Structural Characterization of Nanoscale Intermetallic Precipitates in Highly Neutron Irradiated Reactor Pressure Vessel Steels

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ABSTRACT

Massive, thick-walled pressure vessels are permanent nuclear reactor structures that are exposed to a damaging flux of neutrons from the adjacent core. The neutrons cause embrittlement of the vessel steel that **grows** with dose (fluence), as manifested by an increasing ductile-to-brittle fracture **transition temperature**. Extending reactor life requires demonstrating that large safety margins against brittle fracture are maintained at the higher neutron fluence associated with **beyond 60** years of service. Here synchrotron-based x-ray diffraction and small angle x-ray scattering measurements are used to characterize highly embrittling nm-scale Mn-Ni-Si precipitates that develop in the irradiated steels at high fluence. These precipitates lead to severe embrittlement that is not accounted for in current regulatory models. Application of the complementary techniques has, for the very first time, successfully identified the crystal structures of the nanoprecipitates, while also yielding self-consistent compositions, volume fractions and size distributions.

I. INTRODUCTION

Reactor pressure vessels (RPVs) are the primary permanent component of light water reactors (LWRs). RPVs experience irradiation embrittlement that increases with neutron fluence (see Refs[1–3] for overviews of the embrittlement phenomena and underlying mechanisms). Ensuring that large safety margins are maintained in the face of embrittlement is required to extend LWR service life to beyond 60 years. Embrittlement is marked by increases in the ductile-to-brittle transition fracture temperature (ΔT) of RPV steels. The ΔT is primarily caused by irradiation hardening ($\Delta\sigma_y$) associated with the formation of nm-scale precipitates and solute-defect complexes that act as obstacles to dislocation glide. At low to intermediate neutron fluence, significant hardening and embrittlement is primarily caused by the formation of coherent, transition phase copper rich precipitates (CRP). **Trace impurity amounts of Cu** (< 0.35 at.%) are insoluble in steels and rapidly phase separate due to radiation enhanced diffusion **(RED)** at

RPV service temperatures (around 290°C). RED is due to excess concentrations of vacancies produced by neutron displacement damage. The CRPs are also enriched in Mn, Ni and Si, in the form of a core (primarily Cu)-shell (primarily Mn-Ni-Si) structure. The hardening and embrittlement due to CRPs saturate when the Cu is depleted from the ferrite matrix. However, the Mn, Ni and Si solutes continue to slowly accumulate in the precipitates, that grow to large volume fractions (up to ~3%) at high fluence since there is much more Mn + Ni + Si (e.g. > 2.5%) than Cu in typical low alloy RPV steels. Further, it was long ago predicted [4–6], and more recently shown [7-11] that Mn-Ni-Si precipitates (MNSP) can also form in low or Cu free steels, but only at sufficiently high fluence. Hence the MNSP have also been called late blooming phases. The ΔT approximately scales as $300^\circ\text{C} \times \sqrt{f}$, where f is the volume fraction of the precipitates [1,2,10]. Thus the large volume fractions associated with MNSP could limit safe extended RPV lifetimes. However, late blooming MNSP are not accounted for in current embrittlement regulatory models based on lower fluence databases.

Solute precipitation and embrittlement are complex phenomenon that depend on the combination of both metallurgical (microstructure, composition, product form and heat treatment) and irradiation (neutron flux, fluence, irradiation temperature) variables. RPV steels have a very wide range of compositions that may be vulnerable to MNSP: Cu $\approx$ 0.02-0.35, Mn $\approx$ 0.8-1.6, Ni $\approx$ 0.2-1.6, Si $\approx$ 0.4-1.2 in at.%. Formation of MNSP also depends on the irradiation temperature, flux and fluence. In general, MNSP are promoted by higher Ni and Cu, lower temperatures and flux and, as noted previously, high fluence. Thus there is a pressing need to incorporate MNSP effects into embrittlement models that can reliably extrapolate ΔT predictions to extended life at high-fluence, low-flux service conditions, where little or no data currently exists. This requires robust physical models that are informed and calibrated by well-designed experiments and characterization studies.

The radiation-induced precipitation in RPV steels has primarily been studied by small angle neutron scattering (SANS) and atom probe tomography (APT). The APT studies provide good measures of CRP and MNSP number densities (N), volume fractions (f), size distributions and average sizes (d) and show that their compositions lie in the vicinity of the G ($\text{Mn}_6\text{Ni}_{16}\text{Si}_7$) and Γ_2 ($\text{Mn}_2\text{Ni}_3\text{Si}$) phases in the Mn-Ni-Si ternary projection of the Fe-based quaternary system phase diagram at around 290°C [10,12]. However, neither SANS nor APT provides information on the crystal structure of the MNSP. Phase identification is needed to develop rigorous thermodynamic and kinetic precipitation models. However, characterizing MNSP crystal structures is very difficult, due to their nm-scale sizes, complex chemistry and limited volume fractions [9,13]. In principle, transmission electron microscopy (TEM) can be used for structure identification, but this has had limited success, indexing the G-phase in only a few cases. Of course, the

basic thermodynamics of phase formation can be used to predict the phase selection. Notably, Thermocalc enabled Calphad models predict Γ and Γ_2 phases in the RPV steel region of the Fe-Mn-Ni-Si quaternary phase diagram, with mole fractions and compositions that are reasonably consistent with the APT measurements [10-11].

Standard x-ray diffraction techniques suffer many of the same challenges to phase identification [14,15]. However, in this work, advanced synchrotron x-ray techniques were used to successfully identify the dominant MNISP intermetallic phases in a set of six irradiated RPV steels with systematic variations in Cu and Ni contents. Phase identification was enabled by a combination of small angle x-ray scattering (SAXS) and x-ray diffraction (XRD). The corresponding results of the synchrotron x-ray techniques for MNISP f and d are shown to be internally self-consistent and in good agreement with APT measurements and thermodynamic predictions.

II. MATERIALS AND METHODS

The chemical compositions of the six split melt RPV steels investigated are shown in Table 1. The L-series alloy includes increasing amounts of Cu (LG, LH, LI and LC) and intermediated and higher contents of Ni (LC and LD). The CM6 alloy is nearly Cu free, but contains a large amount of Ni. Specimens in the form of 2×0.5 mm discs were wrapped in three layers of Kapton to prevent any radioactive contamination at the synchrotron beamline. The alloys were previously irradiated to a high-fluence of $\sim 1.10 \times 10^{21}$ n/cm² at 290°C in the Idaho National Laboratory Advanced Test Reactor (ATR) at a neutron flux of $\sim 2.3 \times 10^{14}$ n/cm²-s.

High-resolution XRD measurements were performed at the National Synchrotron Light Source using the high-energy X-rays available at beamline X17A. SAXS measurements were performed at the X-ray Powder Diffraction (XPD) beamline of the new National Synchrotron Light Source-II. All measurements were performed in transmission mode with an amorphous Silicon-based flat panel detector (Perkin-Elmer) mounted orthogonal to and centered on the beam path. The sample-to-detector distances and tilts of the detector relative to the beam were refined using either CeO₂ (XRD), or Silver Behenate (SAXS) powder standards. The wavelengths of the incident X-rays were 0.1839 Å (67.42 keV, X17A) and 0.2361 Å (52.51 keV, XPD). The sample-to-detector distances were calculated to be 780 mm for XRD (with maximum two theta range of 20 degrees) and 2893 mm for SAXS (with a Q-range of 0.01-0.8 Å⁻¹). Multiple patterns were collected to avoid saturation of the detector. Typical count times were 0.5-1 sec (depending on the sample). Each diffraction or scattering pattern consisted of the average of 100-500 individual exposures. All raw two-dimensional patterns were background corrected by subtracting the

dark current image and Kapton/air scattering. Noticeable artifacts in the images (like the beam stop or dead pixels) were masked. The corrected and masked two-dimensional detector images were then averaged and radially integrated to obtain the one-dimensional powder diffraction and SAXS patterns.

The measured SAXS intensities were converted to absolute cross-section units following the methods described in Ref [16]. Precipitate sizes were determined using the nonlinear least square fitting procedures in the IGOR Pro-based software package IRENA [17]. Spherical particles were assumed, consistent with previous APT and TEM measurements [10]. The electron density difference (or atomic density difference) between the matrix and the precipitates were calculated within IRENA based on their respective bulk-phase values.

The Kapton/air background subtracted XRD patterns were Rietveld refined with the TOPAS software package (BRUKER). The peak profiles were modeled by a modified pseudo-Voigt function. The instrument contribution to the broadening of the measured profiles was quantified by fitting a CeO₂ NIST powder standard (38 hkl reflections), with known crystalline-domain size and negligible strain contribution. The Gaussian and Lorentzian-based broadening parameters were subsequently fixed during the analysis of the alloys under investigation. The volume fraction f , domain size, lattice parameter, and strain were allowed to vary during the Rietveld refinements, with the isotropic temperature factors [18] nominally fixed to their bulk values taken from the literature [13,16,19–21]. The strain components for the small austenite fcc phase [22], the cementite (alloyed Fe₃C type phase) and MNSPs (described below) were not included in the refinements due to the known complications to their quantification at such small sizes [23,24]. Therefore, the refined size parameters of the cementite and austenite phases are lower limits. Furthermore, in the case of the irradiated alloys, where the diffraction contributions of the nm-scale MNSP are small, the precipitate size, determined from SAXS, was fixed and only f and the lattice parameter were allowed to vary during the refinement. This method is similar to that employed in the field of mineralogy to determine the structure and fraction of a phase with partial or no known crystal structure (PONKCS) [25,26].

III. RESULTS AND DISCUSSION

A. Small-Angle X-ray Scattering

Figure 1 shows the background corrected SAXS patterns for the (a) LD and (b) CM6 -unirradiated and irradiated alloys (alloys with the highest and lowest Cu content, respectively). The scattering intensity at low- Q , is indicative of features with sizes of ~ 40 -70 nm, that can be attributed to the cementite particles. The SAXS patterns for all the alloys were found to change significantly following irradiation.

The increase in the scattering amplitude at higher Q in the irradiated samples is due to the formation of new nm-scale MNSPs that are remarkably quantitatively consistent with APT measurements [10]. Table 2 summarizes the SAXS and APT d and f .

B. X-ray Diffraction

Figure 2 shows XRD patterns for (a) LD and (b) LG unirradiated and irradiated alloys with the identified phases superimposed for reference. The quantitative Rietveld results (see supplementary information) for the unirradiated samples show that the line broadening from the strain components are small for the ferrite phase. All the unirradiated alloys also display a Fe_3C contribution ($f \approx 2.1\text{-}2.7\%$) and a small fcc phase contribution ($f \approx 0.6\text{-}1.8\%$). These small fcc crystallites are primarily attributable to the austenite phase (fcc Fe), although, in some cases, there may be a minor contribution from fcc Cu that precipitates during heat treatments [1].

Figure 2 shows changes in the XRD patterns after irradiation, including: i) an increase in the structured scattering background; ii) a slight broadening of the ferrite peaks; and iii) partial to complete removal of the peaks associated with the fine scale austenite phase. The only alloys that retain an austenite component after irradiation are LD and CM6, both with higher Ni contents. These alloys also contained the largest austenite crystallites prior to irradiation. The removal of the peaks associated with the retained austenite is attributed to their transformation to ferrite, or a significant decrease in their size (again for LD and CM6), consistent with previous studies [27]. The quantitative Rietveld analysis of the irradiated alloys (see supplementary information) reveals that irradiation induces some subtle changes in the crystalline domain size for the ferrite and cementite phases and a minor increase in the strain broadening in the ferrite phase, compared to their unirradiated counterparts, perhaps due to accumulation of defects like dislocation loops.

The intrinsic broadening of diffraction peaks for nm size particles, and the small volume fractions both result in an increase in the structured diffraction intensity background, rather than generating discernable peaks at bulk phase 2θ angles. However, the peak broadened contribution can be calculated for a given precipitate size and crystal structure, thus fits to the structured background can provide a basis for phase identification and quantification of MNSP structure and f using an appropriate Rietveld refinement model. Thus the diffraction patterns were simultaneously refined while incorporating either the G or the Γ_2 phase with fixed d that were determined from the nearly equivalent SAXS and APT measurements. The only parameters allowed to vary in the refinements were the f and lattice parameters of the MNSPs. Figure 3 shows representative fits for the LD and CM6 alloys. The blue curve identifies the respective

MNSP structures. The quantitative fitting results for the MNSP are given in Table 3 considering one of the two intermetallic phases. All the irradiated alloys, except CM6, could be refined with confidence only for predominantly G-phase, while only the Γ_2 -phase consistently returned non-physical parameters and low f values ($< 0.1\%$ see supplementary information). As also shown in Table 3, the G-phase f from all of the refined XRD analysis are in excellent agreement with those determined from the APT [10] and SAXS measurements described above and in Table 2. The weighted profile R-factor, R_{wp} (see supplementary information for definition), for the irradiated samples decreased with the inclusion of the MNSP, as shown in Table 3. Including the extra phase resulted in R_{wp} values almost identical to their unirradiated counterparts. The lattice parameters determined from the Rietveld refinement are slightly different (averaging $\sim +1.8\%$ for L-series alloys and $\sim -7.1\%$ for the CM6 alloy) compared to their bulk counterparts ($\text{Mn}_6\text{Ni}_{16}\text{Si}_7$: $11.167 \text{ \AA}$ [13] and $\text{Mn}_2\text{Ni}_3\text{Si}$: $6.673 \text{ \AA}$ [12,28]). These differences may be due to the complex MNSP chemistry, in combination with the large surface-to-volume ratios of these nm-scale features coherently or semi-coherently embedded in the ferrite matrix, as has been observed in other comparable nanoparticle ensembles [29–31]. Further, in the medium Ni L-series alloys, the deviations were on average larger in the steels with MNSP appended to copper rich precipitates. Finally, as shown in the supplementary material, refinements considering the possibility of both G and Γ_2 phases also yields good fits. While APT suggests a relatively small range of compositions, the possibility of multiple phases, which is predicted by some thermodynamic databases [11], will be explored in future research.

The phase selection in the Rietveld refinement analysis is also consistent with the Thermocalc II database thermodynamic predictions for the L-series high-Ni, high-Cu alloy LD and the high-Ni, low-Cu CM6 alloy, containing G and Γ_2 -phases, respectively [11]. In the other irradiated intermediate Ni L-series alloys (LG, LH, LI, LC) with intermediate Ni and increasing Cu, the APT measurements generally lie in the vicinity of the average compositions predicted by Calphad models using the Thermocalc II database, as a mixture of G and Γ_2 -phases. Notably, the APT compositions of these alloys lie near the Si rich end of the Γ_2 -phase field. The XRD data suggests the dominant formation of the G phase in these cases, which is consistent with an alternative University of Wisconsin thermodynamic database. The predicted phases based on the chemical compositions are listed in Table 3. Thus our combined SAXS/APT and refined XRD data provide a basis to test and improve the parameterization of the thermodynamic models in a way that was not possible using either technique alone. More generally, our XRD Rietveld refinements confirm the thermodynamic predictions that the MNSPs are indeed crystalline intermetallic phases [11].

It is important to recognize the occurrence and character of MNSP have been a matter of considerable controversy [32-37]. For example, it has been argued, based on computer simulations, that: a) such

features were neither late blooming, in the sense that they evolve to large volume fractions only at high fluence beyond a threshold; or, b) that they were phases at all. Rather, it was proposed that the Mn-Ni features (Si not included) are non-equilibrium sub-nm solute-defect cluster complexes that develop as a result of radiation induced segregation (RIS) [32, 34]. Significant issues in this work with the embedded atom potential predicted repulsive Ni-Mn interactions were addressed in a later paper, with an improved potential [33, 35], that predicted the stability of sufficiently large Mn-Ni B2 coherent clusters, but only at very high solute concentrations and/or low temperatures. The resulting conclusion remained that RIS leads to the formation of non-equilibrium Mn-Ni clusters. However, the Fe-Ni potential used in this paper was not fit to the experimental Ni phase boundary, and as specifically noted by the authors, overestimated the observed solubility in Fe by a factor of 5 [33]. The RIS non-equilibrium precipitate hypothesis is also not consistent with thermally induced MNSP that have been observed in high Ni steels, as an appendage to Cu-rich precipitates [34, 38]; in this case nucleation is promoted by the presence of both the precipitated Cu and grain boundaries. Finally, the models in [32-35] do not consider the role of Si in MNSP.

The results reported here do not speak to the issue of nucleation of MNSPs, nor do we exclude the role of RIS in this process, as well as in possibly slightly modifying the otherwise equilibrium MNSPs, at least at early stages of clustering and precipitation. Indeed, Mn segregation to dislocation loops in irradiated binary alloys is well established [37]. Further, we have long argued that defect-solute (Mn, Ni, Si, P, Cu) cluster complexes formed in high recoil energy neutron induced cascades are the likely precursors to well-formed MNSPs, but again the latter evolve as large volume fraction of equilibrium, or near equilibrium, phases only at high fluence. The controversy that these phases exist has been largely laid to rest by previous APT results and thermodynamic models discussed in [10,11]. However, the phase identification achieved in this study makes the case even more compelling.

More importantly, the current results show the intermetallic nature of MNSP is extremely important to informing rigorous physically based thermodynamic and kinetic models of irradiation enhanced precipitation, including the possibly effects of RIS as well as RED, and the resulting hardening and embrittlement of RPV steels. Such models are needed to more reliably extrapolate to conditions beyond the existing surveillance database.

IV. CONCLUSIONS

In summary, we have shown that a combination of complementary characterization methods can be used to develop a more detailed understanding of embrittlement of RPV steels irradiated up to high neutron

fluence. The MNSP d and f from SAXS, APT and XRD measurements are nearly identical based on the composition and densities of G and Γ_2 phases. Thus truly remarkable self-consistency exists, not only between the various characterization techniques, but also with well-accepted thermodynamic models.

Perhaps most significantly, quantitative Rietveld refinements characterized, for the first time, crystal structures of intermetallic MNSPs in highly irradiated RPV alloys that are also consistent with the thermodynamic models. While the MNSPs are indeed crystalline, the measured lattice parameters differ slightly from their bulk counterparts, especially in the case of the $\text{Mn}_2\text{Ni}_3\text{Si}$ phase.

The combined SAXS/APT/XRD technique and analysis approach is by no means limited to studying precipitates in irradiated RPV steels, and it will also enormously contribute to characterization of relatively small fractions of otherwise unidentified nm-scale phases in a wide variety of other structural materials. The extension of this combined approach to other materials systems, as well as including other relevant techniques, such as small angle neutron scattering and diffraction, will also be explored in the future.

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FIGURES

Figure 1. Background corrected SAXS scattering intensity as a function of scattering vector, Q , for the irradiated LD and CM6 samples. Solid black lines are the fits to experimental data for the irradiated samples.

Figure 2. High-resolution XRD patterns for the unirradiated and irradiated (a) LD (b) LG samples. The peaks attributable to the cementite (Fe₃C), austenite (FCC Fe) and ferrite (BCC Fe) phases are included for reference. The magnified range highlights the specific features (i-iii) discussed in the text.

Figure 3. Modified Rietveld refinements for the (a) LD and (b) CM6 irradiated samples. The components of each phase are included for reference. The magnified range highlights the broad features of the small MNSP component(s). The blue curve identifies the MNSP structures.

TABLES

TABLE 1. Nominal chemical compositions (wt.%) for the RPV samples

Sample ID	Cu	Ni	Mn	Mo	P	C	Si	Fe +imp
LC	0.41	0.86	1.44	0.55	0.005	0.14	0.23	balance
LD	0.38	1.25	1.38	0.55	0.005	0.19	0.23	balance
LG	0.01	0.74	1.37	0.55	0.005	0.16	0.22	balance
LH	0.11	0.74	1.39	0.55	0.005	0.16	0.24	balance
LI	0.2	0.74	1.37	0.55	0.005	0.16	0.24	balance
CM6	0.02	1.68	1.5	0.54	0.007	0.15	0.17	balance

TABLE 2. The precipitate sizes and volume fractions as determined from previous APT measurements [10] and the SAXS analysis.

Alloy ID	diameter (APT) (nm)	f (APT) (%)	diameter (SAXS) (nm)	f (SAXS) (%)
LC	2.9	1.8	2.9 (0.5)	1.8
LD	3.9	2.1	4.0 (1.1)	2.4
LG	2.5	1.3	2.4 (0.5)	1.3
LH	2.7	1.5	2.7 (0.5)	1.4
LI	2.7	1.5	2.5 (0.4)	1.6
CM6	3.0	2.8	3.2 (1.5)	2.9

Table 3. Refined parameters for the irradiated samples from the Rietveld analysis. The predicted phases from [10-11] are included for reference.

Alloy	a	f	d	R_{wp}	R_{wp}	XRD Phase	APT	Calphad/TC	U. Wisc.
ID	(Å)	(%)	(nm)	with Mn-Ni-Si	without Mn-Ni-Si	(Mn/Ni/Si)	(Mn/Ni/Si)	Phase	G/ Γ_2 (Mn/Ni/Si)
LC	11.329	1.8	2.9	6.2	7.2	G	37/44/19	G	33/67
	(0.018)	(0.2)	(fixed)			(21/55/24)			(30/52/18))
LD	11.612	2.1	4.0	6.6	7.5	G	25/52/23	G	73/27
	(0.032)	(0.2)	(fixed)			(21/55/24)			(24/54/12)
LG	11.268	1.3	2.4	4.5	6.3	G	31/46/23	G	100/0
	(0.020)	(0.2)	(fixed)			(21/55/24)			(21/55/24)
LH	11.224	1.4	2.7	5.8	7.5	G	37/43/20	G	22/78
	(0.031)	(0.2)	(fixed)			(21/55/24)			(31/52/18)
LI	11.445	1.6	2.5	7.0	8.5	G	35/44/21	G	92/8
	(0.040)	(0.1)	(fixed)			(21/55/24)			(22/55/23)
CM6	6.197	2.9	3.2	5.4	6.3	Γ_2 (33/50/17)	35/53/12	Γ_2	0/100
	(0.027)	(0.2)	(fixed)						(33/52/15)