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OF HELIUM IN NEUTRON-INDUCED MICROSTRUCTURAL EVOLUTION

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D. S. Gelles and F. A. Garner

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AN EXPERIMENTAL METHOD TO DETERMINE THE ROLE OF HELIUM IN NEUTRON-INDUCED MICROSTRUCTURAL EVOLUTION

D. S. GELLES and F. A. GARNER

Materials Development, Hanford Engineering Development Laboratory, W/A-57, P. O. Box 1970, Richland, WA 99352, USA

A method is presented which allows the determination of the role of helium on microstructural evolution in complex alloys and which avoids many of the problems associated with other simulation experiments. It involves a direct comparison of the materials' response to a primary difference in fission and fusion environments, namely the rate of helium generation. This is accomplished by irradiating specimens in a fission reactor and conducting microstructural analyses which concentrate on alloy matrix regions adjacent to precipitates rich in boron or nitrogen. Such precipitates generate well-defined atmospheres of helium (and other transmuted atoms) due to (n,α) reactions during irradiation. Microstructural comparisons are made between the regions bearing implanted helium and those just beyond the helium range. The method takes advantage of virtually no variation in alloy composition and pre-irradiation microstructure over short distances, and can be used to study any material of interest if the appropriate precipitates can be developed. A variety of helium/dpa ratios can be obtained in one specimen by using precipitates of various sizes. Procedures are outlined for calculation of background and injected helium levels as well as displacement doses generated by neutrons and alpha particles. An example of the analysis method is shown for an experimental austenitic stainless steel containing boride particles and irradiated to 3 and 7 x 10²² n/cm² (E > 0.1 MeV).

1. INTRODUCTION

The evolution of microstructure in metals exposed to neutron environments is known to be sensitive to a large number of material and environmental variables, many of which act synergistically. It is therefore difficult to study the individual action of transmutation-produced helium atoms on microstructural development. In charged particle simulation experiments the evolution of microstructure has also been found to be quite sensitive to the rate, schedule, temperature and manner of helium introduction [1,2]. It is therefore desirable in simulation studies that helium be generated internally at the irradiation temperature and that its generation proceed concurrently with the displacive irradiation.

This paper suggests a method which allows the determination of the role of helium and some other atoms in complex alloys and which avoids many of the problems associated with other simulation experiments. It involves the use of neutron-irradiated specimens which contain precipitate particles rich in elements subject to (n,α) reactions. Such precipitates develop well-defined atmospheres or "halos" of helium and other (n,α) recoil products [3-6]. A microstructural analysis is then conducted in regions bearing the desired atoms and in immediately adjacent regions. This method takes advantage of the minimum variations in alloy composition and preirradiation microstructure over short distances and can be used to study any material if suitable precipitates can be developed.

The following sections develop the quantitative expressions necessary to select material and irradiation conditions and to analyze the data.

2. PARTICLE DEPOSITION RATE WITHIN THE HALO

The precipitate is assumed to be spherical with radius r_p and density ρ_p and to contain a known density of atoms subject to (n,α) events. The energetic particles are born with a distribution of energies $N(E_0)$ and travel in paths assumed to be straight lines with total ranges $R_p(E_0)$ in the precipitate phase and $R_m(E_0)$ in the matrix phase. The rest distribution of atoms about the range is assumed to be gaussian and to be defined by the straggling parameter $\Delta R(E_0)$. Alpha particles which travel through both phases must obey the relation

$$d_p/R_p(E_0) + d_m/R_m(E_0) = 1, \quad (1)$$

where d is the distance traveled in a particular phase. This statement is a direct consequence of the Geiger relationship. Figure 1 shows that the inner and outer limits (R_i and R_o) of the halo can be defined for a given energy in terms of $R_p(E_0)$, $R_m(E_0)$ and r_p .

$$R_o = R_m(E_0) + r_p \quad (2)$$

$$R_i = R_m(E_0) + r_p(1-2m) \quad (3)$$

$$m = \frac{\rho_p \sqrt{\frac{A}{E_0}}}{\rho_m \sqrt{\frac{A}{E_0}}} = \frac{R_m(E_0)}{R_p(E_0)} \quad (4)$$

Fig. 1 - The limits of the halo are determined by (n,α) events occurring on the near and far surfaces of the precipitates.

where A is the molecular weight. Equation (4) states the Bragg-Kleeman rule for alpha ranges.

When $m = 1.0$ and $\Delta R(E_0) \ll R(E_0)$, the distribution of deposition rates $\dot{D}(r)$ within the halo is easy to define. Only those particles born on the portion of the spherical surface defined by radius $R_m(E_0)$, centered at r , and which lies within the precipitate, can be deposited in $dV(r)$, providing that the particle was directed at $dV(r)$. It can be shown that the volumetric deposition rate is

$$\dot{D}(E_0, r)_{m=1} = \frac{\dot{S}(E_0)}{4rR_m(E_0)} (r_p^2 - [r - R_m(E_0)]^2) \quad (5)$$

where $\dot{S}(E_0)$ is the volumetric birth rate of particles.

$$\dot{S}(E_0) = C(t) \phi \bar{\sigma}_{n,\alpha}(E_0) \quad (6)$$

where $C(t)$ is the current concentration of reactive atoms, $\bar{\sigma}_{n,\alpha}(E_0)$ is the spectrum-averaged cross section and ϕ the total flux. Figure 2 illustrates the nature of the profiles for the $^{10}\text{B}(n,\alpha)$ reaction. Note the strong dependence of concentration on particle size.

Fig. 2 - Effect of particle size on normalized deposition rate of reaction products for $^{10}\text{B}(n,\alpha)$ events occurring in spherical precipitates.

Integration of equation (5) over the entire halo yields total conservation of particles as expected.

$$\int_{R_m(E_0)-r_p}^{R_m(E_0)+r_p} \dot{D}(E_0, r) 4\pi r^2 dr = \frac{4}{3} \pi r_p^3 \dot{S}(E_0) \quad (7)$$

For most experimental studies, an appropriate average deposition rate over the area A should be calculated such that

$$\dot{D}_{\text{avg}} = \int_{r_1}^{r_2} \dot{D}(E_0, r) dA(r) / \int_{r_1}^{r_2} dA(r) \quad (8)$$

For some combinations of neutron spectra and (n,α) reactions the particle source is not at a single energy. An integration of equation (5) over the source distribution is thus required.

$$\dot{D}(r) = \int_{E_0(\text{min})}^{E_0(\text{max})} \dot{D}(r, E_0) dE \quad (9)$$

Precipitates rich in nickel and subjected to environments with large thermal and fast neutron components will generate such a source distribution by the time-dependent build-up of the two stage $^{58}\text{Ni}(n,\gamma)^{59}\text{Ni}(n,\alpha)^{56}\text{Fe}$ reaction.

When $m \neq 1.0$ the source surface within the precipitate is not spherical and considerable complexity is introduced. To a good first approximation, however,

$$\dot{D}_{\text{avg}} (m \neq 1) = m^{-1} \dot{D}_{\text{avg}} (m = 1.0) \quad (10)$$

provided the area analyzed is centered in the halo and $R_m \gg 2r_p$.

3. DISPLACEMENT RATE WITHIN THE HALO

For typical (n,α) reactions, the displacement level generated by the particles as they slow down is usually but not always small compared to the displacements generated by neutrons. In thermal neutron environments for instance, where the (n,α) cross section is very large and the displacement rate is small, the additional displacements in the halo may become a substantial fraction of the total. The fractional increase I in displacement rate can be approximated by

$$I = \frac{\dot{D}_{\text{avg}} A_m N_d}{\rho_m \bar{\sigma}_d N_a \phi} \quad (11)$$

where $\bar{\sigma}_d$ is the spectral-averaged cross section of the matrix, N_d is the total number of displacements per particle, N_a is Avogadro's number and ϕ is the total neutron flux.

4. OPTIMUM PARTICLE SIZE

There is an optimum particle radius r_p^* which maximizes the width of the halo, thus minimizing the gradients in deposition, while also ensuring that the two halos do not overlap. As shown later, this latter consideration is quite important.

$$r_p^* = [R_m(\bar{E}_0, 2) - R_m(\bar{E}_0, 1)] / 2m \quad (12)$$

where $\bar{E}_0$ is the mean birth energy of the source and the designations 1 and 2 refer to the shorter and longer range reaction products, respectively.

5. EXPERIMENTAL EXAMPLE

The successful use of this technique requires the identification of the precipitate composition in order to determine $C(t)$. If a variety of source precipitates exist, it is thus necessary to retain the precipitate within the thin foil section employed for the microstructural analysis. If the precipitates are only of one type with well-defined stoichiometry, the latter restriction can be relaxed and r_p calculated from the ring width using expressions (2) and (3). Stereomicroscopy is useful to determine the relative positions of the precipitate and halo with respect to the foil section. The use of non-equatorial sections of the halos requires appropriate geometrical corrections. The identity of the reactive isotope can be ascertained from measurements of the range of the two recoil products. This is best done when the precipitate is retained in the foil. These considerations are all employed in analysis of the following experiment.

Void swelling studies have been conducted in the EBR-II reactor using an experimental precipitation-hardened austenitic stainless steel containing 30 wt. % nickel, 10 wt. % chromium, and lesser amounts of molybdenum, titanium, aluminum, manganese, silicon, and a trace of boron (0.0007 wt. %). The boron has been found to be almost totally contained in small precipitates (about 500 nm) formed prior to irradiation. These precipitates were identified by X-ray lattice parameter determinations as M_3B_2 [7]. In a related alloy containing these same precipitates, the metal atoms have been found to be Mo, Ti, Cr, Fe, Al and Ni in rough order of decreasing concentration [8]. Energy-dispersive X-ray analysis in a scanning transmission microscope confirmed that the precipitates are indeed rich in molybdenum and contain the other elements in roughly that order. Since the nickel concentration of the precipitate is below that of the matrix, only the boron atoms function as extra alpha sources in this case. As shown in Figure 3, a ring of enhanced void nucleation about an M_3B_2 precipitate occurred at a range of about 1.3 μm in a specimen irradiated to $2.2 \times 10^{22} \text{ n/cm}^2$ ($E > 0.1 \text{ MeV}$) at 400°C . This halo is caused by the ^7Li product of the $^{10}\text{B}(n,\alpha)$ reaction; no visible enhancement occurred at about 2.6 μm , the expected range of the alpha particle. The lithium ring width is comparable to the precipitate diameter which suggests that $\rho_p/\rho_m = m \approx 1.0$. Actually $m = 1.06$ according to equation (4).

Using the following parameters the deposition profiles can be calculated for each expected ring. The profiles pertaining to Figure 3 are shown in Figure 4.

$$\begin{aligned} m &= 1.06, r_p = 0.145 \mu\text{m} \\ E_0^{Li} &= 0.84 \text{ MeV}, E_0^\alpha = 1.47 \text{ MeV} \\ R_{Li}(0.84) &= 1.3 \mu\text{m}, R_\alpha(1.47) = 2.6 \mu\text{m} \\ \Delta R_{Li} &= 0.09 \mu\text{m}, \Delta R_\alpha = 0.17 \mu\text{m} \\ \bar{\sigma}_{n,\alpha} &= 2 \times 10^{-4} \text{ barns for the matrix and 1.0 barn for the boron atoms} \end{aligned}$$

$$\bar{\sigma}_d = 417 \text{ barns}, \phi = 2.0 \times 10^{15} \text{ n/cm}^2\text{-sec}$$

According to equation (12), the optimum particle radius r_p^* is 0.75 μm , considerably larger than that of the example problem. The example given in Figure 3 therefore exhibits considerably steeper profiles than those produced by precipitates of radius r_p^* . Note that the peak lithium and helium deposition rates are $6.0 \times 10^{-7} \text{ appm/sec}$ and $1.5 \times 10^{-7} \text{ appm/sec}$, respectively. The latter represents only a 38% maximum increase over the background helium generation rate and is too small to yield an observable halo. There is clearly an effect of the small lithium concentration on void nucleation, however, which confirms the validity of the non-overlapping halo criterion. The ion-induced displacement damage is less than one percent of the total in both halos.

Table 1 shows that halos and associated precipitates were measured in two other specimens at a slightly higher temperature, 430°C , but at fluence levels of 2.8 and $7.0 \times 10^{22} \text{ n/cm}^2$ ($E > 0.1 \text{ MeV}$). In all three specimens there was a noticeable enhancement of void nucleation in the lithium halo while an enhancement in the helium halo was only found at $7.0 \times 10^{22} \text{ n/cm}^2$. Note in Figure 5 that the effect of lithium deposition is more pronounced in the early stages of irradiation but is later overtaken by the effect of the additional helium. The disagreement of measured density changes and local matrix swelling represents not only the normal inhomogeneity of swelling at low fluences but also the influence of the radiation-induced precipitation of other phases, which leads to several tenths of a percent densification at these temperatures.

6. DISCUSSION

The technique described above can be tailored to suit a given alloy by selection of appropriate precipitates, which may occur naturally or which may be deliberately introduced. Several routes are available for the introduction of such precipitates. For alloys containing boron, the particle size distribution and density can be controlled by melting and homogenization procedures. For M_3B_2 , for instance, solutionization of the boron occurs at $1200\text{--}1300^\circ\text{C}$ [8], which suggests that aging at $1150\text{--}1200^\circ\text{C}$ should promote the formation of large M_3B_2 particles. Farrell of Oak Ridge has successfully introduced preformed B_4C particles into many pure metals [9]. In some metals it may be possible to form precipitates with lithium and use the $^6\text{Li}(n,\alpha)^3\text{H}$ reaction to form halos of helium and tritium. For systems forming nickel-enriched phases the use of appropriate neutron spectra may allow the two-step nickel reaction to provide the alpha source.

This technique is quite sensitive to neutron spectra as indicated by Table 2 [10]. This sensitivity allows the study of helium-affected microstructural development under conditions wherein the helium/dpa ratio approaches much larger values. The use of thermal neutron absorber materials around some specimens allows the helium

Fig. 3 - Void swelling produced in an experimental alloy irradiated to 2.2×10^{22} n/cm² (E > 0.1 MeV) at 400°C. An enhancement of void density occurred in the lithium halo associated with the M₃B₂ precipitate. Stereomicroscopy showed that the precipitate lies above the foil section as shown in the inset.

TABLE 1 - ENHANCED VOID FORMATION ABOUT M₃B₂ PRECIPITATES IN VARIOUS SPECIMENS IRRADIATED IN EBR-II

Irradiation Temperature (°C)	Fluence ⁺	Bulk Density Change (-%)	M ₃ B ₂ Particle Diameter (nm)	Void Swelling (%)		Void Density (10 ¹⁴ cm ⁻³)		Mean Void Size (nm)		Back-ground Helium Level (appm)	Enhancement in Halo (appm)	
				Matrix	Void Shells	Matrix	Void Shells	Matrix	Void Shells		He	Li
400	2.2 (11)	-0.03	350	0.17*	0.23 (Li)	4*	16	21*	16	9	4	16
			440		0.20 (Li)		12		15		5.5	22
430	2.8 (14)	-0.23	720	0.086*	0.21 (Li)	2*	9	21*	18	11	22	88
			730		0.27 (Li)		13		16		23	92
430	7 (35)	1.41	800**	0.77	1.7 (Li) 2.8 (He)	3	19 10	35	25 35	28	59	240

+ 10^{22} n/cm², E > 0.1 MeV (dpa).

* Helium halo showed no measurable enhancement above background.

** Estimated.

deposition rate to vary substantially but not the background displacement rate. This allows a number of helium/dpa ratios to be studied in one reactor spectrum. The helium/dpa ratio can also be varied about an order of magnitude in one specimen by analyzing the halos about precipitates of varying size. The latter consideration reflects one of several major strengths of this technique. The use of the two-step nickel reaction in mixed

spectra reactors leads to only one He/dpa ratio unless the nickel is in precipitate form. Studies involving doping of the matrix with boron must not only contend with the chemical effect of boron but also that of lithium. As this study has shown, lithium has a strong influence on microstructural development. The halo method is also applicable in fast reactor spectra as well as that of mixed spectra reactors. The major

TABLE 2 - CROSS SECTIONS AND FLUXES FOR FAST AND THERMAL REACTORS [10]

Spectrum	Mean Neutron Energy, $\bar{E}$ (MeV)	Spectral-Averaged Cross Sections (barns)					
		SS Displacements	SS Composite (n,a)	^{58}Ni (n,y)	^{59}Ni (n,y)	^{59}Ni (n,a)	^{10}B (n,a)
HFIR/PTP	0.42	192.0	1.7×10^{-4}	1.6	35.0	5.4	1.3×10^3
EBR-II Core	0.81	417.0	2.0×10^{-4}	3.2×10^{-3}	0.043	0.0078	1.0
EBR-II Blanket	0.22	162.0	1.2×10^{-5}	2.0×10^{-2}	2.4	0.43	8.4
FTR Gridplate	0.036	40.9	3.1×10^{-9}	9.1×10^{-2}	11.0	2.0	6.8×10^1
FTR Vessel	0.0022	4.31	3.2×10^{-11}	3.2×10^{-1}	18.0	3.0	2.7×10^2
CRBR Core Barrel	0.080	80.0	1.1×10^{-8}	5.2×10^{-2}	6.5	1.2	3.3×10^1

Fig. 4 - Normalized deposition rate of ^7Li and ^4He atoms in halos formed about the M_3B_2 precipitate shown in Figure 3. Fig. 5 - The enhancement of swelling at 400-430°C by lithium and helium atoms deposited in halos surrounding M_3B_2 precipitates.

limitation of the technique is that it cannot be used to study bulk mechanical properties.

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