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RADIATION-INDUCED SEGREGATION IN HT-9 MARTENSITIC STEEL*

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ABSTRACT

Miniature notched-bar specimens of normalized and tempered HT-9 were neutron irradiated to ~13 dpa and broken at liquid nitrogen temperatures in a UHV chamber. Fracture surfaces were analyzed using scanning Auger electron spectroscopy. Following irradiation at 410°C, the fracture surface contained a small number of large relatively smooth facets, which are thought to be prior austenite grain boundaries. Strong segregation of Ni, Cr, Si, and P was detected at these surfaces, the remainder of the fracture surface showing no evidence of segregation. At irradiation temperatures of 520° and 565°C, there was relatively little segregation and none was found in thermal controls.

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INTRODUCTION

Ferritic/martensitic steels, with a tempered martensite lath structure, offer some advantages over austenitic stainless steels for first wall and blanket structural applications in terms of their superior swelling resistance, compatibility with liquid metals and their thermal stress resistance. The effect of neutron irradiation on fracture toughness is of concern, however. In the U.S., the mechanical behavior of HT-9, an Fe-12Cr-1Mo alloy containing W and V, is being studied extensively. An investigation of heat No. 91354 reported by Smidt et al. [1] demonstrated that irradiation to a fluence of ~5 dpa at 419°C increased the Charpy ductile-brittle transition temperature (DBTT) by ~108°C and significantly lowered the upper shelf energy. Further results for the same heat of material were presented by Hu [2]. Irradiation at 380°C to a fluence of 13 dpa increased the DBTT by ~140°C whereas irradiations to the same fluence at temperatures of 450°C and 550°C had virtually no effect on impact properties. Tensile data reported by Klueh and Vitek [3] for the same heat showed that irradiation to 11 dpa at ~400°C increased the yield stress by ~25% whereas irradiation at 450°, 500°, and 550°C had very little effect on strength properties. Higher fluence data reported in these proceedings by Gelles [4] show that the shift in DBTT saturates at ~10 dpa for irradiation temperatures in the range 390°–427°C. Irradiation at temperatures greater than 450°C produces smaller shifts in DBTT which saturate much more slowly with increasing influence. On the basis of fractographic examination, Smidt et al. [1] concluded that irradiation at 419°C increased the incidence of fracture along prior austenite grain boundaries; they postulated that a combination of increased yield strength and radiation-accelerated temper embrittlement was

responsible for the increased DBTT and the reduced upper-shelf toughness. On the other hand, Gelles and Hu [5], in a fractographic study of the specimens reported on by Hu [2], concluded that the fracture appearance was not altered by irradiation and that the reduced capacity for plastic strain was the primary factor involved in the radiation-induced loss of toughness. The present paper describes an attempt to measure, using Auger spectroscopy, the extent of chemical segregation at interfaces exposed by low temperature fracture of neutron irradiated HT-9.

EXPERIMENTAL PROCEDURES

The chemical composition of the test material, determined by Carpenter Technology Corporation, is given in Table 1. Small bar specimens, 1 mm square and 10 mm long were machined with a central 60° notch, 250 μm deep. They were annealed at 1035°C for 1 h, air-cooled and tempered at 760° for 1 h. Irradiation was carried out in EBR-II in the AAXIV experiment by the U.S. Breeder Reactor Cladding/Duct Materials Development Program. The irradiation temperatures were 410°, 520°, and 565°C (±20°C), and the neutron fluence was 2.8×10^{26} n/m^2, which corresponds to a damage level of about 13 dpa. Control specimens were aged at the appropriate temperatures for periods of 15,000 hs to match the times for the irradiated specimens.

Table 1

Composition of HT-9 Alloy (Heat 91354)

	Ni	Cr	Mo	W	Si	Mn	Al	C	S	P	N
Wt %	0.58	12.11	1.03	0.53	0.21	0.50	0.034	0.21	0.003	0.008	0.004
Atoms %	0.54	12.81	0.06	0.16	0.41	0.50	0.07	0.96	0.01	0.01	0.01

Following irradiation or thermal aging, each specimen was chemically cleaned in 10% HF-30% H_2SO_4-H_2O solution and rinsed in deionized water, air-dried, and inserted in a special fracture device in an ultra-high vacuum (UHV) fracture chamber attached to a Physical Electronics Model 590 Auger spectrometer. The fracture chamber was pumped to UHV conditions, the specimen was cooled to approximately 77K and fractured by impact. Without breaking the vacuum, the broken specimen was transferred to the spectrometer examination chamber. The areas of the fracture surface selected for Auger analyses were photographed using the built-in SEM feature. Later, they were recorded under higher resolution in another SEM.

Auger-electron spectroscopy (AES) was used to analyze the fracture surfaces before and after removal of surface layers by argon ion sputtering. Sputtering was done in five steps using 5 keV ions to a depth of 120 nm at normal incidence to the fracture plane. C, Ni, Fe, Cr, P, Si, W, S, Mo, O, V, N, and Mn were determined by measuring the peak-to-trough values in derivative spectra and applying the manufacturers elemental sensitivity factors to the dI/dE curves from each surface examined. The probe size was ~0.2 μm diam. The concentrations were normalized to 100%. Corrections were made for interference between iron and silicon peaks. Oxygen and carbon were not included in the normalization because they are subject to errors due to environmental contamination during long examinations. During impact fracture in the AES helium release was measured using a residual gas analyzer.

RESULTS

All specimens were broken well below the DBTT and exhibited a predominantly brittle fracture. Stereo-micrographs, obtained by SEM, showed randomly oriented

micro-facets of the order 2–5 μm with evidence for ductile-tearing at facet edges. These micro-facets are believed to be related to the underlying lath packet structure. The fracture surface of the specimen irradiated at 410°C is shown in Fig. 1. In addition to the overall micro-facetted structure, the surface contained several much larger facets of the order 25–50 μm diam. These macro-facets were strikingly smooth and clearly represented crack propagation along a different microstructural component. Very few of these macro-facets could be found in specimens irradiated at 520° and 565°C, and none could be found in thermal controls. However, thermal controls, which were first hydrogen charged and then broken at room temperature, did show a few such regions.

In all specimens, AES analysis of the micro-facetted regions yielded elemental concentrations at the same levels of the bulk chemical analyses, indicating no segregation in these regions. The macro-facets exposed in the hydrogen charged thermal controls showed enrichment of Cr and Mo suggesting that the fracture occurred through a region rich in carbides. A slight enrichment of phosphorus at these surfaces was removed by sputtering to less than 10 nm and was thought to be due to equilibrium segregation. On the other hand, the macro-facets in the specimen irradiated at 410°C displayed significant levels of segregation of Ni, Cr, Si, and P. Seven separate analyses were made on each of three macro-facets; the average concentrations are shown as a function of sputtered depth below the original surface in Fig. 2. At the fracture surface, chromium was enriched by a factor of ~1.4 above its bulk concentration; silicon was enriched by a factor of ~10. The concentration of phosphorus was ~1 at. %, representing an enrichment over the average concentration by a factor of ~100. In each case, these concentrations declined with depth and approached bulk

values within ~30 nm below the surface. Completely different behavior was observed for nickel. The measured surface concentration of nickel was ~4 at. %, i.e., about 8 times higher than the average bulk concentration. With increasing depth, the concentration of nickel increased, reaching a value of ~8 wt % at 60 nm, which then persisted to the maximum depth sputtered (120 nm).

During impact fracture in the AES, release of helium from the irradiated specimens was detected using a residual gas analyzer. Approximately twice as much helium was released from the specimens irradiated at 520°C as from the 410°C irradiated specimen.

Foils for TEM examination were prepared from broken specimens. The microstructures consisted of lath shaped subgrains ~0.5 μm wide containing large amounts of blocky carbides. Precipitation was more extensive in the irradiated specimens than in the thermal controls, much of the precipitation being at lath boundaries. Prior austenite grain boundaries were also heavily decorated with precipitates. Very small bubbles were detected at interfaces in the specimens irradiated at 520°C. Energy dispersive X-ray spectroscopy of precipitates in the 410°C-irradiated specimen yielded compositions of approximately 60 at. % Cr, 30 at. % Fe, and 3 at. % Si. Following irradiation at 520°C, Mo was incorporated at the expense of Fe. Ni could not be detected in these precipitates.

DISCUSSION

The existence of chemical concentration gradients at the surfaces of the macro-facets indicates that these surfaces are structural interfaces exposed by propagation of a brittle crack. The size (25–40 μm) and shape of the macro-facets suggests that they are prior austenite grain (PAG) boundaries.

Other possible microstructural features which should be considered include δ-ferrite grains, lath packets, inclusions, and carbides. Although relatively large quantities of δ-ferrite have been reported in HT-9 [6], its occurrence in our Auger specimens is restricted to occasional islands 4–5 μm in diam. The repeated normalizing treatments at 1035°–1050°C, which were used during processing the wrought bar stock from 3.5 cm thick to 0.1 cm thick, drastically reduced the amount of δ-ferrite retained from the ingot stage. The macro-facets appear to be too large by a factor of 4–5 to be related to lath packet boundaries. Inclusions or carbides can be ruled out on the grounds of size.

The occurrence of topographical features consistent with the PAG size, in fracture surfaces irradiated at HT-9, has been observed previously. Smidt et al. [1] reported such features in Charpy specimens made from the same heat of HT-9 (91354) following irradiation to 5 dpa at 412°C. At the lowest test temperature (93°C), these features were heavily micro-facetted while at the highest test temperature (427°C) they exhibited micro-void coalescence. Also, in the same heat of material irradiated at 390°C to 13 dpa and tested at –7°C, Gelles and Hu [5] observed a small number of relatively smooth cleavage regions which they related to failure at PAG boundaries.

The preceding evidence suggests that under the conditions of our experiment we have exposed a small number of PAG boundaries. It is possible that the relative smoothness of these fracture surfaces is related to a layer of retained austenite at the PAG boundaries produced during cooling from the final normalizing treatment. Although we have not examined our material for retained austenite, its existence in HT-9 has been described by Lechtenberg [7] and by Garrison and Hyzak [8]. During tempering, the retained austenite probably transforms to ferrite and $M_{23}C_6$. The existence of retained austenite layers

would make it possible for highly embrittled boundaries to fracture without exhibiting topographical features related to laths or lath packets.

The observation of strong concentration gradients of Ni, Cr, Si, and P at the brittle fracture features in specimens irradiated at 410°C, but not in specimens irradiated at higher temperatures or in thermal controls, suggests that we have detected a radiation-induced segregation phenomenon. The existence of high concentrations of phosphorus is of particular significance. Segregation of phosphorus to PAG boundaries, enhanced by an interaction with chromium, has been shown to be a major factor in the temper embrittlement of a 12Cr martensitic steel [9]. Although significant enrichment of all four elements occurs at the boundary, the behavior of nickel is completely different from the other three elements. Whereas the concentration of Cr, Si, and P decrease rapidly with increasing distance from the boundary, the Ni concentration increases initially and then persists at a high concentration over a distance of at least 120 nm. At present we have insufficient information on grain boundary precipitation reactions or on the nature of solute-point defect interactions in this material to draw any conclusions regarding the behavior of nickel.

It must be emphasized that the brittle fracture features are a relatively infrequent occurrence. This is probably because failure only occurs along those boundaries favorably oriented so as to contain the maximum resolved shear stress. Brittle crack propagation probably also requires the coincidence of favorable metallurgical parameters such as critical concentrations of segregants, thickness of retained austenite layer, and the nature of carbide precipitation. The radiation-induced segregation of Cr, Ni, Si, and P could well have some bearing on the Charpy impact behavior of HT-9. Smidt et al. [1]

observed an almost five-fold reduction in absorbed energy at ~100°C following irradiation at 412°C. This was ascribed to a large increase in yield stress, which inhibits the dissipation of stresses in the vicinity of the crack tip through slip, coupled with a weakening of PAG boundaries by some undefined mechanism. It is suggested that the radiation-induced segregation of Cr, Ni, Si, and P is involved in reducing the fracture resistance of PAG boundaries. The temperature dependence of radiation-induced segregation of these elements in HT-9 is not known, and it may well be significant at lower temperatures. Thermal processes will begin to dominate as temperatures approach 500°C. Smidt et al. [1] have shown that HT-9 is somewhat susceptible to reversible temper embrittlement following aging at 538°C. This process could give rise to reductions in the toughness of material irradiated at temperatures where radiation hardening does not occur.

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FIGURE CAPTIONS

Fig. 1. Scanning electron micrograph of the fracture surface of HT-9 irradiated at 410°C; segregation of Cr, Ni, Si, and P was detected at the central macro-facet.

Fig. 2. Concentration versus depth from the surface of fracture macro-facets on the specimen irradiated at 410°C. The concentrations are the average values from seven areas on three facets.

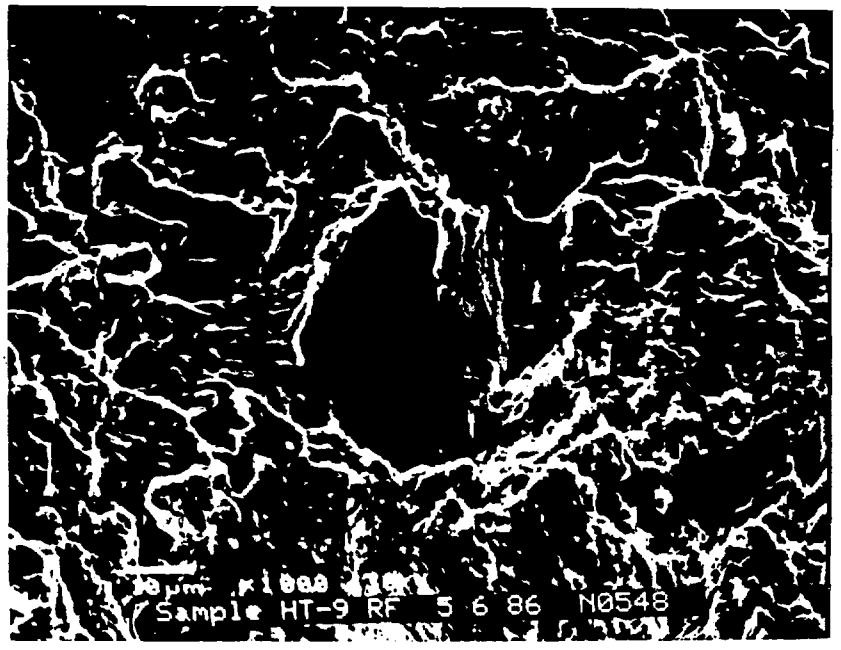
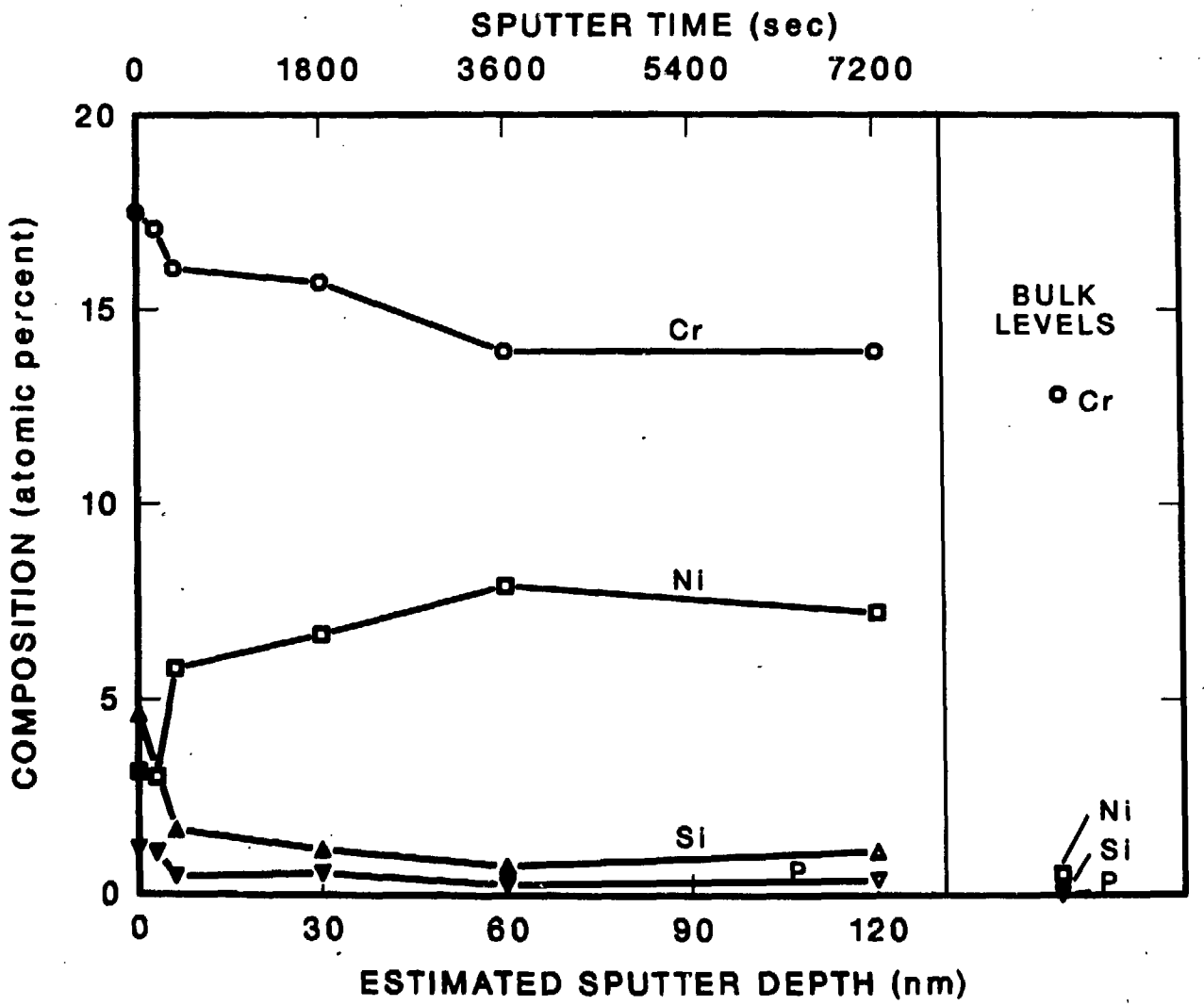


Figure 1

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