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Swelling and microstructure of pure Fe and Fe–Cr alloys after neutron irradiation to ∼26 dpa at 400 °C

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Abstract

The microstructures of pure Fe and various Fe–Cr binary alloys in both the annealed and heavily cold worked conditions were investigated after irradiation to 25.8 dpa at 4×10^{-7} dpa s^{-1} in the BR-10 fast reactor. Microscopy has shown that the largest swelling of 4.5% was observed in the cold worked pure iron while that of annealed Fe is only 1.7%. Additions of 2% chromium resulted in a decrease of swelling, but the swelling of cold worked Fe–2Cr alloy was still higher than that of the annealed condition. Independent of the initial starting condition, swelling in the Fe–6Cr alloy was completely suppressed. In alloys with higher chromium content swelling of 0.04–0.05% was observed only in samples irradiated in the annealed condition. There were also significant changes in dislocation and precipitate microstructure.
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1. Introduction

Metals and alloys possessing a bcc lattice have traditionally been considered as materials with high resistance to swelling, especially when compared to that of fcc metals and alloys. Experimental data provided by Gelles on model iron-base alloys showed low swelling levels after irradiation to doses as high as 200 dpa when irradiated at relatively high displacement rates in the Fast Flux Test Facility (FFTF) [1]. There has been a general perception that the low swelling rate of bcc materials is an intrinsic property of bcc crystal lattice [2]. However, recent data have cast doubt on the general validity of such a perception. The first contrary data showed that V–5%Fe swelled ∼100% after neutron irradiation to 52 dpa at an average swelling rate of ∼2%/dpa [3] while the steady state swelling rate in iron-base alloys with fcc lattice does not exceed 1%/dpa [4].

In one of our earlier reports, pure Fe and Fe–Cr alloys in the lightly cold-worked (5–15%) condition were irradiated near the top of the BR-10 fast reactor to 6 dpa at $\sim 1 \times 10^{-7}$ dpa s^{-1}, which is a relatively low displacement rate for a fast reactor. Microstructural examination showed that the swelling of pure iron reaches 3%, implying an average swelling rate of ∼0.5%/dpa, although the same study showed that additions of Cr resulted in partial but

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strong suppression of swelling [5]. At that time it was suggested that the high average swelling rate of ~0.5%/dpa in pure Fe might be related to the combined effects of cold work as well as to the relatively low dose rate of $\sim 1 \times 10^{-7}$ dpa s^{-1}.

Garner and co-workers later showed that cold working often accelerates the onset of void swelling in metals and alloys, both fcc and bcc, when irradiated under conditions where void nucleation was otherwise rather protracted [6,7]. Garner also showed that the swelling of both Fe–Cr–Ni and Fe–Cr alloys was a transient-dominated process, with the transient duration decreasing very strongly as the atomic displacement rate decreased [7–10]. More importantly, it was shown that the steady state swelling rate of Fe–Cr alloys was at least 0.2%/dpa, significantly larger than previously reported by Gelles after irradiation at higher displacement rates.

Fortunately, the alloys of immediate interest were irradiated in several positions in BR-10. In order to check the possibility that cold-working and lower dpa rates could increase swelling, another set of the same Fe and Fe–Cr alloys were irradiated in-core to 25.8 dpa at 4×10^{-7} dpa/s. While this dpa rate is higher by a factor of four compared to that of our previous study, it is still lower by an order of magnitude compared to studies conducted in FFTF by Gelles [1]. To study the effect of thermal–mechanical treatment, these Fe and Fe–Cr alloys were irradiated in both solution treated and heavily cold-worked conditions.

2. Experimental details

Strips of pure iron with <0.015 C, <0.005 P, <0.05 S, 0.012 Si, 0.001 Al, 0.0015 Cr, 0.0015 Cu, 0.007–0.03 Ni, <0.0015 Mg, 0.001 Mo, 0.18 O, 0.002–0.004 N (wt%), and four Fe–Cr alloys (2, 6, 12 and 18 at.% Cr) with similar low levels of impurities (>99.9% Cr) were used to prepare the specimens. These strips were originally 0.5 mm in thickness and were rolled in one pass to 0.12 to 0.15 mm thickness. The average level of cold work in these foils was ~250 %. Half of these foils were then annealed at 1100 °C for 5 min and then quenched in water. Plates of 6 × 15 mm were prepared from both cold-worked and annealed material. A package containing both types of plates was loosely bound with Nichrome wire and placed vertically in a perforated capsule at 140–155 mm above the core midplane of the BR-10 fast reactor. The irradiation was performed in flowing sodium at 400 °C, reaching 25.8 dpa at 4×10^{-7} dpa s^{-1}.

After irradiation, disks of 3 mm diameter were punched from these plates and thinned for electron microscopy using a STRUERS jet device. Unirradiated archive specimens were similarly prepared. The specimens were investigated using a JEM-100CX electron microscope equipped with a side-entry goniometer stage. The first details describing the microstructure of the pure Fe specimens irradiated to 25.8 dpa were reported earlier [11]. This report covers the final phase of the experiment where all Fe–Cr alloys were examined.

3. Results

In the unirradiated condition (both annealed and cold-worked) Fe and Fe–18Cr were found to have ferritic structure, Fe–6Cr was completely martensitic, and the Fe–2Cr and Fe–12Cr alloys had two-phase structure with 70–80% of ferrite and 20–30% martensite. The ferrite and martensite phase fractions were determined by measuring the grain sizes on micrographs at a low magnification. In the heavily cold-worked materials, ferritic grains were observed to have undergone fragmentation and formation of clearly expressed sub-grain structure. Data on the initial dislocation density in both cold-worked and annealed materials are shown in Tables 1 and 2. The grain size in cold-worked materials was 20–50 μm. The grain size in annealed materials was larger at 50–100 μm.

Neutron irradiation resulted in significant structural changes, namely, formation of voids, dislocation loops and precipitates, and redistribution of dislocations. Data on microstructural characteristics of the irradiated materials are also shown in Tables 1 and 2.

3.1. Voids

As seen from data shown in Tables 1 and 2, pure iron exhibits the highest swelling, with cold-worked iron at 4.5%, but annealed iron is only 1.7% (Fig. 1(a) and (b)). Adding 2% chromium results in a decrease of swelling for both conditions, but the swelling of cold-worked Fe–2Cr is still higher than that of the annealed alloy, however. Voids and dislocation loops formed only in ferritic grains in Fe–2Cr. The swelling of Fe–6Cr was suppressed completely, independent of the initial thermal–mechanical treatment. The relative swelling behavior of the

Table 1
Characteristics of the microstructure in Fe–Cr alloys (250 % C.W.) irradiated in BR-10 at 400 °C to 25.8 dpa

Chromium content (at.%) Structure		0 F	2 F + M	6 M	12 F + M	18 F
Dislocation density ρ_d^{unirr} (10^{14} m^{-2})	F	10–20	10–20	–	10–20	10
	M	–	10–20	10–20	10–20	–
Dislocation density $\rho_d^{irr.}$ (10^{14} m^{-2})	F	0.4	0.5	–	10	10
	M	–	10	10	10	–
Mean void diameter $\langle d_v \rangle$ (nm)		120	44	–	–	–
Void number density N_v (10^{20} m^{-3})		0.32	1.2	–	–	–
$\Delta V/V$ (%)		4.5	1.1	–	–	–
Mean loop diameter $\langle d_l \rangle$ (nm)		85	36	–	–	–
Loop number density N_l (10^{20} m^{-3})		0.9	10	–	–	–
Mean diameter of α'-precipitates $\langle d_p \rangle$ (nm)		–	–	–	n.m.	10
Number density of α'-precipitates N_p (10^{22} m^{-3})		–	–	–	n.m.	2

n.m. = Not measured; F = ferrite; M = martensite.

Table 2
Characteristics of the microstructure of Fe–Cr alloys (1100 °C/5 min + quenched) irradiated in BR-10 at 400 °C to 25.8 dpa

Chromium content (at.%) Structure		0 F	2 F + M	6 M	12 F + M	18 F
Dislocation density ρ_d^{unirr} (10^{14} m^{-2})	F	<0.1	1	–	2	0.1
	M	–	5–10	10	10	–
Dislocation density $\rho_d^{irr.}$ (10^{14} m^{-2})	F	0.3	0.5	–	0.5–1.0	0.5
	M	–	5	5	5	–
Mean void diameter $\langle d_v \rangle$ (nm)		55	16	–	8	5/30–100
Void number density N_v (10^{20} m^{-3})		1.2	5	–	5	≈1.7/0.1
$\Delta V/V$ (%)		1.7	0.3	–	0.04	0.05
Mean loop diameter $\langle d_l \rangle$ (nm)		117	40	–	25	12
Loop number density N_l (10^{20} m^{-3})		0.75	6	–	5	20
Mean diameter of α'-precipitates $\langle d_p \rangle$ (nm)		–	–	–	14	14
Number density of α'-precipitates N_p (10^{22} m^{-3})		–	–	–	0.7	2

two starting conditions was reversed at higher chromium contents, with swelling of 0.04–0.05% observed in the annealed condition and none in the cold-worked condition.

3.2. Dislocation structure

After irradiation the dislocation evolution was different in martensite and ferrite grains. The character of dislocation structure changes in martensite grains was similar in both cold-worked and annealed conditions, and was expressed in an approximately two-fold decrease of the initial dislocation density and also in the formation of clusters of small dislocation loops (Fig. 2(a)).

The dislocation structure of ferrite grains irradiated in the annealed condition consisted of quite uniformly distributed dislocation lines, segments and loops with the total length per unit volume in the range of $3–7 \times 10^{13}$ m^{-2} (without counting of loops) (Fig. 2(a)). The largest loops were formed in pure iron with a mean loop diameter of 117 nm. With increasing chromium content the loop size decreases monotonically to 12 nm. The lowest loop concentration was observed in iron. Alloying of iron with chromium has resulted in a substantial increase of loop concentration.

In pure Fe and Fe–2Cr irradiated in the cold-worked condition the initial cellular dislocation structure of $(10–20) \times 10^{14}$ m^{-2} in density has transformed to a uniform dislocation network with density of $(4–5) \times 10^{13}$ m^{-2}. Meanwhile, the dislocation structure of ferrite grains in Fe–12Cr and Fe–18Cr alloys in the cold-worked condition has demonstrated a high resistance to irradiation, having kept the initial dislocation density after the irradiation. In all cases, the habit planes and Burgers vectors of loops in ferrite grains were identified as {1 0 0} planes and a $\langle 1 0 0 \rangle$ Burgers vectors. From observations conducted in martensite grains one

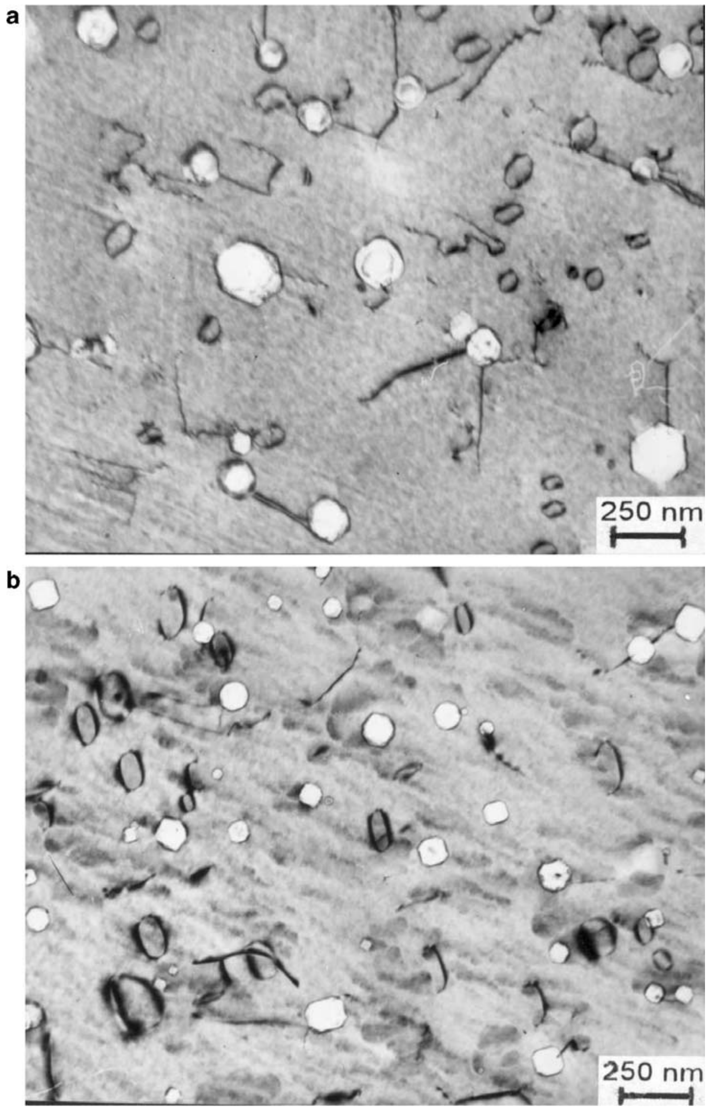

Fig. 1. Microstructure of pure Fe after irradiation in BR-10 at 400 °C to 25.8 dpa. (a) Specimen in ~250% cold deformed condition and (b) annealed condition.

can conclude that some dislocation loops lay also on planes of {1 0 0} type.

3.3. Precipitates

After irradiation finely dispersed precipitates of α′-phase formed the Fe–12Cr and Fe–18 alloys in the bulk of grains in both cold-worked and annealed specimens (Fig. 3(a)). Precipitate-free zones of ⩽150 nm in width were observed along grain boundaries. In annealed samples the mean precipitate diameter was approximately identical at ~14 nm. In cold-worked alloys the α′-phase precipitates have a slightly smaller size, ~10 nm. Along with the α′-phase precipitates, a low concentration of rod-like or plate-like precipitates of 100–500 nm in length and 10–40 nm in thickness was observed at grain boundaries and in the matrix of annealed Fe–12Cr and Fe–18Cr alloys. In many cases these precipitates were attached to largest voids (Fig. 3(a)). An analysis of micro-diffraction patterns has shown that these precipitates are M_7C_3 carbides. The chemical composition of both the α′-phase precipitates and M_7C_3 precipitates was not determined in the present work. The structures of these precipitates were determined using micro-diffraction methods.

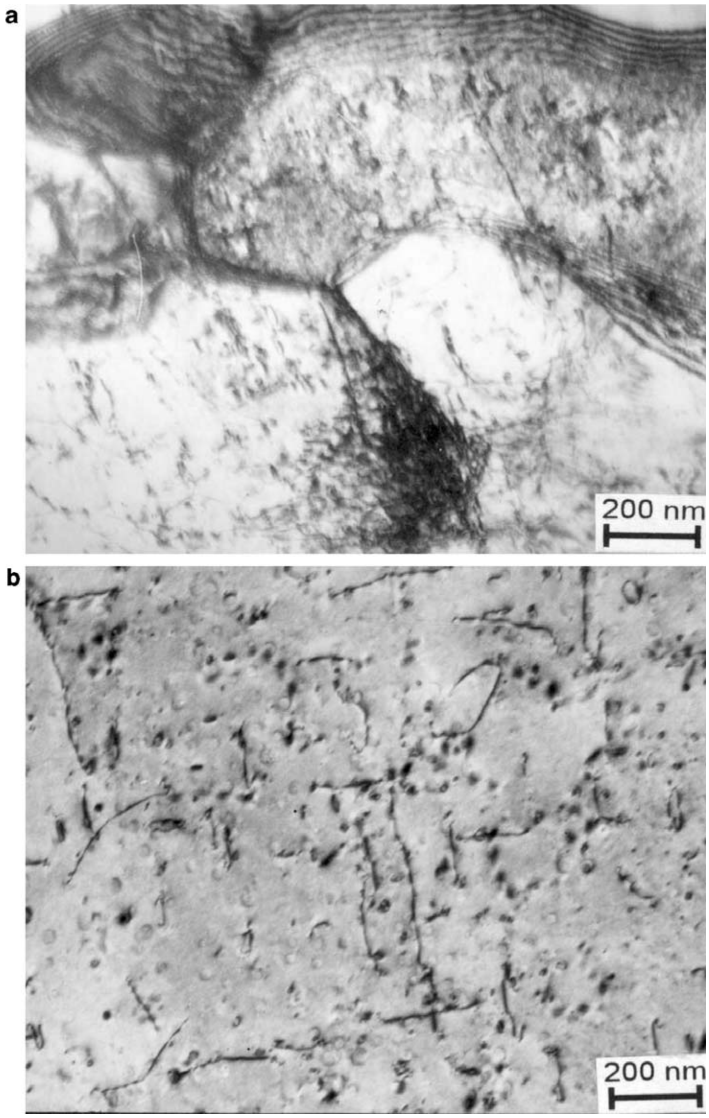

Fig. 2. Dislocation structure of Fe–Cr alloys after irradiation in BR-10 at 400 °C to 25.8 dpa. (a) Fe–6Cr alloy, ~250% cold deformed, martensite and (b) Fe–12Cr alloy, annealed condition, ferrite.

4. Discussion

Having reached 3% swelling in pure, lightly cold-worked iron at 6 dpa and 1×10^{-7} dpa s^{-1}, one might expect to reach more than 4.5% swelling in heavily cold-worked pure iron at 25.8 dpa and 4×10^{-7} dpa s^{-1}. However, such an expectation is not necessarily warranted, when one considers not only that the cold-work level is very different, but also there is a significant difference in dpa rate. Garner and coworkers have shown that relatively small increases in dpa rate can strongly extend the transient regime of both fcc and bcc iron-base alloys and thereby lower the swelling [7–10].

The most significant observation is that in pure Fe and Fe–2Cr irradiated side-by-side, cold-working strongly increased swelling, consistent with the earlier observations of Garner [6,7]. At higher chromium levels no swelling or very small levels of swelling were observed. In the high-chromium specimens containing radiation-induced α'-phase, voids were observed only in the annealed specimens and not in the cold-worked specimens. Unlike the observations at 0–2% Cr, this behavior is in agreement with

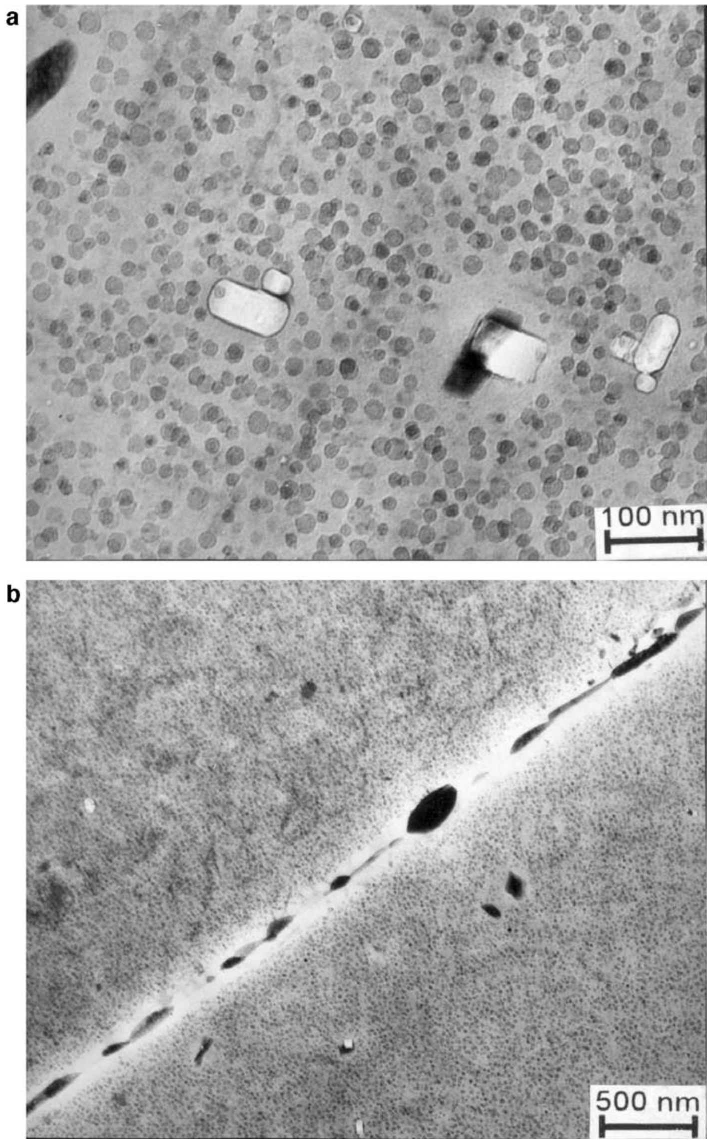

Fig. 3. Precipitation of α′-phase (a) and M_7C_3 (b) in annealed Fe–8Cr after irradiation in BR-10 at 400 °C to 25.8 dpa.

the general perception that cold working suppresses swelling.

The other significant observation of these studies was the radiation-induced decrease in dislocation density. In order to describe the radiation-induced recovery of dislocation structure in cold-worked materials one can write the following equation for the rate of change in the total length of dislocations and dislocation loops per unit volume $L(t)$:

$$\frac{\mathrm{d}L(t)}{\mathrm{d}t} = I(t) - R_{\mathrm{d}} v L^2(t), \tag{1}$$

where $I(t)$ is the dislocation source which is determined by the rates of loop nucleation and growth, v is the dislocation climb velocity (assumed be equal to the loop growth rate), R_{d} is the effective radius of annihilation. The velocity v can be expressed in terms of the voidage rate as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\Delta V}{V} = bvL(t), \tag{2}$$

where b is the Burgers vector length.

Inserting the Eq. (2) in Eq. (1) and integrating, one obtains the following solution satisfying the initial condition:

$$L(t) = L(0)\exp\left(-\frac{R_d}{b}\frac{\Delta V}{V}(t)\right) + \int_0^t I(t') \times \exp\left(\frac{R_d}{b}\left[\frac{\Delta V}{V}(t') - \frac{\Delta V}{V}(t)\right]\right)\mathrm{d}t'. \quad (3)$$

Because of the lack of information on both $I(t)$ and dose dependence of voidage in the Fe–2Cr alloy (250% C.W.), the expression Eq. (3) can be used for determining the ratio R_d/b only for iron in the cold-worked condition. In the cold-worked iron a relatively low dislocation loop length per unit volume of $0.23 \times 10^{14}\ \mathrm{m}^{-2}$ has formed after irradiation to 25.8 dpa, so that only the first term in the right side of Eq. (3) is of significance. Taking for iron in the 250% cold-worked condition $L(0) = (10\text{–}20) \times 10^{14}\ \mathrm{m}^{-2}$, $L(t) = 0.4 \times 10^{14}\ \mathrm{m}^{-2}$ and $\Delta V/V = 4.5\%$ one obtains $R_d/b = 61\text{–}76$, which is a relatively large number compared to the original dislocation spacing in this heavily cold-worked material, thereby providing a strong driving force for reduction in dislocation density, as was observed in this study.

5. Conclusions

The results of the present work confirm our perceptions that relatively high neutron-induced swelling levels can be reached in pure iron compared with Fe–Cr alloys, and that cold-working leads to an enhancement of swelling in iron and low-chromium alloys. It also appears that unexpectedly high levels of swelling can be reached when the irradiation is conducted at displacement rates that are significantly lower than those of many earlier studies.

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