Embrittlement of Irradiated F82H in the Absence of Irradiation Hardening—
R. L. Klueh (Oak Ridge National Laboratory), K. Shiba (Japan Atomic Energy Agency), and M. A. Sokolov (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this work is to develop an understanding of the effect of irradiation on microstructure and mechanical properties of ferritic/martensitic steels for fusion applications and to use that knowledge to develop steels with improved properties.

SUMMARY

Neutron irradiation of 7-12% Cr ferritic/martensitic steels below 425–450ºC produces microstructural defects and precipitation that cause an increase in yield stress. This irradiation hardening causes embrittlement, which is observed in a Charpy impact or fracture toughness test as an increase in the ductile-brittle transition temperature. Based on observations that show little change in strength in steels irradiated above 425–450ºC, the general conclusion has been that no embrittlement occurs above these temperatures. In a recent study of F82H steel, significant embrittlement was observed after irradiation at 500ºC. This embrittlement is apparently due to irradiation-accelerated Laves-phase precipitation. Observations of the embrittlement in the absence of hardening has been examined and analyzed with thermal-aging studies and computational thermodynamics calculations to illuminate and understand the effect.

PROGRESS AND STATUS

Introduction

The effects of neutron irradiation on the mechanical properties of commercial and reduced-activation ferritic/martensitic steels have been studied extensively [1-9]. Below 425–450ºC, irradiation damage hardens the steels, causing an increase in yield stress and ultimate tensile strength and a decrease in ductility [1-5]. Irradiation hardening affects toughness, and the effect is observed qualitatively in a Charpy impact test as an increase in the ductile-brittle transition temperature (DBTT) and a decrease in upper-shelf energy (USE) [6-11]. The magnitude of the shift varies inversely with irradiation temperature, similar to the variation in hardening.

For irradiation above 425–450ºC, the tensile properties are generally unchanged, although there may be enhanced softening over that caused by thermal aging alone, depending on fluence and temperature [3-5]. In this paper, embrittlement of F82H at irradiation temperatures above the hardening regime will be examined and discussed.

Experimental

The reduced-activation steel F82H (nominally Fe-7.5Cr-2.0W-0.15V-0.02Ta-0.09C) was irradiated in the High Flux Isotope Reactor (HFIR) in the normalized-and-tempered condition [12,13]. Normalization involved austenitizing at 1050ºC to transform the steel to austenite, after which it was air cooled to form 100% martensite. Tempering was at 750ºC for 1 h.

One-third-size pre-cracked Charpy (PCVN), Charpy V-notch (CVN), and 0.18T disk-compact fracture-toughness [DC(T)] specimens were irradiated in HFIR to ≈3-5 and 20 dpa at 300 to 500ºC [12,13]. The PCVN, CVN, and DC(T) specimens were tested to determine the transition temperature before and after irradiation. Tensile specimens were irradiated to 4.7 dpa and 20 dpa at 300 and 500ºC and tested at -100ºC, room temperature, and at the irradiation temperature [12].

Results

A large increase in yield stress was observed after irradiation at 300ºC to 4.7 and 20 dpa, with most of the change occurring for the 4.7 dpa irradiation [12,13]. There was only a slight further increase after 20 dpa [Fig. 1(a)]. Irradiation at 500ºC to 4.8 and 20 dpa had no effect on yield stress [12].

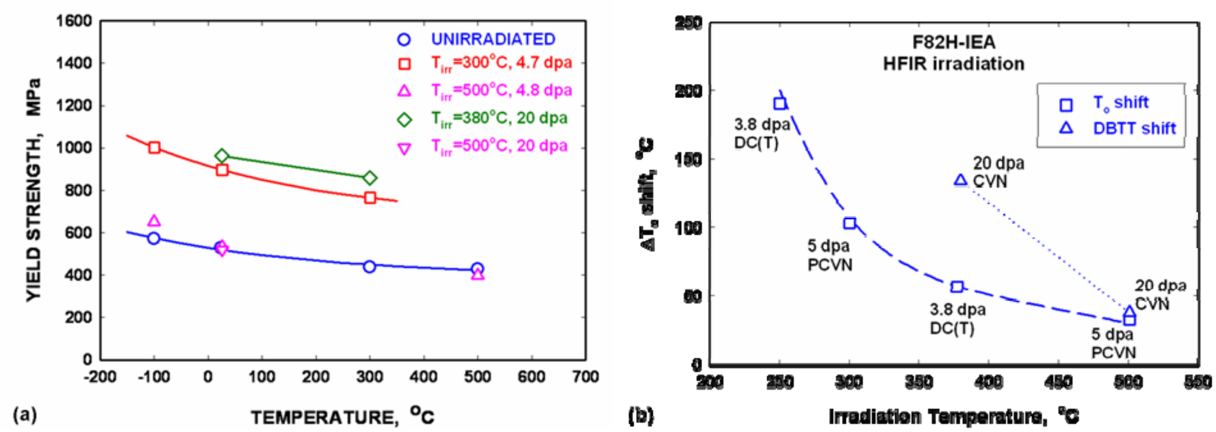

Figure 1. The (a) transition temperature as a function of irradiation temperature and (b) yield stress as a function of test temperature for F82H irradiated in HFIR in the range 250-500ºC [13]

Fracture toughness transition temperature shifts were evaluated with the master curve methodology [12], and the shifts showed a pronounced effect of irradiation temperature [Fig. 1(b)]. The greatest effect occurred for the lowest temperature irradiations, with the shift decreasing with increasing temperature. Unexpectedly, there was a shift of 33ºC for the 5 dpa CVN specimen irradiated at 500ºC, and this was corroborated by a 38ºC shift for the 20 dpa CVN specimen [13].

Analysis

Based on thermal-aging observations of F82H discussed below, it is postulated that the increase in transition temperature in the absence of irradiation hardening can be traced to irradiation-accelerated Laves-phase [$(Fe,Cr)_2W$] precipitation. For normalized-and-tempered F82H tempered at 750ºC, the major precipitate is chromium-rich $M_{23}C_6$ with a small amount of MX, where M is vanadium and tantalum rich, and X is carbon and nitrogen. Calculations with the computational thermodynamics program JMatPro [14] predicted 1.9 wt % $M_{23}C_6$ and 0.06 wt % MX form during tempering at 750ºC, with little change as temperature is decreased. Laves phase is predicted to be stable below ≈650ºC. The calculations indicate an abrupt cutoff temperature for Laves: at ≈640ºC, where 1.22% Laves is predicted, after which it drops to zero by ≈650ºC. However, M_6C is predicted to form below 756ºC and increase to 1.15% at 650ºC, where it then drops abruptly to zero at 639ºC. Calculated amounts of Laves, $M_{23}C_6$, M_6C, and MX present at 400-800ºC are shown in Fig. 2.

Shiba thermally aged tensile and Charpy specimens of F82H for 1000, 3000, 10000, and 30000 h at 400 (aged 30000 h only), 500, 550, 600, and 650ºC. Although aging caused a reduction in room-temperature strength that was quite large at the highest aging temperatures and longest times [Fig. 3(a)], there was an adverse effect on impact properties [Fig. 3(b)] [15,16]. The largest strength decreases occurred at 600 and 650ºC; at 650ºC, a 33% decrease occurred after 30000 h.

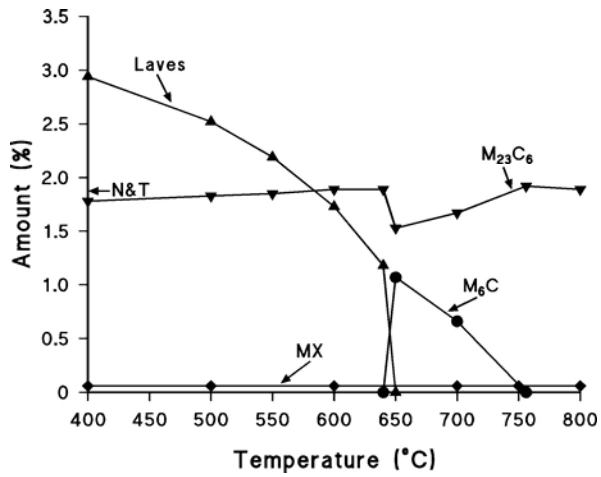

Figure 2. Equilibrium amounts of $M_{23}C_6$, Laves phase, M_6C, and MX precipitates calculated to form in F82H steel at 400–800ºC. Calculations were made with the computational thermodynamics program JMatPro.

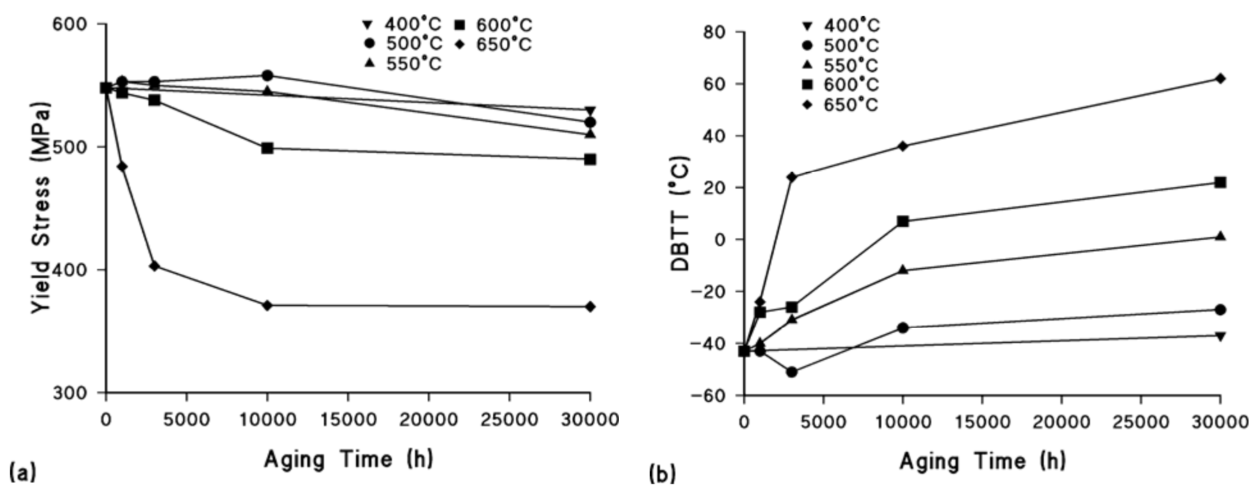

Figure 3. The (a) yield stress and (b) ductile-brittle-transition temperature as a function of aging time at 500, 550, 600, and 650ºC [15,16].

Despite the large decrease in strength after aging at 650ºC, the largest increase in Charpy DBTT (105ºC) also occurred at this temperature after 30000 h. The DBTT also increased at the other temperatures, with the magnitude of the increase decreasing with decreasing aging temperature. The change was relatively small at 400 and 500ºC, even after 30000 h.

Extracted precipitates from normalized-and-tempered and thermally aged specimens were analyzed by x-ray diffraction and EDX analysis using SEM and TEM [15,16]. For aging times up to 3000 h, the total amount of precipitate increased at 600 and 650ºC. After 10000 and 30000 h, the largest increase in the amount of precipitate occurred at 600ºC. The EDX analysis indicated that the largest elemental increases in the precipitate were tungsten, iron, and chromium, all three of which are expected to be present in Laves phase; M_6C will be tungsten rich. X-ray diffraction of the precipitate verified the presence of Laves phase at 550, 600, and 650ºC after aging for 10000 h. TEM observations indicated Laves phase formed on $M_{23}C_6$ particles on prior-austenite grain boundaries and lath boundaries.

When the total amount of precipitate calculated with JMatPro (the sum of the two curves in Fig. 2) is compared to the measured precipitate after 30000 h, the effect of kinetics versus equilibrium is evident (Fig. 4). Equilibrium was reached by 30000 h at 650ºC [15], and it is being approached after aging 30000 h at 600ºC. Significant amounts of precipitate formed at 550ºC, but because of the reduced kinetics at 400 and 500ºC, little precipitate formed at these aging temperatures, even after 30,000 h. Much more is to be expected with longer aging times. However, from observations on the increase in transition temperature that occurred during irradiation of F82H at 500ºC in HFIR, it is concluded that irradiation accelerates precipitation kinetics, thus causing embrittlement, even though there was no irradiation hardening.

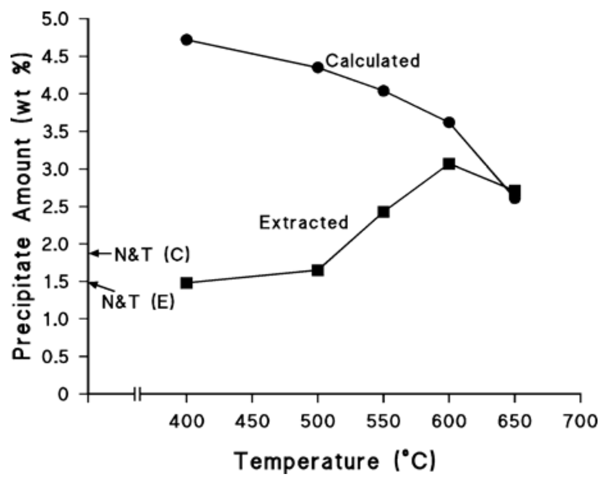

Figure 4. Amount of extracted precipitate in normalized-and tempered F82H steel thermally aged 30000 h at 400, 500, 550,600, and 650ºC compared to calculated equilibrium amount of $M_{23}C_6$, Laves, M_6C, and MX phases. Amounts extracted and calculated for steel tempered at 750ºC are indicated by N&T (E) and N&T (C), respectively.

Discussion

The observations of embrittlement of F82H in the absence of irradiation hardening appeared to be caused by Laves-phase precipitation that occurred during irradiation. Fracture in steels is generally initiated at precipitate particles and/or inclusions with the critical stress to propagate a crack being inversely proportional to crack length [17,18]. If it is assumed fracture initiation occurs at a Laves-phase particle and the crack length at initiation equals the diameter of a particle, then fracture stress will decrease with increasing precipitate size.

In the HFIR experiment containing the F82H-IEA heat that was irradiated to 5 and 20 dpa at 500ºC, the F82H-IEA heat with a different heat treatment (F82H-HT2), ORNL 9Cr-2WVTa steel (Fe-9.0Cr-2.0W-0.25V-0.06Ta-0.11C), and JLF-1 steel (Fe-9.0Cr-2.0W-0.20V-0.07Ta-0.10C) were also irradiated at 500ºC (Table 1) [19]. The latter two steels have compositions only slightly different from F82H. All of

Table 1. Shift in transition temperature of steels irradiated in HFIR at 500ºC

Material	Dose (dpa)	DBTT (ºC)	ΔDBTT (ºC)	Grain Size No.
F82H-IEA	5	-54	30	3.3
	20	-46	38	
F82H (HT #2)	5	-92	9	6.5
ORNL 9Cr-2WVTa	5	-78	16	6
JLF-1	5	-66	19	6

these steels had a positive ΔDBTT, but they all had a smaller ΔDBTT after the 5 dpa irradiation at 500ºC than the F82H-IEA heat. Laves phase in an amount similar to that in F82H is calculated to form at 500ºC in all of these tungsten-containing steels.

The objective of the different heat treatment for F82H was to obtain a smaller prior-austenite grain size than the large grain size of F82H-IEA. After austenitizing at 920ºC instead of 1050ºC, the estimated ASTM grain size number increased from 3.3 to 6.5, corresponding to average grain sizes of ≈114 and ≈38 µm, respectively. The ORNL 9Cr-2WVTa and JLF-1 steels had ASTM grain-size number 6, corresponding to ≈45 µm. They had smaller ΔDBTTs than the F82H-IEA, although they were somewhat larger than F82H-HT2.

Laves phase forms preferentially on prior-austenite grain boundaries, but the amount of Laves formed does not depend on grain size. Therefore, if the ΔDBTT at 500ºC is caused by Laves phase, the difference in the F82H with different heat treatments could be the result of the different grain sizes, assuming all else remains the same. If most of the Laves forms on prior-austenite grain boundaries, then a smaller grain size would provide a larger area for heterogeneous nucleation. This would be expected to result in a larger number of smaller precipitates, which could explain the observations based on the proposed crack-nucleation mechanism.

Thermodynamics calculations indicate that the amount of Laves phase in the reduced-activation steels at 500ºC depends mainly on tungsten content, and since ORNL 9Cr-2WVTa and JLF-1 contain 2% W similar to the F82H, similar amounts of Laves are predicted for these steels as for F82H. ORNL 9Cr-2WVTa and JLF-1 have similar compositions, and they have similar prior-austenite grain sizes, which are smaller than that of F82H-IEA. The ΔDBTTs for the two steels at 500ºC are similar and somewhat higher than for F82H-HT2 and about half that of F82H-IEA (Table 1). With time at temperature or for higher irradiation doses, the Laves phase precipitation will be completed, and the particles will coarsen. It is expected that this will have a major effect on toughness, but needs to be determined by long-time thermal aging and/or higher-dose irradiation experiments.

Odette and co-workers [20,21] discussed fracture under similar circumstances to those presented in this paper, which they labeled non-hardening embrittlement (NHE). To describe the behavior, a multiscale model based on a model proposed by Ritchie, Knott and Rice [22], which is "based on the observation that cleavage occurs by the propagation of microcracks emanating from brittle trigger-particles, like large grain boundary carbides…" [21]. They write that, "Local stress–strain concentrations due to incompatible matrix particle deformation cause some of the brittle ceramic trigger-particles to crack."

Summary and Conclusions

In the past, irradiation-effects studies in ferritic/martensitic steels have focused on temperatures where irradiation hardening occurs (<425-450ºC) that is accompanied by embrittlement caused by a reduction in toughness. Embrittlement due to irradiation-enhanced precipitation in the absence of irradiation hardening has received relatively little attention.

In this report, F82H steel was embrittled when irradiated at 500ºC where no hardening occurred in a tensile test. The embrittlement was attributed to Laves-phase precipitation. It occurred for a relatively low dose (≈20 dpa) and a relatively low temperature (500ºC). Because of the low dose (relatively short thermal exposure time) and relatively low temperature for extensive precipitation, the ultimate effect of the precipitates on properties has yet to be determined. Therefore, need exists for high-dose irradiations at higher temperatures (500-600ºC) than most previous irradiation experiments.

References

[1] R. L. Klueh, D. R. Harries, High-Chromium Ferritic and Martensitic Steels for Nuclear Applications (American Society for Testing and Materials, West Conshohocken, Pennsylvania, 2001).

[2] C. Wassilew, K. Herschbach, E. Materna-Morris, K. Ehrlich, in: Ferritic Alloys for Use in Nuclear Energy Technologies, Eds J. W. Davis, D. J. Michel (The Metallurgical Society of AIME, Warrendale, PA, 1984) p. 607.
[3] R. L. Klueh, J. M. Vitek, J. Nucl. Mater. 132 (1985) 27.
[4] R. L. Klueh, J. M. Vitek, J. Nucl. Mater. 137 (1985) 44.
[5] R. L. Klueh, J. M. Vitek, J. Nucl. Mater. 182 (1991) 230.
[6] R. L. Klueh, D. J. Alexander, in: Effects of Radiation on Materials: 15th International Symposium, ASTM STP 1125, Eds R. E. Stoller, A. S. Kumar, D. S. Gelles (American Society for Testing and Materials, Philadelphia, 1992) p. 1256.
[7] W. L. Hu, D. S. Gelles, in: Influence of Radiation on Material Properties: 13th International Symposium (Part II) ASTM STP 956, Eds F. A. Garner, C. H. Henager, Jr, N. Igata (American Society for Testing and Materials, Philadelphia, 1987) p. 83.
[8] R. L. Klueh, D. J. Alexander, J. Nucl. Mater. 179-181 (1991) 733.
[9] R. L. Klueh, D. J. Alexander, in: Effects of Radiation on Materials: 16th International Symposium, ASTM STP 1175, Eds A. S. Kumar, D. S. Gelles, R. K. Nanstad (American Society for Testing and Materials, Philadelphia, 1994)p. 591.
[10] C. Wassilew, K. Ehrlich, J. Nucl. Mater. 191-194 (1992) 850.
[11] V. K. Shamardin, A. M. Pecherin, O. M. Vishkarev, V. P. Borisov, G. A. Tulyakov, in: Proc. Int. Conf. on Radiat. Mater. Sci. (Alushta, USSR, 1990) p. 3.
[12] M. A. Sokolov, R. L. Klueh, G. R. Odette, K. Shiba, H. Tanigawa, in: Effects of Radiation on Materials: 18th International Symposium, Volume 1, ASTM STP 1447, Eds M. L. Grossbeck, T. R. Allen, R. G. Lott, and A. S. Kumar (ASTM International, West Conshohocken, PA, 2004) p. 408.
[13] M. A. Sokolov, H. Tanigawa, G. R. Odette, K. Shiba, R. L. Klueh, J. Nucl. Mater. 367-370 (2007) 68.
[14] N. Saunders, X. Li, P. Miodownik, JPh. Schillé, in: Proc. Symp. Mater. Design Approach and Experiences, Eds J.-C. Zhao, M. Fahrmann, T. Pollock (The Materials Society; Warrendale, PA, 2001) p. 185.

[15] K. Shiba, in: Proceedings of the IEA Working Group Meeting on Ferritic/Martensitic Steels, November 3-4, 1997 (Japan Atomic Energy Research Institute, Tokai, Japan, 1998) 119.

[16] K. Shiba, Y. Kohno, A. Kohyama, in: Report of IEA Workshop on Ferritic/Martensitic Steels, November 2–3, 2000 (Japan Atomic Energy Research Institut, Tokai, Japan, 2001) 79.

[17] R. W. Hertzberg, Deformation and Fracture Mechanics of Engineering Materials, 3rd ed. (Wiley, New York, 1989) p. 253.
[18] C. J. McMahon, Jr., Fundamental Phenomena in the Materials Sciences, Eds L. J. Bonis, J. J. Duga, J. J. Gilman, Vol. 4 (Plenum, New York, 1967) p. 247.
[19] H. Tanigawa, M. A. Sokolov, K. Shiba, R. L. Klueh, Fusion Sci. and Tech, 44 (2003) 206.
[20] G.R. Odette, T. Yamamoto, H.J. Rathbun, M.Y. He, M.L. Hribernik, J.W. Rensman, J. Nucl. Mater. 323 (2003) 313.
[21] T. Yamamoto, G. R. Odette, H. Kishimoto, J. W. Rensman, P. Miao, J. Nucl. Mater. 356 (2006) 27.
[22] R.O. Ritchie, J.F. Knott, J.R. Rice, J. Mech. Phys. Solids 21 (1973) 395.