

Helium Migration and its Influence on Cavity Formation in Irradiated Materials

Nasr M. Ghoniem

School of Engineering and Applied Science, University of California at Los Angeles,
Los Angeles, CA 90024, USA

(Received: 20 April 1983)

ABSTRACT

The introduction of helium atoms in irradiated structural materials is now recognized to impair their useful properties. In this paper, we outline the theoretical foundations for the mechanisms of helium transport and subsequent clustering in irradiated alloys. Under typical reactor irradiations, helium is trapped in vacancies or vacancy complexes, and then detrapped by a variety of thermal and displacement mechanisms. The effective helium diffusion rate is described, in view of the influence of material and irradiation variables. Cavity formation and stability are then presented, with emphasis on the theoretical understanding of nucleation mechanisms.

1. INTRODUCTION

During the past few years, there has been a growing interest in the effects of helium atoms introduced in solids on their properties. Of particular concern is the influence of the synergistic interaction between helium and displacement damage on the mechanical properties of structural alloys in a nuclear environment. It has now been established that cavities form and grow in the cladding and duct materials in Fast Breeder Reactors (FBRs). And it is also recognized that such cavity formation is a serious impediment to a long service

life of fuel elements, because of the induced deformations and associated stresses under irradiation. Even though the helium generation rate due to nuclear reactions in a fast breeder reactor is not very high, it is still believed to be one of the key factors which lead to cavity formation. The growth of nucleated cavities is nevertheless dictated mainly by displacement damage and radiation temperature.

In Magnetic Confinement Fusion Reactors (MCFRs), the situation is expected to be quite different. Whereas helium concentrations typical of FBR steel cladding are in the range 10^{17} – 10^{18} atoms/cm³ during its lifetime, much higher concentrations are expected for MCFRs. Generation rates are projected to be on the order of 10^{18} atoms/cm³/year in a fusion reactor based on the deuterium–deuterium (D–D) fusion fuel cycle, and about 3×10^{19} to 6×10^{19} atoms/cm³/year in a deuterium–tritium fusion reactor.¹ While the amount of displacement damage accumulated during one year of irradiation is expected to be ~ 0.2 – 0.8 of the corresponding amount of an FBR cladding material, the presence of large helium concentrations is still of primary concern.

Simulation experiments using dual ion beams² and thermal reactor irradiations in HFIR³ have consistently shown that helium concentrations introduced during irradiation can be well correlated to cavity concentrations. The nature of those cavities (bubbles or voids) is also shown to depend on the level of helium.³ In this brief paper, we discuss the major findings of our theoretical research on helium migration and its effect on cavity formation in irradiated structural materials.

2. HELIUM MIGRATION

A variety of migration mechanisms have been proposed for the transport of helium atoms introduced in solids. Many possibilities exist where helium residing in an interstitial position, a substitutional position or with a cluster of helium and vacancies, can migrate. Transport of helium in the solid can therefore be accomplished solely or in coordination with point defects. Under irradiation, the possibilities become even more numerous, since both self-interstitials and vacancies and their clusters are produced. Philips and co-workers^{4,5} have recently measured effective values for helium diffusion in nickel at both high⁴ and low⁵ temperatures. At the high

temperature, the effective migration energy was attributed to the difference between the helium–vacancy dissociation energy and the vacancy formation energy. At low temperatures, however, it was possible to measure an interstitial helium migration energy.

Under irradiation conditions, where helium atoms are introduced concurrently with displacement damage, three more features complicate the understanding of helium transport. The first is the competition between self-interstitials and helium atoms to react with vacancies. Next, helium atoms tend to agglomerate with available vacancies, which effectively immobilize helium. Finally, displacement collision cascades may supply enough energy to remove helium ‘bound’ in deep traps such as vacancy helium clusters. During irradiation, it is concluded that the major helium reactions are: (1) trapping and thermal detrapping of helium in single vacancies, divacancies and higher order complexes; (2) helium trapping at dislocations and grain boundaries; (3) replacement of helium bound to single vacancies by self-interstitials; (4) helium clustering into vacancy–helium complexes; (5) displacement of trapped helium atoms by collision cascades; and (6) migration of helium as an interstitial atom or in a divacancy.

We have recently constructed a mathematical rate theory based on the previously described reactions.⁶ The theory provides a detailed description of the time-dependent concentrations of various helium–vacancy complexes. In this work, rate equations are developed for unoccupied single vacancies, single self-interstitials, interstitial helium, unoccupied divacancies, and various complexes containing m vacancies and n helium atoms. It is found that helium migration, past a transient period, can be roughly described by two characteristic temperatures: $T_1(S, G)$ and $T_2(S, G)$, where $T_2 > T_1$. Here G represents the displacement damage rate (dpa/s) and S is the effective sink density (cm^{-2}). Both T_1 and T_2 are found to increase with G giving an effective temperature shift with displacement damage rate, and to have weak dependencies on the sink strength S . During quasi-steady state, which is achieved at times longer than a vacancy mean-lifetime, helium migration is controlled by trapping and thermal detrapping at single vacancies for temperatures greater than T_2 . It is therefore simple to show that the effective migration energy for helium is the difference between the energy needed to dissociate it from a vacancy, and the vacancy formation energy. Between the temperatures T_1 and

T_2 , helium diffusion is controlled mainly by trapping at single vacancies and detrapping by self-interstitials. At steady state the effective migration energy is close to that of a single vacancy in this temperature regime. Around T_1 , divacancies contribute to the transport of helium, rendering it greater mobility than only single vacancies. Below temperature T_1 , steady state is achieved over a long time, on the order of years. When such a steady state situation is achieved, collision cascades become the most dominant mechanism for the detrapping of helium, and thereby dictate its mobility. During the transient time, which may prove to be important in pulsed fusion reactors, helium mobility is higher; its detrapping is primarily controlled by the large self-interstitial flux.

3. STABILITY OF VACANCY-HELIUM CLUSTERS

3.1. Thermal dissociation

Once a cluster of vacancies and helium atoms has formed, it will be subject to destabilizing mechanisms leading to its dissociation. If the dissociation mechanisms are less vigorous than the formation processes, nucleation of cavities proceeds until it is terminated at saturation. The presence of helium in vacancy-helium clusters is found to be a key factor in the stabilization of these clusters. We will discuss here two aspects of the dissociation of an already formed cluster. The first is by thermal emission of a vacancy or helium atom, and the second is by the effects of collision cascades created in the vicinity of a cavity.

In rate-theory calculations, the determination of the thermal emission rates of vacancies and helium from cavities is essential. The thermal emission of a helium atom from a cluster is found to be a difficult process. Helium is insoluble in most metals and the energy required to force a helium atom into the metals lattice is high, on the order of 4–5 eV. However, and for small clusters, if the number of helium atoms per vacancy is significantly larger than unity, the internal gas pressure is so high that the energy change in an emission process is larger than the dissolution energy. Another competing process may occur, however: a Frenkel pair can be created in the vicinity of the cluster in order to relieve the excessive pressure. In any event, a high ratio of helium to vacancies is not likely, and is limited by helium

emission into the solid or by the creation of a Frenkel pair leading to interstitial loop 'punch out'.

In the classical drop model proposed by Wiedersich and co-workers,⁷ the idea of detailed balance on a hypothetical equilibrium Boltzmann distribution is used to calculate the emission rates of vacancies. The calculation depends on evaluating $\Delta F(m, n)$, the free energy change during the emission process for m vacancies and n helium atoms. Equivalently, for small size vacancy-helium clusters, the emission rate is calculated using the binding energy of the last vacancy to cluster, E_v^B . It is shown that:

$$E_v^B = \Delta F(m, n) + E_v^F \quad (1)$$

where E_v^F is the vacancy formation energy. For a cluster containing m vacancies and n helium atoms, $\Delta F \rightarrow 0$ as both m and $n \rightarrow \infty$. Using the parameters of nickel, for example, the binding energy of the last vacancy increases from 0.25 eV at $m = 2, n = 0$, to 1.4 eV at $m = \infty, n = 0$. Including more helium into the cluster ($n/m > 0$) is found to increase E_v^B as compared to the previous example. Calculations indicate that if helium does not exist, homogeneous cavity nucleation by vacancy condensation alone may be impossible. The low binding energies for small vacancy clusters results in immediate dissociation at temperatures high enough for vacancy mobility. During the early stages of cavity formation, it is found that the most stable helium-vacancy clusters are those with $m \approx n$, where m and n are both small (1–10). Once this is accomplished, larger size cavities will continue to grow, largely by the absorption of vacancies. Generally, $m \gg n$ during the growth stage of cavities, but m/n is somewhat dependent upon the He/dpa ratio, the prevailing sink structure, and the irradiation temperature.

3.2. Dynamic re-resolution of cavities

The importance of the dynamic re-resolution of fission gas bubbles by fission fragments is widely accepted in swelling calculations of nuclear fuels.⁸ We have recently established that the direct interaction of neutrons or cascades with gas-filled cavities can lead to their ultimate destruction. This mechanism is extremely important to evaluate, for it may partially explain differences between swelling of alloys in different neutron spectra. The re-resolution parameter is defined as the

probability per second that a gas atom in the cavity receives an energy greater than a minimum energy, T_{\min} , which a struck gas atom must acquire to be considered re-dissolved by a collision. This may occur directly by a neutron–helium gas atom collision or by recoil in an iron atom–helium gas atom collision.

The re-resolution parameter for direct collisions between neutrons and helium gas atoms is found to be:

$$b_d \approx \sigma_s(n, \text{He}) \phi(\bar{E}_n) \quad (2)$$

where $\sigma_s(n, \text{He})$ is the scattering cross-section between neutrons and helium atoms, and $\phi(\bar{E}_n)$ is the neutron flux at an average neutron energy \bar{E}_n , provided that $\Lambda \bar{E}_n \gg T_{\min}$. Λ is a kinematic factor given by $\Lambda = 4M_1M_2/(M_1 + M_2)^2$. The direct collision re-resolution parameter is thus independent of the gas density within the cavity and the minimum energy for the re-resolution. This implies that every direct neutron collision with a helium atom will result in a re-resolution event.

Collision cascades created by primary knock on atoms (PKAs) in the near vicinity of a cavity can cause significant energy transfer to the gas atoms. Consider gas-filled cavities each containing m gas atoms immersed in a spatially uniform flux of recoil atoms, $\phi(E_r)$. To evaluate the re-resolution probability per atom due to collision cascades, b_c , expressions for the recoil flux spectrum and the differential energy-transport cross-section between recoils and gas atoms, $\sigma_{\text{Fe-He}}(E_r, T_r)$, need to be derived. Using simplifying assumptions for evaluating both $\phi(E_r)$ and $\sigma_{\text{Fe-He}}(E_r, T_r)$, where T_r is the transferred energy to helium atoms, we obtain

$$b_c = BK\phi \left[\frac{\Lambda'^3 \Lambda_n \bar{E}_n}{6T_{\min}^2} + \frac{\Lambda'}{\Lambda_n \bar{E}_n} \left(\ln \left(\frac{T_{\min}}{\Lambda'} \right) + 1 \right) + \frac{\bar{E}_n}{\Lambda_n E_{n,\min}^2} \left(\frac{T_{\min}}{3\Lambda_n E_{n,\min}} - \frac{\Lambda'}{2} \right) - \frac{1}{\Lambda_n \bar{E}_n} \left(\Lambda' \ln(\Lambda_n E_{n,\min}) + \frac{T_{\min}}{\Lambda_n E_{n,\min}} \right) \right] \quad \text{s}^{-1} \quad (3)$$

In this expression B and K are constants, ϕ is the neutron flux, \bar{E}_n is the average neutron energy, $E_{n,\max}$ is the maximum neutron energy, and Λ' is the kinematic energy transfer parameter between Fe and He

atoms.¹ According to this simple model, the re-resolution rate of gas from bubbles is estimated to be on the order of 1–10 times the displacement damage rate.

4. CONCLUSIONS

The presence of helium gas in irradiated materials is now established, on theoretical and experimental grounds, to be a key factor during the nucleation phase of cavities. During the growth phase at intermediate temperatures, however, the role of helium seems not to be so direct. Helium modifies cavity growth indirectly by changing the nucleated sink structure of the irradiated matrix. However, at temperatures below $\sim 0.3T_m$ or above $\sim 0.6T_m$, helium may force cavities to grow by 'pumping up' their size regardless of vacancy behavior.

Our studies show that there exists a 'critical path' to the ultimate formation of cavities in irradiated materials. This path is found on a two-dimensional space containing m vacancies and n helium gas atoms, and is defined for only the ratio $R(m, n) = m/n$. During the early stages, this ratio is ~ 1 , while the later stages of formation are associated with $m/n \gg 1$. The vacancy-to-helium ratio is obtained by finding the maximum concentrations of vacancy-helium clusters for given combinations of m and n . It is found that during early cavity formation, if $R(m, n) \gg 1$ the vacancy-helium complex is unstable against thermal dissociation. Conversely, clusters for $R \ll 1$ do not normally form because of the possibilities of helium ejection into the matrix and Frenkel pair formation.

Neutron collisions with helium atoms in cavities, or collisions between displacement cascades and helium atoms, have been found to result in cavity destabilization. Using a simplified model for the energy transfer process during the primary damage stage, the re-resolution rate of helium atoms into the matrix is estimated to be 1–10 times the displacement damage rate. This dispersal process is particularly important at low temperatures, where ejected helium atoms do not immediately migrate to the original cavity. Re-resolution is found to result in a 'refinement' of the cavity microstructure at temperatures $< 450^\circ\text{C}$ for reactor irradiations. At higher temperatures, re-resolution has a very small effect. The most drastic effects of re-resolution are found in the 300–500°C temperature range for typi-

cal reactor irradiations. Due to re-solution cavity density increases and the average size decreases even faster, resulting in lower swelling.

Simulations of pulsed fusion irradiations show interesting results. During the off-time, vacancy traps are depleted from the matrix by absorption at sinks. Unstable vacancy-helium complexes dissociate thermally during the off-time, leaving helium to migrate at a fast rate as an interstitial atom. Combining the on-time and the off-time behavior of helium, it is found that the effective mobility is higher than corresponding steady-irradiation. An interesting consequence is that pulsing leads to a faster nucleation of helium cavities, as well as more absorption at dislocation sinks. The net number of matrix cavities is therefore smaller than in the corresponding steady-irradiation.

ACKNOWLEDGEMENTS

The author is grateful for the help of his students, Ms Myra Takata and Mr Shahram Shrafat. Also, discussions with Mr Philip Maziasz of ORNL are greatly appreciated. This research was supported in part by the United States Department of Energy under contract number DE-AM03-76SF00034 with UCLA.

REFERENCES

1. Ghoniem, N. M. and Takata, M. L., A rate theory of swelling induced by helium and displacement damage in fusion reactor structural materials, *J. Nucl. Mater.*, **105** (2 & 3) (1982) 276-92.
2. Farrell, K., *Rad. Effects*, **53** (1980) 175.
3. Maziasz, P. J., Some effects of increased helium content on void formation and solute segregation in neutron irradiated type 316 stainless steel, *J. Nucl. Mater.*, **108/109** (1981) 359-84.
4. Philips, V., Sonnenberg, K. and Williams, J. M., Diffusion of helium in nickel, *J. Nucl. Mater.*, to be published.
5. Philips, V. and Sonnenberg, K., Interstitial diffusion of helium in nickel, *J. Nucl. Mater.*, to be published.
6. Ghoniem, N. M., Sharafat, S., Mansur, L. K. and Williams, J., The theory of helium transport and clustering in metals under irradiation, *J. Nucl. Mater.*, to be published.
7. Wiedersich, H. and Hall, B. O., *J. Nucl. Mater.*, **66** (1977) 187.
8. Griesmeyer, J. M., Ghoniem, N. M. and Okrent, D., A dynamic intragranular fission gas behavior model, *Nucl. Eng. Design*, **55** (1979) 69.