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THE PRECIPITATION RESPONSE OF 20%-COLD-WORKED TYPE 316 STAINLESS STEEL TO SIMULATED FUSION IRRADIATION*

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The precipitation response of 20%-cold-worked type 316 stainless steel has been examined after irradiation in HFIR at 380–600°C, after irradiation in EBR-II at 500°C, and after thermal aging at 600 to 750°C. Eta phase forms during exposure to all environments, and it constitutes a major portion of the precipitation response. It is not normally reported in 20%-cold-worked type 316 stainless steel. Qualitatively, for eta phase, $M_{23}C_6$, Laves, sigma and chi, the precipitate phases appear at similar temperatures after HFIR, EBR-II, or thermal exposure. There are, however, some differences in relative amounts of phases, size, and distribution when compared among the various environments. Eta phase is the only carbide-type phase observed after irradiation in HFIR from 380–550°C. The large cavities associated with it at 380°C contribute significantly to swelling. Precipitate re-solution and re-precipitation of massive particles of sigma, $M_{23}C_6$ and chi are observed after recrystallization in HFIR.

1. INTRODUCTION

Austenitic stainless steel has been studied in many reactor environments and is a leading near-term candidate in the Department of Energy's (DOE) Magnetic Fusion Energy Alloy Development Program [1]. Both swelling and postirradiation tensile properties have been shown to be sensitive to preirradiation microstructure in a radiation environment that simutaneously produces helium and displacement damage at near fusion levels [2–4]; these properties can be improved by 20% cold working prior to irradiation. Irradiation conditions and the preirradiation microstructure have a direct influence on the microstructure that evolves during irradiation, which in turn affects the properties. Precipitation is one component of the damage structure that can have direct or indirect (changing the matrix chemistry) effects on the properties. There have been efforts to characterize precipitation in 20%-cold-worked 316 in both thermal aging [5,6] and fast reactor environments [7–10]. Clearly, in either a thermal aging or fast reactor environment, cold working changes the precipitation response relative to annealed material. A study of the precipitation response of 20%-cold-worked 316 irradiated under conditions closely related to fusion irradiation seems necessary to guide the design of alloys for optimum performance in a fusion environment.

2. EXPERIMENTAL

The composition (in weight percent) of the 316 examined in this work is 18 Cr, 13 Ni, 2.6 Mo, 1.9 Mn, 0.8 Si, 0.05 Ti, 0.05 C, 0.013 P, 0.016 S, 0.05 N, balance Fe. The final steps in specimen preparation from rod involved a 50% reduction in area by cold swaging, annealing for 1 h at 1050°C, 20% further reduction, and finally machining into buttonhead tensile specimens. Details of the irradiation experiments have been published [2–4,11]. Specimens were irradiated in HFIR (High Flux Isotope Reactor) at temperatures of 370–680°C to neutron fluences producing up to 60 dpa and 4100 at. ppm He. Specimens of the same material were aged at 750°C for 1000 h and 600 and 650°C for 10 000 h. A specimen of the same steel, but cross rolled to a 20% reduction in thickness and fabricated into sheet specimens, was examined after irradiation in EBR-II at 500°C to a neutron exposure producing ~9 dpa. The irradiation temperatures in HFIR were calculated from previously determined nuclear heating values, but new measurements by Grossbeck [12] indicate that the temperatures could be as much as 75°C higher than calculated. For continuity with previous work, the samples will be identified by their calculated temperatures, but the temperature difference will be taken into account in the interpretation of the data. Further temperature measurement in HFIR is in progress.

TEM disks were thinned using a two-step thinning method developed by DuBose and Stiegler [13]. All specimens were examined using either a JEOL 100-C (120 kV) AEM or a Hitachi 1000 (1 MeV) CTEM. Several low-order zones were obtained from each precipitate particle examined, and compared with the literature to identify the crystal structure [14]. Chemical analysis using energy dispersive x-ray analysis in CTEM on precipitate particles extracted on carbon replicas from aged samples of 316 has been performed.

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3. RESULTS

The most striking result is the unexpected appearance and dominance of a diamond cubic phase with $a_0 \sim 10.7$ Å in 20%-cold-worked 316 irradiated in HFIR below 600°C. The same type of phase is found in both annealed and 20%-cold-worked 316 after thermal aging at 650°C for 10 000 h. Its crystal structure, lattice parameter and chemistry after thermal aging are similar to "H-phase" found in other steels by H. Hughes [15] and Tither and Clark [6]. However, as discussed later, this phase should be referred to as eta phase. The experimental results for the various samples observed are presented in Table 1.

Intergranularly, eta phase is the only phase observed in 20%-cold-worked 316 after irradiation at 380°C, and it appears together with Laves phase at 460°C (see Fig. 1a,b). At 380°C (and to a lesser extent at 460°C), large cavities (∿100 nm in dia) are attached to eta phase precipitates. A total cavity swelling $\Delta v/v_0$ of 2.5% is measured, and 1.0% swelling is due to the large cavities [4]. Discontinuous grain boundary precipitation of eta phase is observed at 380 and 460°C. At 550°C, eta and Laves phases are observed intragranularly and large isolated sigma phase particles are observed at the grain boundaries along with larger than average cavities (40 nm in diameter at grain boundary, 21 nm in the matrix).

At 600°C, after irradiation to 60 dpa in HFIR, 20%-cold-worked 316 is completely recrystallized. Two samples were observed at these conditions — one contained massive sigma phase and $M_{23}C_6$ (∿5 μm), while the other showed massive sigma and chi phases with smaller $M_{23}C_6$ particles (0.2–0.5 μm) (see Table 1). The precipitation is quite coarse, but optical metallography indicates the distribution of large phases to be reasonably uniform on a macroscopic scale. After 1.5 dpa at ∿600°C, no recrystallization is observed, but partial recrystallization does occur at 3.3 dpa. Laves, some eta, and large sigma phase particles are observed in the recrystallized portion of the material; the unrecrystallized portions of each sample contain $M_{23}C_6$, Laves, and sigma phase particles (see Table 1). The $M_{23}C_6$, eta, and Laves phase precipitate particles are smaller (100–300 nm) and more finely distributed than the coarse precipitate particles observed after high fluence irradiation (Fig. 2). Laves and eta phases are conspicuously absent after high fluence and complete recrystallization.

Gamma prime is not observed in any of the 20%-cold-worked 316 samples irradiated in HFIR, particularly at 380°C where it might be expected based on fast reactor irradiation [9]. Indeed, gamma prime is the dominant intragranular phase in annealed 316 irradiated in HFIR at 370°C to neutron fluences producing ∿9 dpa, whereas 20%-cold-worked 316 irradiated at the same conditions has almost no precipitation at all.

There is concern about the formation of magnetic phases like ferrite. Magnetic susceptibility measurements were made on the TEM disks of 20%-cold worked 316 irradiated in HFIR at 550 and 600°C to 42 and 60 dpa, respectively, by Billington [17]. No significant magnetic material was indicated and no microstructural evidence of ferrite formation could be found in any sample.

Table 1. Precipitate phases present in 20%-cold-worked 316 exposed to various environments

HFIR irradiated, 3000–4100 at. ppm He, 42–60 dpa

380°C*	460°C
η phase; g.b., m.	η phase, g.b., m Laves; m
550°C	**600–610°C, 100% Rx**
η phase; m. Laves; m, g.b. σ phase	Massive χ phase or massive $M_{23}C_6$ Massive σ phase $M_{23}C_6$, m.

580–600°C

1.5 dpa, 30 at. ppm He	3.3 dpa, 85 at. ppm He (10–15% Rx)	
	Deformed	Rx
$M_{23}C_6$	$M_{23}C_6$	η phase
Laves	Laves	Laves
σ phase	σ phase	σ phase

Thermally Aged or EBR-II Irradiated

600°C, 10 000 h	650°C, 10 000 h (<5% Rx)
$M_{23}C_6$; g.b., m η phase; m Laves; m Massive σ phase	Deformed or Rx $M_{23}C_6$; g.b., m η phase; m Laves; m Massive σ phase

750°C, 1000 h, ∿20% Rx

Deformed	Rx	EBR-II Irradiated (∿9 dpa, 500°C)
$M_{23}C_6$; m	$M_{23}C_6$ (?)	
Laves; m	Laves	
χ phase; m	χ phase	$M_{23}C_6$; g.b.
	σ phase	η phase; m

Note: g.b. = grain boundary; m = matrix, Rx = recrystallized.

*These are the calculated irradiation temperatures.

The precipitation response of 20%-cold-worked 316 after thermal aging at 600 and 650°C for 10 000 h and 750°C for 1000 h is shown in Table 1 and Fig. 3. Eta phase is found in significant amounts mixed with $M_{23}C_6$ at 600 and 650°C and is morphologically indistinguishable from $M_{23}C_6$. It is not observed at 750°C. Eta phase is also found in annealed 316 aged 10 000 h at 650°C and its chemistry along with $M_{23}C_6$ was determined by quantitative energy dispersive x-ray analysis on individual precipitates extracted on a carbon replica [18]. Eta phase contains (by weight percent) 6 Si, 31 Mo, 29 Cr, 13 Fe, 21 Ni, and ∿0 Mn; $M_{23}C_6$ is <1 Si, 16 Mo, 64 Cr, 13 Fe, 5 Ni, <0.5 Mn. The eta phase and $M_{23}C_6$ compositions

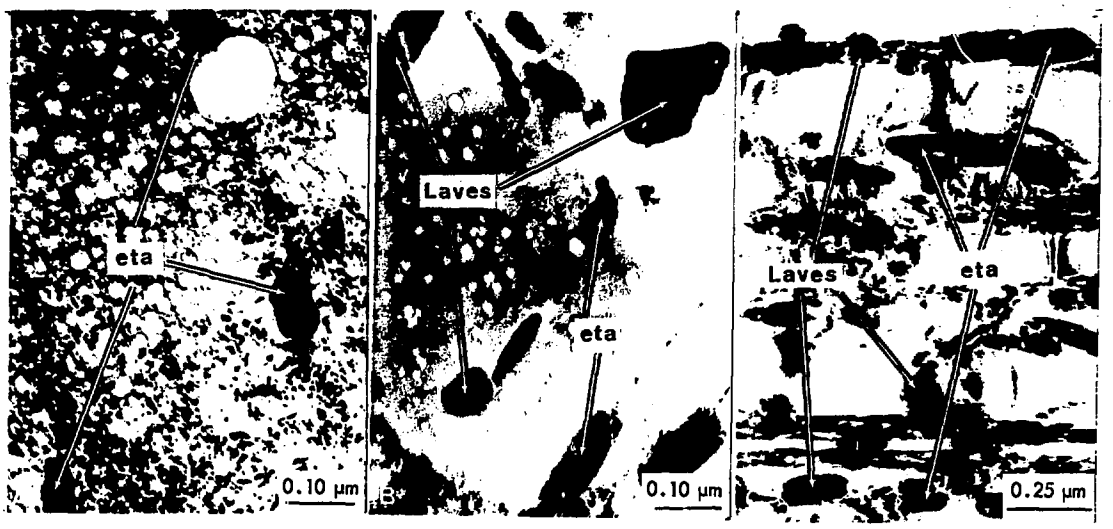

Fig. 1. 20%-cold-worked 316 irradiated in HFIR to 42–60 dpa and 3000–4100 appm He at (a) 380°C, (b) 460°C, and (c) 550°C.

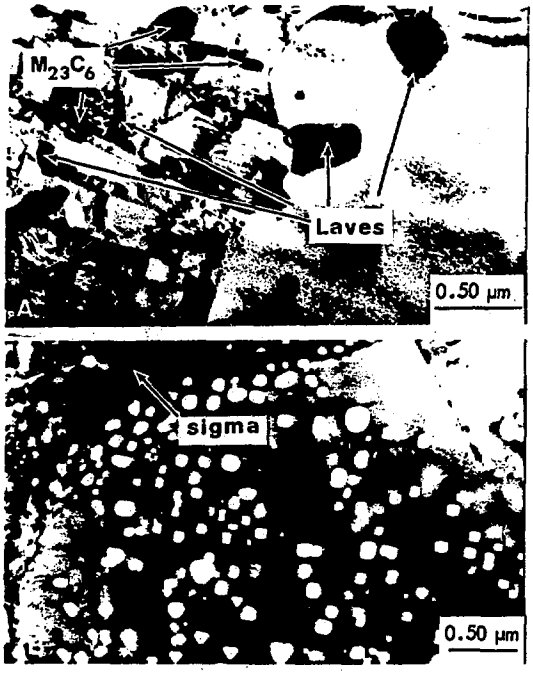

Fig. 2. 20%-cold-worked 316 irradiated in HFIR at ∿600°C to (a) 3.3 dpa and 80 at. ppm He (partially recrystallized) and (b) 60 dpa and 4070 at. ppm He (completely recrystallized).

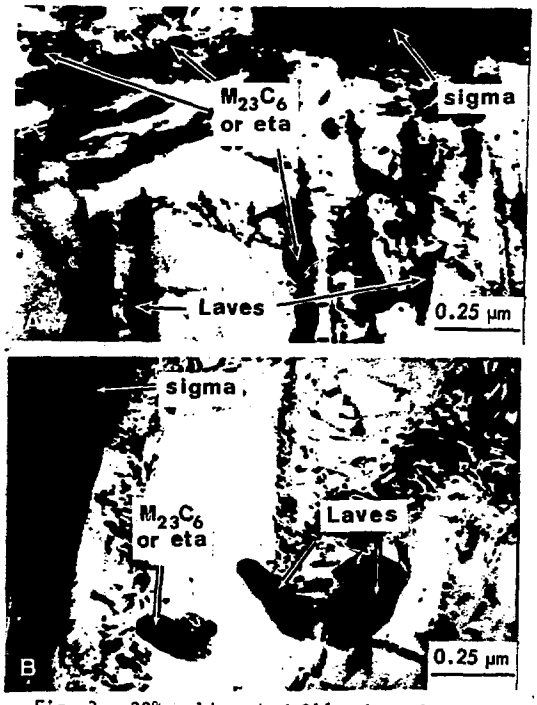

Fig. 3. 20%-cold-worked 316, thermal aged at (a) 600°C for 10 000 h, and (b) 650°C for 10 000 h.

in 20%-cold-worked 316 after the same aging treatment are similar to those reported above.

Laves phase, $M_{23}C_6$ and massive sigma phase particles are observed in all thermally aged samples. Chi phase is observed only after 1000 h at 750°C. As shown in Fig. 3, the precipitate density decreases and the size coarsens with increasing temperature. The relative amount of carbides to intermetallic Laves phase tends to decrease as the temperature increases. Slight (<5 vol fraction) recrystallization is observed at 650°C after 10 000 h and considerable recrystallization (∿20%) is observed after 1000 h at 750°C.

Finally, 20%-cold-worked 316 has been examined after EBR-II irradiation at 500°C to neutron fluences producing 9 dpa. Small blocky eta phase particles are observed intragranularly with $M_{23}C_6$ particles at the grain boundaries.

4. DISCUSSION

The widespread appearance and dominance of the diamond cubic phase in 316 stainless steel after thermal aging, HFIR or fast reactor irradiation were unexpected based upon previous reports in the literature [4–13]. However, after thermal aging, a similar phase has been observed in other steels. Hughes [15] first observed a phase he termed "H phase" together with $M_{23}C_6$ in a 12 Cr–4 Ni–0.1 C steel (3% Mn, 3% Si, 1% V). "H phase" was identified as diamond cubic (space group Fd3m) by x-ray diffraction and found to be high in silicon by chemical analysis. Tither and Clark [16] also observed "H phase" in 18 Cr–15 Ni–0.03 C steel (4.5 wt % Si, 1 wt % Mn), but incorrectly identified it as fcc (Fm3m) when their published x-ray data indicated diamond cubic. The structure factor for diamond cubic (Fd3m) crystal structure predicts systematic absences of (200), (420), etc. [14]. Tither and Clark analyzed "H phase" to contain (in atomic percent) 11 Si, 8 Fe, 44 Cr, and 37 Ni, but did not analyze for carbon. They assumed it was $M_{23}Si_6$, while Hughes had assumed an MSi_x compound with $x > 1$. Hughes, however, did not directly analyze the "H phase" for carbon either. It is unclear whether it is a carbide or a silicide. This phase should not be confused with a class of carbon- or nitrogen-containing compounds having a hexagonal close-packed structure ($c/a = 4.9$), also termed H phase [19].

The appearance of a diamond cubic "H phase" makes suspect the observations of "M_6C," also diamond cubic, in other work on 316 [11]. A review of eta phase by Stadlemair [19] indicates that an eta-carbide structure proposed by Westgren [20] could well encompass $M_3M_3'X$, $M_6M_6'X$ (X is C, N, or O), or $M_2M_3'Si$-type phases with lattice parameters ranging from ∿1.07 to 1.22 nm, depending upon phase composition. The composition and stiochiometry of the phase in turn depend on the composition of the matrix [19,20, 21]. Both "H phase" and "M_6C" fit into the general classification of eta phase, which would be a safe designation until carbon (and/or nitrogen) can be measured to further specify stoichiometry and composition.

The data in the literature on 20%-cold-worked 316 show that during thermal aging cold work accelerates the formation of $M_{23}C_6$, sigma and chi phases in time relative to annealed material, but not in temperature [5,6]. After fast reactor irradiation, behavior similar to thermal aging is observed for $M_{23}C_6$, sigma and chi, but Laves phase formation is shifted to lower temperature in cold-worked relative to annealed 316 [7–10]. A rod-shaped, hexagonal ($c/a = 0.6$), phosphorus-containing phase is observed above 500°C and below 625°C in annealed 316 but not in 20%-cold-worked 316 after fast reactor irradiation [7–10, 23–25]. Gamma-prime (nominally Ni_3Si) is observed in both annealed and 20%-cold worked 316 below ∿480 to 525°C in fast reactors [9,26]. The results reported here on thermally aged or EBR-II irradiated material are generally consistent with the literature, except that $M_{23}C_6$ and eta phase are found where normally only $M_{23}C_6$ had been reported.

The temperatures at which $M_{23}C_6$, eta, Laves, sigma and chi phases form during HFIR irradiation are similar to those observed during thermal aging, if the calculated irradiation temperatures are corrected upwards by ∿75°C. There are, however, differences in the particle density, size, and relative amounts of the various phases. Figures 1c and 3b indicate that at comparable temperatures, the total precipitate particle density is greater after HFIR irradiation than after thermal aging. The carbides appear to be a mix of $M_{23}C_6$ and eta phase after thermal aging, but are nearly all eta phase after HFIR irradiation up to 550°C (calculated). The trend of decreasing amount of $M_{23}C_6$ and/or eta phase relative to Laves with increasing temperature is the same for both HFIR irradiated and thermally aged material.

HFIR-irradiated material that has recrystallized contains massive sigma and chi phases much larger than those observed after thermal aging, but the presence of massive $M_{23}C_6$ particles is an anomaly relative to thermal aging. Annealed 316 irradiated in HFIR at 600°C contains only Laves and sigma phases [11]. The re-solution of precipitates following recrystallization is not usually observed in other environments [5–7], and the absence of Laves is conspicuous. However, the finely distributed phases present prior to recrystallization (see Table 1) should result in a different matrix chemistry than in annealed material. The low dislocation density after recrystallization presents a new sink structure in the matrix as well, and it is quite possible that prior phases could become unstable with the new matrix conditions.] The displacement cascades and enhanced point defect concentrations present during irradiation could also obviously contribute to precipitate

re-solution, as well as changes in matrix chemistry. This type of behavior is disconcerting if preirradiation thermomechanical treatments produce precipitate phases that could become unstable during irradiation.

Comparing HFIR- with EBR-II-irradiated 20%-cold worked 316 indicates that the carbides and Laves phase form at similar temperature if the calculated temperatures in HFIR are corrected as mentioned above. Comparing the data on the EBR-II irradiated material at 500°C (reported in Table 1) with the literature data, it is possible that the carbides or "carbosilicide" phases reported [7–10] are really a mixture of $M_{23}C_6$ and eta phase. In that case, the relative amount of $M_{23}C_6$ and eta phase changes from a mixture of the two during EBR-II irradiation to exclusively eta phase after HFIR irradiation at 550°C (calculated) and below.

The behavior with respect to gamma-prime (Ni_3Si) formation also changes. After HFIR irradiation at 380°C (calculated) and 48 dpa, no gamma prime is observed. Gamma prime would be expected to form in 20%-cold-worked 316 based on fast reactor data [9,26], even with + 75°C correction in HFIR irradiation temperatures. The formation of eta phase, which is also high in nickel and silicon, may preclude formation of gamma prime. Indeed, annealed 316 irradiated in HFIR at 370°C (calculated) at ∿9 dpa precipitates copious gamma prime intragranularly and no eta phase.

Finally, Porter and Wood [27] observe ferrite formation in 20%-cold-worked 316 irradiated in EBR-II at 550°C to ∿4 × 10^{26} n/m^2, and attribute its formation to depletion of nickel in the matrix. The differences in the precipitation produced in HFIR as compared to EBR-II indicate that the microchemical evolution of the matrix should not be expected to be the same. The fact that no ferrite is observed after HFIR irradiation clearly supports this. The inclusion of significantly higher simultaneous helium in the damage products for HFIR relative to EBR-II is coincident with these changes in behavior. The results presented above indicate that helium must be considered as influencing all components of the microstructure, including precipitation.

5. CONCLUSIONS

1. Eta phase is an unexpected and dominant portion of the precipitation response of 20%-cold-worked 316 to thermal aging and EBR-II or HFIR irradiation. It is associated with large cavities after HFIR irradiation at 380°C (calculated).

2. Qualitatively, ($M_{23}C_6$, eta), Laves, chi and sigma phases appear at similar temperature for HFIR irradiation compared to EBR-II irradiation or thermal aging. There are, however, differences in density, size and relative amounts of the various phases.

3. Re-solution of fine precipitate particles of $M_{23}C_6$, eta, and Laves and re-precipitation of massive $M_{23}C_6$, sigma and chi phase particles follows recrystallization at 600°C (calculated) and above in HFIR.

Measurements need be made to determine the composition of eta(η) phase formed in HFIR especially whether or not it contains carbon. This information can then guide both major and minor alloying changes to try and eliminate uncontrolled phase instability.

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