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Abstract

To assist in the characterization of microstructural changes associated with irradiation damage in low alloy steels, the technique of quantitative x-ray mapping using a field emission gun scanning transmission electron microscope (FEG-STEM) equipped with an x-ray energy Dispersive spectrometer (XEDS) has been employed. Quantitative XEDS microanalyses of the matrix and grain boundaries of irradiated specimens have been compared with previous quantitative analyses obtained using 3D-Atom Probe Field-Ion Microscopy (3D-APFIM). In addition, the FEG-STEM XEDS maps obtained from the irradiated steel have revealed the presence of 2 to 3 nm Ni-enriched "precipitates" in the matrix, which had previously been detected using 3D-APFIM. These quantitative FEG-STEM XEDS results represent the first direct and independent microchemical corroboration of the 3D-APFIM results showing ultra-fine irradiation-induced hardening features in low alloy steel.

Introduction

The properties of engineering materials are controlled by the microstructure developed during processing or thermal treatment. These microstructures frequently contain various transformation products and fine-scale precipitates that are intended to uniformly strengthen the material. However, solute redistribution leading to segregation or depletion at interfaces can give rise to other extraneous microstructural features that can significantly alter the properties of the material. Therefore, the ability to quantitatively assess local microchemical variations can provide critical insight necessary for understanding material behavior and optimizing the microstructure. The FEG-STEM approach combined with XEDS is a direct technique for elemental analysis of electron-transparent thin-film specimens. Recently, with the development of improved x-ray collection efficiencies and quantitative computation methods, it has proved possible to map out composition and thickness variations in thin-foil specimens with a spatial resolution approaching 1-2 nm and a sensitivity of less than 10 atoms in the analyzed volume [1,2].

In this investigation, the FEG-STEM XEDS technique has been applied to study the complex microstructural changes that occur in low alloy steel as a result of neutron irradiation. Irradiation induces hardening in the steels due to the formation of ultra-fine solute-enriched "clusters/precipitates"which have previously been identified using the APFIM technique, and vacancy-related defects [3]. The quantitative x-ray maps obtained using the FEG-STEM technique have been compared with the 3D-APFIM results for irradiated high Ni A508 Gr 4N steel.

Experimental

Material

The steel studied in this investigation was an A508 Gr 4N low alloy forging steel, the composition of which is listed in Table 1. This type of steel is generally bainitic (typically lower bainite). The steel was tempered at ~615°C for ~20 to 50 h after water-quenching from the reaustenitization temperature of 927°C. After tempering, the steel was aged at 565°C for 50 h, and slowly cooled to room temperature.

This steel had been neutron-irradiated at ~250°C to a damage level of 68 milli displacements per atom (mdpa).

Microstructural Analysis

Electron-transparent thin-foil specimens were prepared using conventional jet-polishing techniques in an electrolyte of 20% $HClO_4$ – 80% CH_3OH at a temperature of ~-35°C. Quantitative XEDS microanalysis and quantitative x-ray mapping were performed using the Lehigh University HB603 FEG-STEM operated at 300 kV. For quantitative microanalysis, x-ray spectra were acquired for 50 s. X-ray maps for the elements of interest (Fe, Cr, Ni, Mn, and Mo) were acquired with a dwell time per pixel of 200 ms. The discrete spot analyses and maps were obtained with an incident probe of ~1.5 nm (full width – tenth max). To quantify the x-ray maps, background intensities were subtracted from the characteristic x-ray maps and the ζ-factor method [4] was applied. The Cliff-Lorimer *k* factors [5] and the ζ-factors required for quantification were determined experimentally using standard specimens with known compositions.

Results and Discussion

TEM characterization revealed a tempered bainitic microstructure with well-developed laths that were sometimes decorated with Cr-enriched M_7C_3 or Fe-rich M_3C carbides. Fine Mo_2C and M_7C_3 carbides were also detected within some laths. Prior austenite grain boundaries contained some $M_{23}C_6$ carbides in addition to the M_7C_3 and M_3C carbides.

Discrete XEDS spot analyses were performed at prior austenite grain boundaries, lath boundaries, and at adjacent locations within the matrix to assess the presence of interfacial segregation. The results of these analyses are shown in Figure 1. The FEG-STEM analyses of the prior austenite grain boundaries revealed some measurable segregation of P and Mo compared to the matrix. The levels of P at the prior austenite grain boundaries were not sufficient to promote intergranular fracture in this material. This material exhibited a transgranular cleavage fracture morphology [6]. One example of limited Cr and Mn segregation to a prior austenite grain boundary was observed. Lath boundaries exhibited very little segregation, as anticipated. Quantitative FEG-STEM XEDS microanalysis of the matrix is summarized in Table 1.

Quantitative FEG-STEM XEDS maps obtained from the irradiated A508 Gr 4N specimen showed non-uniform or localized enrichments of Ni on a very fine scale. Figure 2 contains the bright-field STEM image of the analyzed region as well as the corresponding Ni and Mn XEDS maps and the thickness map (obtained using the ζ-factor technique). Detailed examination of the high magnification images revealed that highly localized regions (~3 nm in size) enriched in Ni were present. Some regions of Mn enrichment were also detected in association with the Ni enrichments.

Comparison of the FEG-STEM XEDS and 3D-APFIM Data

The matrix composition measured by XEDS was generally consistent with the results of the 3D-APFIM analysis. However, the XEDS-measured Mn levels were slightly higher than those measured by 3D-APFIM. The increased Mn contents measured by XEDS is related to the intrinsic Mn K signal generated by irradiated Fe-base materials. In addition, the matrix levels of Cr appeared to be lower on average than the Cr contents measured via 3D-APFIM. This reflects the local variation in Cr carbide precipitation within the microstructure. The FEG-STEM XEDS analyses obtained near prior austenite grain boundaries showed Cr levels as much as 40% lower than the APFIM matrix measurements. The prior austenite grain boundaries are preferential sites for the precipitation of Cr-rich $M_{23}C_6$ as well as M_7C_3. Thus, Cr depletion of the local matrix is expected.

It is important to note that the maximum Ni level measured, ~ 8%, is consistent with the incorporation of an irradiation-induced solute-enriched "precipitate" within the analyzed volume. 3D-APFIM analysis of

these "precipitates" yielded a composition of ~33% Ni - ~15% Mn -~6% Cu. (3) With the quantitative XEDS maps, it was also possible to estimate a number density of these solute-enriched "features"/ "precipitates". An estimate of ~2 X $10^{23}/m^3$ was obtained from the XEDS and thickness maps. This value is remarkably consistent with the ~5 X $10^{23}/m^3$ number density determined by 3D-APFIM of a relatively small volume of material (~16 nm X ~16 nm X ~85 nm).

Conclusions

These XEDS results provide the first independent direct microchemical analyses confirming the presence of irradiation-induced solute-enriched "precipitates" in high Ni A508 Gr 4N steel. Previous microchemical identification had only been possible using APFIM techniques. Although the 3D-APFIM can uniquely identify the complete microchemistry of the irradiation-induced solute-related hardening features within the microstructure, the complementary data obtained by FEG-STEM XEDS maps and discrete spot analyses are very important in the quantitative characterization of the material. The FEG-STEM XEDS mapping technique combined with the ζ-factor quantitative analysis represents a valuable complementary technique for the characterization of ultra-fine scale microchemical changes within an irradiated steel. Important advantages include the ability to analyze larger regions of the microstructure via mapping as well as performing quantitative spot analyses of specific microstructural features, such as grain boundaries or precipitates.

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Table 1. Comparison of A508 Gr 4N Steel Composition (wt.%, balance Fe)

		C	Mn	Ni	Si	Cr	Mo	Cu	Al	P	S
nominal		0.18	0.20	3.75	0.03	1.59	0.57	0.08	0.003	0.009	0.011
FEG-STEM XEDS	matrix	-	0.5-0.7	3.0-3.3	-	0.7-1.0-	0.2-0.3	-	-	0-0.05	-
3D-APFIM	matrix	0.01	0.2	3.02	0.03	1.18	0.39	0.08	-	0.01	-

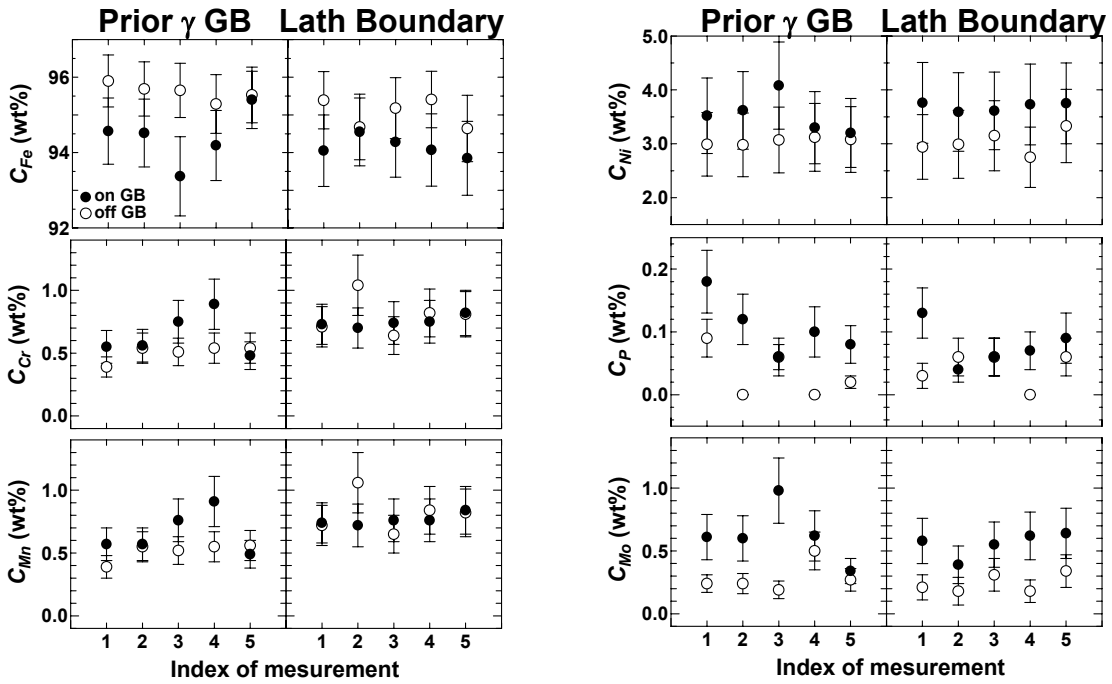

Figure 1. FEG-STEM XEDS discrete analyses obtained on and off of prior austenite grain boundaries and lath boundaries. The filled and open symbols represent the boundary analyses and the adjacent matrix analyses, respectively. The error bars represent 3σ.

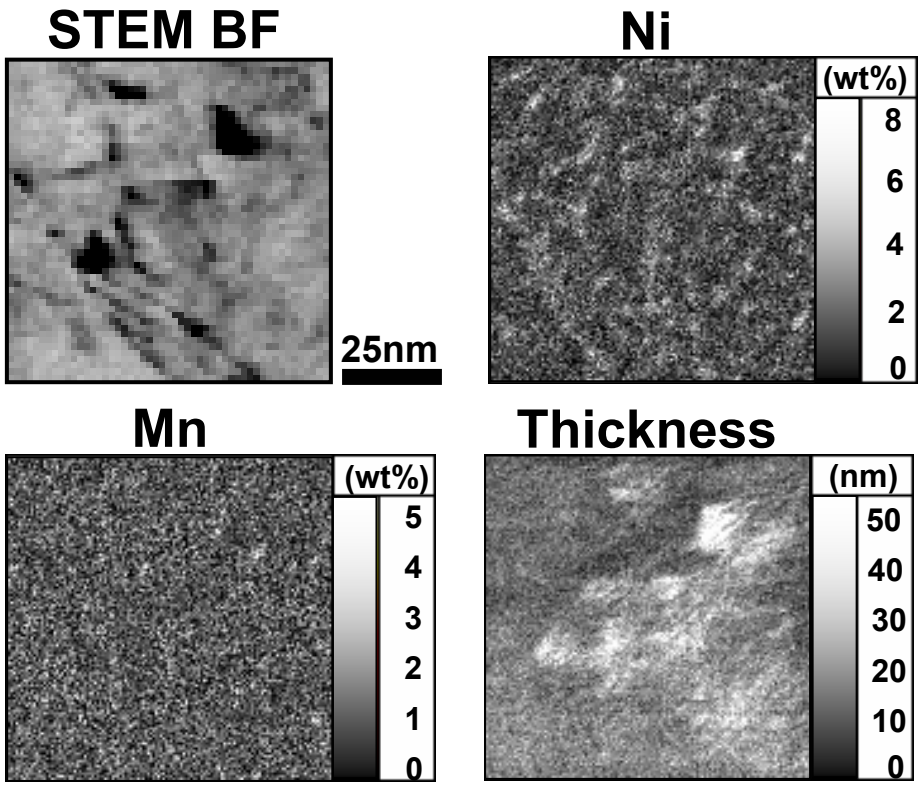

Figure 2. A bright-field STEM image obtained from the irradiated A508 Gr 4N steel and corresponding Ni and Mn compositional maps. By applying the ζ-factor method, the thickness map can be extracted from X-ray intensity data.