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PRECIPITATION AND CAVITY FORMATION IN AUSTENITIC STAINLESS STEELS DURING IRRADIATION*

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Microstructural evolution in austenitic stainless steels subjected to displacement damage at high temperature is strongly influenced by the interactions between helium atoms and second phase particles. Cavity nucleation occurs by the trapping of helium at partially coherent particle-matrix interfaces. The recent precipitate point defect collector theory describes the more rapid growth of precipitate-attached cavities compared to matrix cavities where the precipitate-matrix interface collects point defects to augment the normal point deflect flux to the cavitry. Data are presented which support these ideas. It is shown that during nickel ion irradiation of a titanium-modified stainless steel at 675°C the rate of injection of helium has a strong effect on the total swelling and also on the nature and distribution of precipitate phases.

INTRODUCTION

Austenitic stainless steels with compositions close to AISI 316 are currently under development for first wall/blanket applications. The ability of these alloys to sustain the necessary dimensional stability and mechanical properties for economic lifetimes is largely dependent upon the manner in which displaced atoms and helium are accommodated in the microstructure. The accommodation of radiation damage in these materials is closely linked to phase instabilities and microchemical changes which occur during irradiation. The effects of irradiation on the precipitation behavior of austenitic stainless steels were summarized recently by Lee, Maziasz, and Rowcliffe [1]. In a companion paper, Mansur, Hayns and Lee [2] developed the theory necessary to treat several mechanisms believed to be important in coupling precipitation behavior and the phenomenon of void swelling, which is a major source of dimensional instability in these alloys. One of the important aspects of the coupling is the development of voids physically associated with second phase particles; the growth of precipitate-attached cavities is often the major source of swelling in austenitic stainless steels. In this contribution we explore several aspects of the interaction between cavities (voids, bubbles) and precipitate phases in titanium-modified austenitic stainless steels.

EXPERIMENTAL

The work reported here is part of a continuing effort to understand the radiation response of austenitic stainless steels stabilized with titanium. Several heats with variations in major and minor alloying element concentrations have been investigated. These heats were designated the LS1 series and data have previously been reported on heats LS1,[3] LS1A [4] and LS1B [5]. The compositions of these heats fall within the ranges shown in Table 1.

Table 1. Alloy Composition, wt %

Fe	Bal
Cr	14–17
Ni	14–17
Mo	1.5–2.5
Mn	1.5–2.0
C	0.04–0.08
Ti	0.15–0.25
Si	0.4–1.0

Irradiations were carried out on 3-mm-dia and 0.3-mm thick disks which were either in a solution-annealed condition (1100°C) or in a solution annealed plus 25% cold-worked condition. Neutron irradiations were carried out in EBR-II at a damage rate of ~10^{-6} dpa/s and a helium generation rate of ~0.4 appm/dpa. Nickel ion irradiations were carried out in the ORNL dual ion beam Van de Graaff facility at a damage rate of 6×10^{-3} dpa/s; helium was injected simultaneously with the nickel ions at various rates. Displacements were calculated using the EDEP-1 code and a value of 40 eV for the effective threshold energy. Techniques used for specimen preparation and analytical transmission electron microscopy are described elsewhere [1].

NUCLEATION AND GROWTH OF CAVITIES ON PARTICLES

Previous work involving titanium-modified steel heats LS1A, LS1B showed that voids did not develop during 4 MeV Ni ion irradiations to high doses when helium was not injected into the microstructure [4,5]. When helium was simultaneously injected at a rate >0.2 appm/dpa, voids developed in association with particles of G and η silicides over the range 600–700°C. This is in contrast to the behavior of nonstabilized steels sich as AISI 316 and 304 in which voids develop readily in the absence of helium. It was proposed that this behavior occurs because titanium traps residual gases which would otherwise be available to stabilize three-dimensional vacancy clusters. However, when helium is simultaneously injected, migrating helium is trapped at particle-matrix interfaces where it stabilizes void embryos.

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Subsequently it was found that thermal aging of these alloys for periods of time and at temperatures corresponding to ion irradiations (i.e., 1–5 h at 500–750°C) resulted in the precipitation of the MC phase. This phase contained both molybdenum and titanium and nucleation on dislocations occurred rapidly at temperatures >600°C. On the other hand, during irradiations of solution-annealed alloys with simultaneous helium injection at 0.2–0.4 appm/dpa, G, η and γ′ phases developed and MC formation was very limited. The relative proportions of G, η, MC and γ′ varied from heat to heat with changes in Cr, Si and Ti concentrations. In general, η phase was encouraged in alloys with high chromium concentrations, and γ′ was prominent in alloys with high silicon contents.

The early stages of cavity formation at G phase particles in alloy LS1B were examined by irradiating with 4 MeV Ni ions to a peak dose of 5 dpa. Helium was simultaneously injected at a rate of 20 appm/dpa. At this dose, the damage structure consisted of a uniform dispersion of defects, ~100 nm dia exhibiting many of the contrast features associated with faulted loops. It was shown, however, that these defects were thin precipitate particles rather than faulted loops by (a) the existence of Moire′ fringes [Fig. 1(a)], and (b) the existence of precipitate reflections in convergent beam diffraction patterns. The diffraction patterns were consistent with the presence of thin disks of G phase which appeared to have nucleated on interstitial loops. In some instances the G phase appeared to have developed inside the loop, but in other instances the particle and the loop were growing on adjacent planes. It was also observed that at certain sites, particle growth developed initially along several different directions giving rise to complex shapes. Careful imaging showed that helium bubbles (1–3 nm dia) had nucleated at the particle-matrix interface; ~100 bubbles were associated with each particle [Fig. 1(b)]. Bubble nucleation in the rest of the matrix was confined to the occasional dislocation line segment.

It was shown previously [6] that very significant levels of silicon and nickel are segregated at interstitial loops at an early stage of irradiation (1–3 dpa). The present work suggests that in this alloy the segregation stage is followed by the nucleation of G phase at interstitial loops. Even at the earliest stage of growth this phase appears to be an efficient collector for helium. Presumably the trapping occurs as the result of elastic interaction between the small helium atom and the particle-matrix coherency strains or the particle-matrix misfit dislocations. With increasing dose, the matrix dislocation density increases and eventually circumstances become favorable for the bias-driven growth of the attached bubbles at the top of the size distribution.

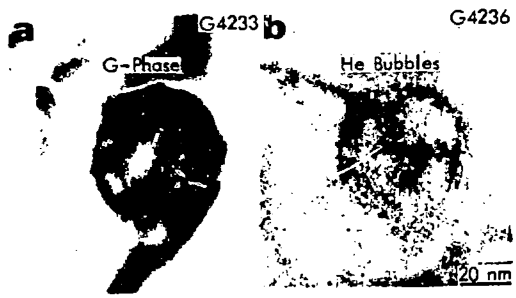

Fig. 1. Solution-annealed LS1B irradiated with 5 MeV Ni ions to 5 dpa at 675°C with simultaneous helium injection. (a) G phase Moire′ fringe contrast; (b) helium bubbles at particle-matrix interface.

The growth of cavities attached to particles has been treated theoretically by Mansur [7]. In this work it is assumed that the particle-matrix interface acts as a collector for point defects. It is considered that this interface also provides a path for the diffusion of point defects to a cavity which has achieved the critical size for void growth. This collector effect augments the absorption of point defects at the cavity-matrix interface. It is shown that the ratio of the growth rate of a cavity attached to a particle to the growth rate of a cavity in the matrix may be expressed in terms of three multiplicative functions:

$$\frac{dr_{cp}}{dr_c} = \frac{r_c r_b}{r_{cp}^2} \cdot b \cdot e \qquad (1)$$

where r_{cp} is the radius of a cavity attached to a precipitate and r_c is the radius of a cavity in the matrix. The quantity r_b is the effective radius of the cavity-precipitate pair. Its exact form is given in ref. [7]. However, it can be approximated as $r_b = (r_{cp}^2 + r_p^2)^{1/2}$, where

r_p is radius of the precipitate. The second term in Eq. (1) is a composite bias modification function which involves the products and differences of the capture efficiencies and densities of all sinks in the material. When the precipitate does not misfit greatly in terms of volume per atom, this term may be taken as unity. The third term is a sink strength modification function. When the growth rates of attached cavities and matrix cavities are being compared in the same microstructure this function also reduces to unity and the ratio of growth rates of attached and unattached cavities is given by:

$$\frac{dr_{cp}}{dr_c} = \frac{\left(r_{cp}^2 + r_p^2\right)^{1/2}}{r_{cp}^2} \cdot r_c \qquad (2)$$

It is predicted that for cavities of the order of or less than the attached precipitate size, the enhancement in growth rate is significant. For typical parameter values the precipitate-attached cavity grows several times larger than the matrix cavity in the time required for the matrix cavity to increase to several times its initial size. This model suggests that for a given precipitate number density, swelling is dictated by precipitate size, provided that the cavities are not the dominant sink in the material. It is expected, for example, that if precipitate size exhibits a characteristic behavior with temperature, then swelling will reflect this behavior.

Some aspects of this model were evaluated with the aid of data obtained from the irradiation of a titanium-modified stainless steel, designated LS1C, irradiated in EBR-II to a fluence of ~35 dpa. At ~400°C, a dense dispersion of γ′, G and η phases developed. Voids formed in the matrix and also at the particle-matrix interfaces of these phases, the attached cavities being significantly larger than those in the matrix [Fig. 2(a)]. With increasing temperature, both the average void and particle size coarsened initially. However, for an irradiation temperature of ~480°C, the volume fraction and average particle sizes of the G and η phases declined sharply, and precipitate structure was dominated by the γ′ phase. This reduction in particle size was accompanied by a corresponding reduction in attached cavity size. At higher temperatures the average particle size of the G phase increased rapidly. Above ~510°C, the G phase was replaced by a Laves phase which provided the major site for the development of large voids at high temperatures [Fig. 2(b)]. The average particle diameter and the average diameter of cavities attached to precipitates were determined for each irradiation temperature, Fig. 3. There is obviously a close similarity between the variation in particle size with temperature and the variation in cavity size. Furthermore, the cavity size at each temperature closely approaches the particle size. Both of

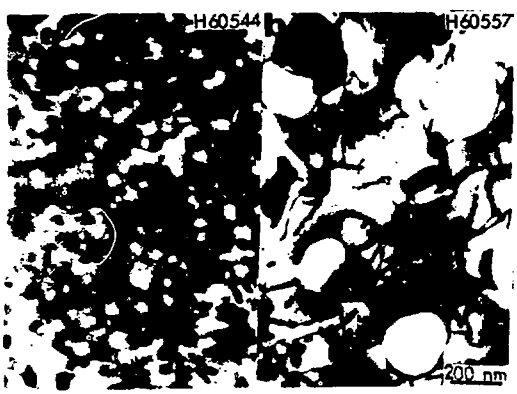

Fig. 2. Cavity-particle association in LS1C irradiated to ~35 dpa in EBR-II at (a) 425°C, (b) 600°C.

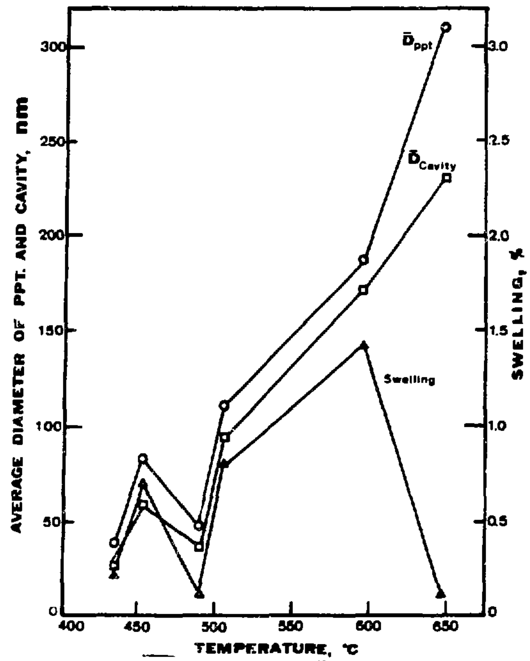

Fig. 3. Temperature dependence of cavity and precipitate size in SA LS1C neutron irradiated to ~ 35 dpa.

these observations are consistent with the model outlined above. The importance of this phenomenon is emphasized by the observation that the temperature dependence of the total swelling is similar to the temperature dependence of the other two parameters in Fig. 3. At temperatures >600°C, the total swelling falls rapidly because of the sharp reduction in void number density.

The integrated effect of point defect collection at the particle interface on cavity size is shown in Fig. 4 for a range of particle sizes. In this particular example, the particle size is taken to remain constant with time. This plot predicts, for example, that in the dose interval required for the matrix cavity to grow by a factor of 3, the precipitate-attached cavity grows by a factor of ~6 for an initial precipitate to cavity radius ratio of 15. These predictions were tested in a set of ion irradiation experiments.

Heat LS1B in a solution-annealed condition was first irradiated with 4 MeV ions to a peak dose of 70 dpa at 675°C without the injection of helium. This irradiation produced a dispersion of G phase particles, but did not produce any detectable voids. Irradiation was then resumed with α-particles only, and a total helium concentration of 400 appm was injected at 675°C. This resulted in the development of helium bubbles nucleated on the damage dislocations and

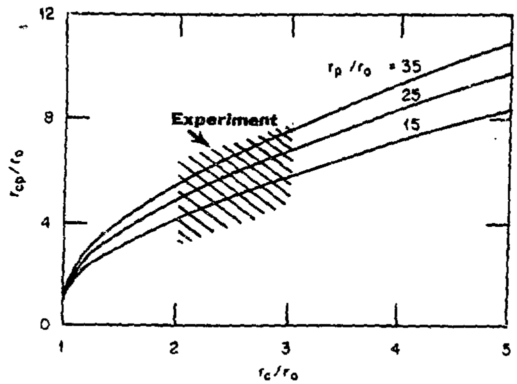

Fig. 4. Comparison of experimental data with the precipitate point defect collector theory predictions.

at the interfaces between the G phase particles and the matrix [Fig. 5(a)]. The average size of the bubbles at the particles and on the dislocations was about the same at this stage. The injection of helium was discontinued and a further irradiation carried out with 4 MeV Ni ions to a peak dose of 20 dpa. During this final irradiation, the size of the G phase particles remained essentially constant. Growth occurred of both the dislocation nucleated and the particle nucleated cavities; however, the latter grew at a substantially faster rate than the former [Fig. 5(b)]. It was found that during the final irradiation, the dislocation-nucleated cavities increased their radii by factors of 2–3. During the same time interval, the precipitate-attached cavities grew by factors of 4–8. The initial precipitate to cavity size ratio was in the range 15–30. This experimental data is represented by the cross-hatched area in Fig. 4. These initial results thus appear to be consistent with the predictions of the precipitate point defect collector theory.

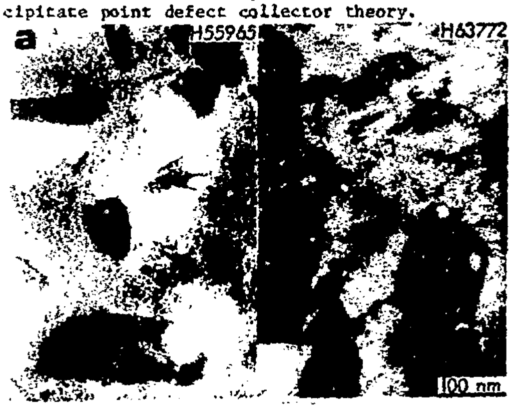

Fig. 5. Accelerated cavity growth on G phase particles in LS1B. (a) Nickel ion irradiated to 70 dpa at 675°C followed by helium injection at 675°C. (b) Same as (a) followed by nickel irradiation to 20 dpa at 675°C.

THE EFFECT OF HELIUM ON PRECIPITATION BEHAVIOR

The effects of helium generation rate on cavity formation and on the precipitation of the G and MC phases were examined using alloy LS1B in a solution-annealed condition. Irradiations were carried out to peak doses of 5 or 70 dpa at 675°C and helium was introduced by simultaneous injection at rates of 0.4, 4.0 or 20 appm/dpa. The total swelling increased linearly with helium injection rate from <0.1% with 0.4 appm/dpa to a value of 2.0% with 20 appm/dpa (Fig. 6). At the lowest injection rate voids nucleated exclusively at G phase particles but with increasing helium injection rate, nucleation occurred at other sites as well. With increasing injection rates, the average size of the G phase particles decreased significantly while the number density remained approximately constant (Fig. 7). With increasing injection rate, the fraction of G phase particles associated with voids increased as shown in Fig. 6. A population of small (2–5 nm dia) helium bubbles also developed, their number and size increasing with injection rate.

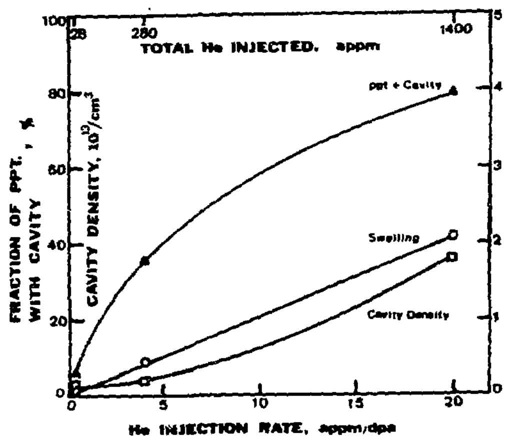

Fig. 6. Swelling and cavity data for SA LS1B nickel ion irradiated with simultaneous injection of helium.

The reduction in growth rate of the G phase with increasing injection rate is believed to be related to the increase in bubble nucleation rate. Because of the increased sink density the recombination rate is increased and the flux of point defects to any individual sink is reduced. Furthermore, the available solute is distributed over a larger number of sinks. The reduction in particle growth rate has no significant effect on total swelling since voids develop elsewhere in the matrix with increasing helium injection rate.

These irradiations were repeated with the alloy in a 25% cold-worked condition. A completely different microstructural response to increasing helium injection rate was observed. An initial

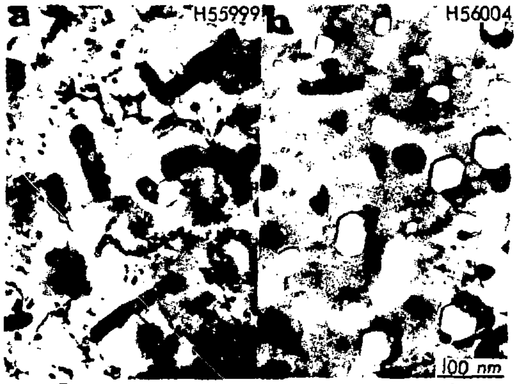

Fig. 7. SA LS1B nickel ion irradiated to 70 dpa at 675°C with simultaneous injection of helium. (a) 0.4 appm/dpa; (b) 20 appm/dpa.

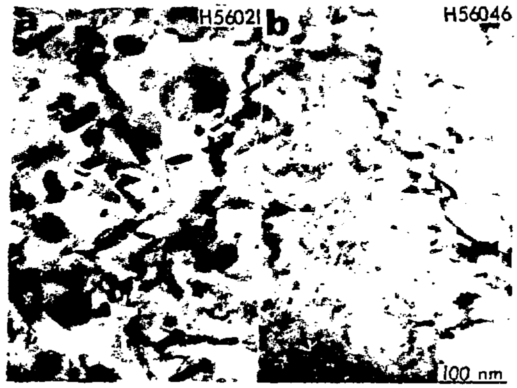

Fig. 8. CW LS1B nickel ion irradiated to 70 dpa at 675°C with simultaneous injection of helium. (a) 0.4 appm/dpa; (b) 20 appm/dpa.

irradiation was carried out at 675°C to a peak dose of 5 dpa with a helium injection rate of 0.4 appm/dpa. At this stage it was found that precipitation consisted entirely of the MC phase nucleated on the cold work dislocation network. This situation was not maintained, however, and after a dose of 70 dpa it was found that in many areas the cold-worked structure had substantially recovered and that nucleation of G phase had occurred in conjunction with the dissolution of the MC phase. The average swelling at 70 dpa was <0.2%. However, every void was associated with a G phase particle. In areas where dislocation recovery was retarded, precipitation of G phase was inhibited and voids did not develop. With increasing injection rate, G phase nucleation became increasingly difficult and MC became the dominant phase. With injection rates of 4 or 20 appm/dpa G phase developed only in isolated patches where the dislocation density was lower than average; these were the only areas containing voids. In the rest of the matrix, a fine (>10^{16} cm^{-3}) dispersion of helium bubbles developed (Fig. 8). High-resolution TEM examination showed that the great majority of bubbles were directly associated with small MC precipitates (Fig. 9). The bubble diameters ranged from 2–5 nm while the MC particles ranged from 3–10 nm. The smallest particles were associated with a single bubble, whereas larger particles were associated with several bubbles. In contrast to the solution-annealed case, swelling did not increase with increasing helium injection rate and was limited to ~ 0.2% in all cases; compare Figs. 7 and 8.

The metastability of the MC phase during irradiation was reported earlier [1]. It was noted that pre-existing MC particles may dissolve under certain irradiation conditions and may be replaced by G or Laves phases. We have also found recently that under certain thermal aging conditions, although the MC phase nucleates very rapidly, it will subsequently undergo dissolution concurrently with the precipitation of other phases rich in molybdenum and titanium. In the present experiments, the initially high dislocation density provides sites for the rapid nucleation of MC. As the displacement dose is increased at the lowest helium injection rate, the dislocation structure relaxes, and conditions become favorable for the interstitial loop–G phase nucleation mechanism. As the G phase develops, absorbing titanium and molybdenum, the MC particles dissolve. It is thought that cascade dissolution plays an important role in this process [4]. When the helium injection rate is increased, however, the MC → G transformation is arrested and the fine dispersion of dislocation nucleated MC is maintained. Since G phase is suppressed, large voids do not develop. The major factor involved in the suppression of G phase and the inhibition of void swelling appears to be the rapid nucleation of small bubbles at the MC particle–matrix interface. Under these conditions the stability of the MC particles is increased possibly because (a) the development of G phase is suppressed because of the high sink density, and (b) the presence of bubbles at the interface relieves some of the misfit strain in the lattice. It was pointed out by Maziasz [8] that because of the large positive volume misfit involved, the MC phase should behave as a strongly biased vacancy sink while the particle is growing. This is thought to be a significant factor in the development of associated bubbles at such small particle sizes. The fine dispersion of MC-bubble entities retards recovery of the cold work thus maintaining conditions inimical to G phase nucleation. The pinning of the dislocation structure also probably reduces the net bias of the system and retards the transformation of bubbles into voids.

SUMMARY AND CONCLUSIONS

These experiments, together with those reported earlier clearly demonstrate that the introduction of helium has a strong impact on microstructural evolution in Ti-modified stainless steels subjected to high temperature displacement damage. It has been observed that during

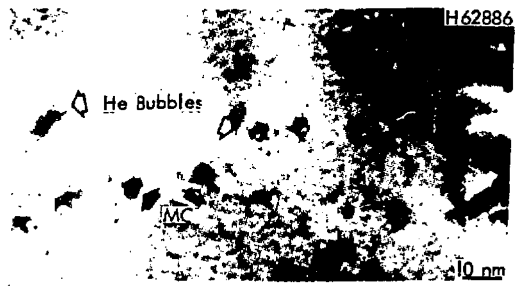

Fig. 9. MC particles and helium bubbles in CW LS1B.

irradiation to a dose of 70 dpa at 675°C and at a damage rate of $\sim 10^{-3}$ dpa/s

(a) Void swelling in the solution annealed alloy increases in proportion to the rate of helium generation.

(b) Void swelling in the cold-worked alloy is insensitive to helium generation rate.

(c) The average particle diameter of the major phase (G) in the SA alloy decreases with increasing helium generation rate.

(d) In the CW alloy, the stability of the MC phase increases with helium generation rate and the development of G phase is inhibited.

It was pointed out earlier that helium could modify the dislocation structure by either enhancing interstitial clustering or by increasing the survival rate of interstitial clusters through the immobilization of vacancies [5]. It is now evident that the trapping of helium at particle-matrix interfaces is also an important factor in the evolution of the damage structure and the development of void swelling.

It has been shown that the variations in cavity size and precipitate size with neutron irradiation temperature are consistent with the precipitate point defect collector theory. Measurements of the relative growth rates of cavities in the matrix and cavities attached to precipitates in a nickel ion irradiation experiment have provided further support for the theory.

It has been suggested that void swelling is coupled to precipitation primarily because the development of certain phases results in the depletion of nickel from the matrix [9]. This explanation is based upon the observed sensitivity of swelling to nickel content in high swelling Fe-Cr-Ni ternary alloys [10]. However, it is unlikely that the same sensitivity will persist in complex structural alloys containing high concentrations of particles ($>10^{15}$ cm^{-3}) and/or significant concentrations (>100 ppm) of solutes such as silicon and carbon which interact strongly with point defects. While matrix nickel concentration may have an influence on void growth rates, there are many other effects associated with precipitation which may dominate swelling behavior. Mansur, Hayns, and Lee [2] have classified three general modes of precipitate action — i.e., direct, e.g., precipitate point defect collector effect, indirect, e.g., changes in overall sink strength or dislocation capture efficiency, and mediated, e.g., depletion of point defect traps in the matrix. The work described here emphasizes some direct effects, namely, the interaction between helium atoms and particles and the collector effect of particles on void growth. Consideration of these effects alone indicates both that helium will be most succesefully accommodated and that void swelling will be minimized if a high density of small particles is maintained in the microstructure. The development of coarse particles which provide a large collector interface must be minimized if the formation of large voids is to be controlled.

Acknowledgments

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References

[1] E. H. Lee, P. J. Maziasz, and A. F. Rowcliffe, "The Structure and Composition of Phases Occurring in Austenitic Stainless Steels in Thermal and Irradiation Environments," Proc. of the AIME Symposium on Irradiation Phase Stability, Pittsburgh, PA (1980).

[2] L. K. Mansur, M. R. Hayns and E. H. Lee, "Mechanisms Affecting Swelling in Alloys with Precipitates," Proc. of the AIME Symposium on Irradiation Phase Stability, Pittsburgh, PA, 1980.

[3] E. E. Bloom, J. O. Stiegler, A. F. Rowcliffe, and J. M. Leitnaker, Scripta Met. 10 (1976) 303–308.

[4] E. H. Lee, A. F. Rowcliffe, and E. A. Kenik, J. Nucl. Mater. 83 (1979) 79–89.

[5] E. A. Kenik and E. H. Lee, "The Influence of Injected Helium on the Phase Instability of Ion-Irradiated Stainless Steel," Proc. of the AIME Symposium on Irradiation Phase Stability, Pittsburgh, PA (1980).

[6] E. A. Kenik, Scripta Met., 10 (1976) 733.

[7] L. K. Mansur, "Theoretical Evaluation of a Mechanism of Precipitate-Enhanced Cavity Swelling During Irradiation," to be published in Philosophical Magazine.

[8] P. J. Maziasz, "Helium Trapping at Ti-Rich MC Particles in Neutron Irradiated Type 316 + Ti Steel," Proc. of the AIME Symposium on Irradiation Phase Stability, Pittsburgh, PA, 1980.

[9] H. R. Brager and F. A. Garner, Effects of Radiation on Structural Materials, ASTM-STP-683 (1979), p. 207.

[10] W. A. Johnston, J. H. Rosolowski, and A. M. Turkalo, J. Nucl. Mater. 54 (1974) 24.