons knock atoms away from their matrix positions, generating vacancy interstitial pairs, and also creating helium by transmutation reactions.

Through the formation of immobile extended defect structures and preferential absorption of interstitials at microstructural sinks, a supersaturation of vacancies is generated within the material. In combination with helium, the excess vacancies can coalesce into bubbles and, after further accumulation of helium atoms and vacancies, into void which can grow by vacancy accretion alone.

It has been known for some time that the cavities formed under irradiation are not purely helium supported, at least once they are readily visible. Cawthorne and Fulton demonstrated that there were too few helium atoms produced by α radiation emitting reactions in a fast reactor to fill all the cavities observed to equilibrium pressure.[1] However, although it is possible for voids to form through classical nucleation mechanisms of vacancy accumulation, driven by the supersaturation of vacancies in the material, this alone cannot account for the numbers of voids observed in irradiated metals.[2]

In this paper, the authors apply the interstitial solid solution model of Mclellan and Dunn to helium in iron. This model has been successfully applied to previous problems, particularly regarding the properties of carbon in iron.[3] It is known that helium will cluster and self-trap in metals under certain conditions,[4] and it is therefore assumed that helium atoms in solution have an attractive pairwise interaction energy. A calculation assessing the importance of this interaction on the nucleation of helium bubbles can then be carried out.

Quasi-chemical model

Gas potential in void

The chemical potential per atom, $\mu_g(T,P)$, of a real gas is given by

$$\mu_g = \mu^\circ(T) + kT\ln f \qquad (1)$$

where $\mu^\circ(T)$ is the chemical potential in the standard state, f is the fugacity of the gas, k is Boltzmann's constant, and T is the absolute temperature.

The fugacity is given by

$$f = P + \frac{B_{i,2}P^2}{RT} + \frac{1}{2}\frac{(B_{i,2}^2 + B_{i,3})P^3}{RT} + \dots \qquad (2)$$

where P is pressure, R is the molar gas constant and $B_{i,n}$ are the virial coefficients for the gas (described, for helium, in Ref. 5).

Gas potential in solution

Helium, when dissolved in ferritic iron, sits at the octahedral interstices. The chemical potential per atom

[1]Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK
[2]EURATOM/UKAEA Fusion Association, Culham Science Centre, OX14 3DB, Oxfordshire, UK

*Corresponding author, email rk237@cam.ac.uk

for an interstitial solid solution is[6]

$$\mu_s = \bar{E}_u - T\bar{S}_u^v + kT\ln\frac{\dfrac{\theta}{\beta}}{1-\dfrac{\theta}{\beta}} -$$

$$\frac{zkT}{2}\ln\left[\left(\frac{\dfrac{\theta}{\beta}}{1-\dfrac{\theta}{\beta}}\right)^2\left(\frac{1-\dfrac{\theta}{\beta}-\phi}{\dfrac{\theta}{\beta}-\phi}\right)e^{\left(-\frac{\omega}{kT}\right)}\right] \quad (3)$$

in which $\bar{E}_u$ is the partial energy of the solute atoms in the infinitely dilute solution, $\bar{S}_u^v$ is the partial excess (non-configurational) entropy, θ is the atom fraction of the solute, β $(=3)$ is the number of relevant interstitial sites per solvent atom, z $(=4)$ is the nearest neighbour coordination number for the interstitial sites and ω is the pairwise interaction energy between nearest neighbour solute atoms.

ϕ is given by

$$\phi = \frac{1-\left\{1-4\left[1-e^{\left(-\frac{\omega}{kT}\right)}\right]\dfrac{\theta}{\beta}\left[1-\dfrac{\theta}{\beta}\right]\right\}^{1/2}}{2\left[1-e^{\left(-\frac{\omega}{kT}\right)}\right]} \quad (4)$$

The deviation from Henrian behaviour is all contained in the last term of equation (3), so

$$\mu_s = \mu^\infty - \frac{zkT}{2}ln\left[\left(\frac{\dfrac{\theta}{\beta}}{1-\dfrac{\theta}{\beta}}\right)^2\left(\frac{1-\dfrac{\theta}{\beta}-\phi}{\dfrac{\theta}{\beta}-\phi}\right)e^{\left(-\frac{\omega}{kT}\right)}\right] \quad (5)$$

in which μ^∞ is the chemical potential of an infinitely dilute interstitial solution. It should be noted that as $\omega\to0$ or $\theta\to0$, $\mu_s\to\mu^\infty$ as expected.

At equilibrium, the chemical potential in the gas phase must be the same as in solution. Equating the potentials therefore gives

$$f = e^{\left(\frac{\mu^\infty - \mu^\circ(T)}{kT}\right)}$$

$$\left(\frac{\dfrac{\theta}{\beta}}{1-\dfrac{\theta}{\beta}}\right)^{-z}\left(\frac{1-\dfrac{\theta}{\beta}-\phi}{\dfrac{\theta}{\beta}-\phi}\right)^{-z/2}e^{\left(-\frac{z\omega}{kT}\right)} \quad (6)$$

For an ideal gas, $f=P$ and so this equation directly provides the pressure, P_e, in equilibrium with the dissolved gas atoms. For a non-ideal gas, equation (2) must be solved to find P_e.

The latter part of equation (6) describes the deviation from ideal solution behaviour. Interstitial helium in body centred cubic (bcc) iron has a helium–helium binding energy of ~0.5 eV, meaning that the atoms are attracted to one another in solution.[7] This has the effect of increasing the solubility of helium in iron at low temperature (and hence, decreasing P_e), as shown in Fig. 1.

Helium concentration under irradiation

Helium is highly insoluble in iron with a solution energy, for interstitial helium, of 5·25 eV atom^{-1} (Ref. 7). As
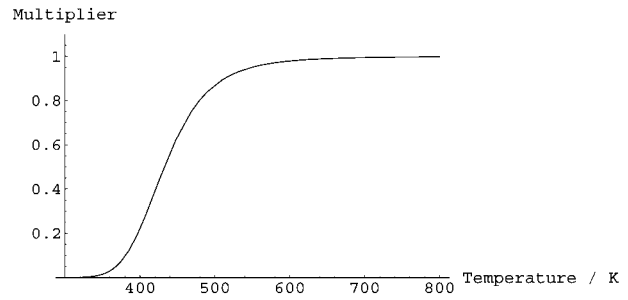
1 Value of quasi-chemical term for deviation from ideal behaviour with temperature in bcc iron ($\theta = 1\times10^{-6}$ mole fraction, $\beta=3$, $z=4$)

the migration energy is very low, 0·078 eV, this means that helium migrates very rapidly to microstructural traps such as dislocations and vacancies, and once in these traps, the atoms can no longer be regarded as being in solution.

It will therefore be necessary to estimate the helium concentration in solution in steady state with these traps. Ghoniem, Sharafat, Williams and Mansur provide a framework for a complete treatment of this problem,[8] but here the authors will concentrate on just two detrapping mechanisms – radiation resolution from extended traps such as dislocations and thermal detrapping from vacancies.

Equating the detrapping rate with that of impingement on sinks gives the rate equation

$$C_{He}^T b + C_{He}^V v e^{\left(-\frac{E_d}{kT}\right)} = D_{He}C_{He}k_{He}^2 + RC_vC_{He} \quad (7)$$

in which C_{He}^T is the concentration of helium (per iron atom) in non-vacancy traps, C_{He}^V is the concentration of helium trapped at vacancies, b is the radiation resolution rate,[9] v is the vibration frequency of a trapped atom, E_d is the helium detrapping energy from a vacancy, D_{He} is the helium diffusion coefficient in solution, k_{He}^2 is the microstructural sink strength for helium, R is a reaction rate coefficient (described in Ref. 8), C_v is the vacancy concentration and C_{He} is the concentration of helium in solution. Additionally, to conserve helium

$$C_{He}^T + C_{He}^V + C_{He} = C_{He}^0 \quad (8)$$

where C_{He}^0 is the total helium concentration in the material. Assuming most of the helium is trapped at any one time (i.e. $C_{He}^T, C_{He}^V \gg C_{He}$) allows an estimate of dissolved helium concentration (Fig. 2).

Discussion

It is clear that the estimated steady state concentration of helium atoms in solution is too low, under a wide range of conditions, for the quasi-chemical correction to be significant. The correction affects equilibrium pressures, at low temperatures (below ~400 K), at concentrations of 10^{-9} mole fraction and above.

This steady state concentration, of $\sim10^{-15}$ mole fraction, is still associated with an equilibrium fugacity of $\sim2\times10^{36}$ Pa (an unphysically high pressure, from equation (2), of $\sim3\times10^{22}$ Pa in helium). On the other hand, a bubble with a radius of 1 nm in which the gas pressure is balanced by the surface energy ($P=2\gamma/r=4$ GPa) would theoretically be in equilibrium,
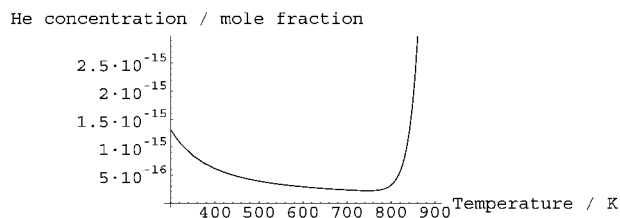
2 **Estimate of dissolved He concentration in bcc iron under fusion conditions: at low temperatures radiation resolution dominates; at high temperatures vacancy detrapping dominates ($b=10^{-5}$ s^{-1}, $k_{He}^2=10^{12}$ m^{-2}, $C_{He}^0=100$ appm, $C_v=10^{-9}$)**

at 800 K, with a bulk helium concentration of $\sim 10^{-24}$ mole fraction or, at 1000 K, 10^{-17} mole fraction.

During irradiation, therefore, any dissolved helium will always be at a huge supersaturation. Under such conditions, the critical radius for nucleation is extremely small (bubbles that would be in equilibrium with anything approaching the supersaturation conditions would be less than one atom across), meaning that the nucleation barrier is very small. In such circumstances, all available nucleation sites would be activated rapidly, leading to site saturation. This justifies the usual assumption made in helium bubble studies, that the process simply involves the growth of a fixed number density of bubbles.

The calculations show that it is reasonable to neglect the nucleation stage of bubbles in the steel irradiated in the fusion reactor. It is the number density of nucleation sites that determines the number density of bubbles. The evolution of the bubbles from minute size then depends on the rate of impingement of helium atoms on the bubble surface. The work presented here justifies models which begin with an assumed number density of bubbles, although it is also true that the number density of nucleation sites will change under irradiation.

Of course, the approach laid out above is not the only model available for the nucleation of helium bubbles under irradiation and there are behaviours that it ignores, for example the possibility of bubble growth by loop punching,[7] vacancy accumulation as a response to over pressure,[10] and bubble growth as a response to an external applied stress or plastic yield.[11,12] In particular, these alternative approaches explicitly include a surface energy term γ allowing heterogeneous nucleation to be considered. However, because the critical bubble size is calculated to be so small using the approach laid out in this paper, there is no particular energetic advantage for helium bubble nucleation at such sites, although it may be easier for a bubble to grow on the grain boundary owing to an increased helium flux (pipe diffusion) along the boundary.[13]

Acknowledgements

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