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Fe-Cr-Ni AUSTENITIC ALLOYS

F. A. Garner
T. Lauritzen
M. A. Mitchell

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Pacific Northwest Laboratory
Richland, Washington 99352

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Frank. A. Garner¹, Thor Lauritzen², and Matthew A. Mitchell³

**THE COMPLEX ACTION OF MAJOR SOLUTES ON RADIATION-INDUCED SWELLING OF
Fe-Cr-Ni AUSTENITIC ALLOYS**

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ABSTRACT: The radiation-induced swelling of simple Fe-Cr-Ni austenitic alloys is known to be very sensitive to solute additions. It is shown in this paper that three of the most common solute elements (P,Si,Mo) exert a very complex and often non-monotonic influence on swelling with increasing solute level. The complexity of this influence and its dependence on other variables appears to be the result of a closely balanced competition between two or more roles played by each solute in its interaction with both vacancies and interstitials. This competition yields a variety of different swelling behaviors in response to changes in solute or solvent composition, displacement rate, and irradiation temperature.

Key Words: Fe-Cr-Ni alloys, void swelling, atomic size difference, silicon, molybdenum, phosphorus, neutron irradiation, ion irradiation.

INTRODUCTION

When addressing the influence of individual solutes on radiation-induced void swelling in simple Fe-Cr-Ni austenitic alloys, it is often assumed that each solute element exerts a monotonic influence with solute level at a given set of irradiation conditions. The nature of this influence is often linked to the sign and magnitude of the size difference between the solute and solvent atoms, implying a single role of the solute in the migration and segregation of point defects created by irradiation.

Recent studies conducted in EBR-II have shown, however, that silicon and phosphorus additions lead to significantly non-monotonic swelling

¹Staff Scientist, Pacific Northwest Laboratory, Richland, WA 99352

²Senior Engineer, General Electric Corporation, Sunnyvale, CA 94086

³Graduate Student, University of Illinois, Urbana, IL 61801

behavior under some irradiation conditions[1], as shown in Figs. 1 and 2. Similar behavior has also been observed in several charged particle irradiation studies.[1-4] Such behavior has been described to result from a competition between two or more separate roles played by an individual solute, with the outcome determined not only by the solute concentration but by the details of the irradiation environment, such as temperature and displacement rate.[1,5-8] As reviewed in refs. 1, 5 and 8, silicon and phosphorus are each known to interact with both interstitials and vacancies, with each interaction exhibiting a different dependence on composition and temperature. These elements, for example, are thought to bind with interstitials[9,10] and thus strongly accelerate nucleation of Frank loops [9] and the development of the dislocation network that precedes void nucleation. They also are thought to increase the overall level of vacancy mobility, which reduces the vacancy supersaturation and thereby decreases the void nucleation rate.[1,10,11] These two mechanisms alone, acting in the absence of other mechanisms, could produce the non-monotonic swelling behavior, especially at lower irradiation temperatures where interstitial binding would exert its largest influence. Both silicon and phosphorus also exhibit a tendency toward radiation-induced segregation and precipitation, however, leading to an additional time-dependent complexity in their influence on diffusion of vacancies and interstitials in the alloy matrix. The precipitates themselves may also play some direct role in determining the sink strengths for point defects and gas atoms, as well as affecting dislocation mobility.

Current studies in the experimental series described in this paper are directed toward the determination of the various roles of three solutes (P, Si, Mo) while either in solution or in precipitates. This paper presents a summary of results of both unpublished and recently published studies conducted in either the EBR-II or FFTF fast reactors. Some previously unpublished ion bombardment data are also included in addition to published ion bombardment data from other researchers to illustrate that similar solute-induced behavior occurs in a variety of irradiation environments.

Figure 1. Influence of phosphorus on neutron-induced swelling of annealed Fe-15Cr-25Ni in EBR-II.[1]

Figure 2. Influence of silicon on neutron-induced swelling of annealed Fe-15Cr-25Ni in EBR-II.[1]

Experimental Details

All specimens examined in this study were irradiated in the form of 3 mm diameter microscopy disks that were ~0.25 mm thick. Three irradiation facilities were employed. Specimens irradiated in EBR-II were irradiated in contact with sodium, with temperatures calculated from knowledge of gamma heating rates. Uncertainties range from $\pm 5^\circ\text{C}$ at 400°C to $\pm 25^\circ\text{C}$ at 650°C . The irradiation proceeded at displacement rates that ranged from 0.6 to 1.1×10^{-6} dpa/s. The neutron spectra in EBR-II yield ~5 dpa for each 1.0×10^{26} n/m² ($E > 0.1$ MeV). Specimens irradiated in FFTF in the Materials Open Test Assembly (MOTA) were also in contact with sodium but were actively maintained at $\pm 5^\circ\text{C}$, independent of the target temperature. For FFTF irradiations the displacement rates were $\sim 1.4 \times 10^{-6}$ dpa/s, but the dose conversion factor ranged from 4.2 to 4.6 dpa per 10^{26} n/m² ($E > 0.1$ MeV) depending on which reactor cycle was involved.[12] The radiation-induced changes in density were measured by an immersion density technique known to be accurate to $\pm 0.16\%$ swelling.

The Fe-15Cr-20Ni-Mo alloys were irradiated not only with neutrons but also with 5 MeV Ni⁺ ions at 2×10^{-2} dpa/s by Johnston and coworkers fifteen years earlier.[2] These previously unpublished data were derived using a masking and step height analysis procedure described in their earlier papers.[2] Some microstructural data on γ' formation were also obtained by microscopy in this study by reexamining some of Johnston's previously examined Fe-15Cr-20Ni-Si specimens, still in excellent condition after so many years.

RESULTS AND DISCUSSION

Fe-15Cr-25Ni-P Alloys

The behavior shown in Figure 1 at the lower two irradiation temperatures was thought to be very surprising at first. Therefore, an expanded version of this experiment was repeated in FFTF using the same alloys that were irradiated in EBR-II. Both annealed and 30% cold-worked specimens were irradiated at 420°C , 520°C and 600°C to doses of 36.6, 34.7 and 31.8 dpa, respectively. As shown in Fig. 3, a non-monotonic

Figure 3. Influence of phosphorus, temperature and cold-work on swelling of Fe-15Cr-25Ni in FFTF.[8]

swelling behavior was observed at 420°C for both the annealed and cold-worked specimens. Cold-working reduced the swelling at all phosphorus levels at 420°C, in agreement with the general observation of cold-work's influence on swelling. The swelling also fell with increasing irradiation temperature in the annealed low-phosphorus alloy, as was also observed in the EBR-II study. The swelling of the annealed phosphorus-containing alloys at 520 and 600°C also exhibited the same trends with phosphorus content observed earlier in EBR-II.

A new surprise arose, however, in the observation that at 520 and 600°C the cold-worked specimens swelled more than the annealed specimens, with the difference being dependent on both temperature and phosphorus content. While initially perplexing, this finding was supported by a number of observations that at higher irradiation temperatures simple Fe-Cr-Ni ternary alloys (without phosphorus) often exhibit a reversal of the conventional role of cold-work on swelling.[8,13] This reversal was attributed to the role of cold-work in overcoming the difficulty of generating and maintaining a stable dislocation network in solute-free (and therefore relatively soft) alloys at high irradiation temperatures. A similar behavior has also been observed in a variety of pure metals and other alloys.[14-16]

Another example of the interactive roles of phosphorus and cold-work on void swelling is shown in Fig. 4 for another EBR-II experiment, confirming once again that the various phenomena shown in Figs. 1 and 3 are relatively reproducible.[8] In this study it was also shown that the formation of phosphide precipitates at 500 and 600°C was delayed by cold-working. Phosphides did not form at 425°C in either the annealed or cold-worked specimens.

The non-monotonic behavior observed in FFTF at 420°C (Fig. 3) does not arise from the influence of phosphide precipitation, however, since no phosphides were observed at any phosphorus level in either alloy starting condition.[8] This is in agreement with the results of Muroga and co-workers[6] who examined the microstructures of the EBR-II specimens shown in Fig. 1 and found that phosphides did not form during either the increasing or decreasing portions of the swelling curves at relatively low irradiation temperatures. Phosphides did form in these alloys at higher irradiation temperatures and in a very reproducible manner, as shown in Fig. 5. The boundary of the phosphide regime is strongly dependent on both temperature and phosphorus level, but it may also be sensitive to displacement rate, nickel level and cold-working.[8]

Most previous irradiation experiments directed toward the influence of phosphorus did not explore the low-phosphorus regime in sufficiently small increments to allow observation of the possible existence of non-monotonic behavior. However, in two studies on simple Fe-Cr-Ni ternary alloys in the annealed condition, each having lower nickel levels but encompassing relatively low phosphorus levels, only monotonic swelling behavior was observed after neutron irradiation.[17,18] At lower nickel levels voids are known to nucleate much more easily and there may not be much of a nucleation barrier for phosphorus to help overcome. The difference between monotonic and non-monotonic behavior with phosphorus content may be due to the relative ease of nucleating voids in ternary Fe-Cr-Ni alloys and thus may reflect only a difference in nickel levels. If this proposal is correct, one might expect to observe non-monotonic behavior in low-nickel phosphorus-bearing alloys in which void nucleation was made more difficult by cold-working and/or additions of other solutes such as silicon and titanium. In fact, this type of behavior has recently been observed in another series of irradiations conducted in EBR-II on relatively complex alloys.[7] Some examples are shown in Fig. 6. Of particular interest in these studies was the observation that non-monotonic swelling behavior in these more complex

alloys often extended to higher temperatures ($\geq 600^\circ\text{C}$) than observed in simple ternary alloys.

Figure 4. Comparison of swelling in Fe-15Cr-25Ni with two phosphorus levels (0.005 and 0.055 wt% P) and two starting conditions after irradiation in EBR-II to 14 dpa[8].

Figure 5. Phosphide formation observed in Fe-15Cr-25Ni following irradiation in either EBR-II or FFTF[8].

Figure 6. Influence of phosphorus and cold-work on swelling of Fe-16.2Cr-13.8Ni-2.5Mo-2.0Mn-1.5Si-0.2Ti-0.04C in EBR-II.[7]

Fe-15Cr-XNi-Si Alloys (x=20,25)

The action of low levels of silicon to increase swelling (Fig. 2) was also unexpected and a more detailed experiment to explore this phenomenon is currently in progress in FFTF. Of particular interest is the observation that the non-monotonic behavior of the 25Ni-Si alloy series in EBR-II extends over a larger temperature range than that of the 25Ni-P alloys. Both alloy series were irradiated in the same experiment, and thus the different behavior must reflect similar but slightly different roles of each solute with respect to point defect interactions.

Sekimura and coworkers [5] have examined the microstructures of the 25Ni-Si alloys and found that at three out of the five irradiation temperatures where swelling increased initially with silicon addition, precipitation of γ' (Ni_3Si) did not occur, as shown in Fig. 7. This suggests, but does not prove that γ' formation was unrelated to the increase in swelling. At higher silicon levels, however, γ' was found to have formed at all five temperatures while swelling decreased from its peak value. It is therefore not possible to determine from these data alone whether the decrease in swelling arose primarily from the higher level of silicon initially in solution, or whether it was due to some direct action of the γ' precipitates themselves.

It is known, however, that γ' precipitation is also a strong function of nickel content. In the EBR-II experiment under discussion, several Fe-15Cr-20Ni-Si alloys were also irradiated. Fig. 8 shows that reducing the nickel level from 25 to 20% leads to a strong reduction in the temperature regime of γ' formation. As shown in a comparison of Figs. 2 and 9, swelling is increased by the lower nickel level and then decreased by

Figure 7. Formation of γ' precipitates observed in Fe-15Cr-25Ni-Si alloys irradiated in EBR-II to 8.2-14.3 dpa[5].

Figure 8. Formation of γ' precipitates observed in annealed Fe-15Cr-20Ni-Si alloys irradiated in EBR-II to 12-14 dpa[5].

Figure 9. Swelling observed in three conditions of Fe-15Cr-20Ni-Si alloys irradiated in EBR-II to 12-14 dpa[5].

silicon addition. At the two higher irradiation temperatures, however, this decrease occurs without formation of γ' . It is obvious that the role of silicon on swelling in these two alloy series is expressed primarily while silicon is in solution and that any direct effects of γ' formation are negligible or at least secondary in importance. The major role of γ' precipitates is, therefore, only to remove some fraction of the nickel and silicon from the alloy matrix, a process which controls only in small part the duration of the void incubation period.

The formation of γ' precipitates also is very sensitive to the displacement rate, as illustrated in Fig. 10. In this comparison the γ' regime is observed to shift upwards in temperature when the displacement rate is increased three orders of magnitude.[19,20] The swelling regime also shifts upward a comparable amount.[2] Note that γ' does not form (even at these high levels) in the range $\leq 0.3\%$ Si. The relatively low γ' volume fractions formed during ion irradiation[19] also indicate that most of the silicon stays in solution at these nickel levels. It appears from the comparison shown in Fig. 10 that higher levels of silicon are required to produce γ' at higher

Figure 10. Comparison of γ' formation in Fe-15Cr-20Ni-Si alloys produced by EBR-II neutrons at -1×10^{-6} dpa/s and 5 MeV Ni^+ ions at 2×10^{-2} dpa/s. The γ' volume fractions are shown in parentheses.

displacement rates and higher temperatures.

Unfortunately, the Fe-15Cr-20Ni-Si alloys irradiated in EBR-II did not employ sufficiently small increments in silicon content to observe the possibility of non-monotonic behavior at low silicon levels. As shown in Fig. 11, it is quite possible that the non-monotonic behavior observed at 25Ni might have occurred at 20Ni as well. It appears, however, that at lower nickel levels (<20Ni) even more complexity can develop in the dependence of void swelling on silicon content. An example is shown in Fig. 12 for silicon-modified AISI 316. [21] At the higher silicon levels, extensive precipitation strongly changes the matrix composition and the sink density for point defects. Note that the regime between 0.0 and 0.48% silicon was not explored in this experiment, possibly overlooking potential non-monotonic behavior in this range.

Fe-Cr-Ni-Mo Alloys

The Fe-15Cr-20Ni alloy was also irradiated along with several molybdenum modifications in a variety of experiments. Johnston, Lauritzen and their coworkers used 5 MeV Ni⁺ ions to study the compositional dependence of swelling in a wide range of simple austenitic alloys. [2] Only a fraction of the Fe-Cr-Ni-Mo data was reported, however. As shown in Fig. 13, small additions of molybdenum significantly increased swelling at all temperatures studied. Further increases in molybdenum caused a reversal in swelling behavior at 675°C, leading to a decrease in swelling. Similar behavior has now been observed in Fe-15Cr-20Ni-Mo alloys irradiated in EBR-II (Fig. 14b) and FFTF (Fig. 15b), but non-monotonic behavior was not observed at the

Figure 11. Two possible interpretations of the swelling behavior in EBR-II of Fe-15Cr-20Ni-Si alloys at 420°C.

Figure 12. Density changes observed in five silicon variations of 316 stainless steel irradiated in EBR-II to exposures ranging from 45 to 60 dpa [21].

Figure 13. Influence of molybdenum on swelling of Fe-15Cr-20Ni after 20 appm helium injection followed by Ni^+ irradiation to 170 dpa.

lowest neutron irradiation temperature.

In Fe-18Cr-8Ni the effect of molybdenum appears to be less pronounced, as shown in neutron irradiations in EBR-II (Fig. 14a) and FFTF (Fig. 15a). The dependence of swelling on molybdenum content is influenced by the base composition and as is further illustrated by the range of swelling behavior observed in several published studies [4,22] involving ion bombardment (Figs. 16 and 17). In none of the studies described in this section, however, were the formation of any precipitates observed during microscopy of these Fe-Cr-Ni-Mo alloys.

The tendency toward monotonic reduction in neutron-induced swelling at lower irradiation

temperatures while tending to increase swelling at higher temperatures is often preserved in more complex alloys, as shown in Fig. 18.

SUMMARY AND CONCLUSIONS

The common features of the various results presented in this paper are as follows:

1. Elements such as phosphorus, silicon and molybdenum can either increase or decrease the swelling of simple Fe-Cr-Ni alloys.
2. The action of each individual solute is influenced by the base composition, displacement rate and irradiation temperature.
3. In each case studied here, the primary effect of each of the three solutes appears to be exerted while the solute is in solution. Precipitation plays either no role or is secondary in importance.

These common features are viewed as indications of a competition between two or more mechanisms involving the action of each solute with vacancies and interstitials. The competition is thought to be so closely balanced that under some conditions, especially involving variables that influence point defect concentrations and their mobility, the competition can be tilted in favor of one mechanism dominating over the influence of the other. Temperature and displacement rate are obviously important in this respect, but so is the concentration of the base alloy. Both the nickel and chromium concentrations are known to affect vacancy mobility in Fe-Cr-Ni alloys [1,11,23], and their influence must compete with those of the various solutes discussed in this paper.

Figure 14. Effect of composition and temperature on neutron-induced swelling of three different model Fe-Cr-Ni-Mo alloys irradiated to 14 dpa in EBR-II.

Figure 15. Effect of composition and temperature on neutron-induced swelling of three Fe-Cr-Ni-Mo alloys irradiated to 31.8 to 36.6 dpa in FFTF.

Figure 16. Ion-induced swelling in Fe-20Cr-12Ni-Mo alloys reported by Sethi and Okamoto[22].

Figure 17. Ion-induced swelling in Fe-7.5Cr-20Ni-Mo alloys reported by Gessel and Rowcliffe[4].

Figure 18. Influence of molybdenum on neutron-induced swelling observed in a complex titanium-modified stainless steel irradiated in EBR-II to 23 and 56 dpa at 425°C and 32, 50 and 75 dpa at 540°C.

It is important to note that the non-monotonic behavior observed in these studies calls into question the tendency to label the action of each solute solely in terms of its size difference. While phosphorus and silicon are usually considered to be subsize elements, molybdenum is an oversized element[24-27], and yet each of these elements can either increase or decrease swelling.

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