Evolution of manganese–nickel–silicon-dominated phases in highly irradiated reactor pressure vessel steels

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Abstract

Formation of a high density of Mn–Ni–Si nanoscale precipitates in irradiated Cu-free and Cu-bearing reactor pressure vessel steels could lead to severe unexpected embrittlement. Models long ago predicted that these precipitates, which are not treated in current embrittlement prediction models, would emerge only at high fluence. However, the mechanisms and variables that control Mn–Ni–Si precipitate formation, and their detailed characteristics, have not been well understood. High flux irradiations of six steels with systematic variations in Cu and Ni contents were carried out at ≈24295°C to high and very high neutron fluences of ≈1.3 × 1020 and ≈1.1 × 1021 n cm−2. Atom probe tomography shows that significant mole fractions of Mn–Ni–Si-dominated precipitates form in the Cu-bearing steels at ≈1.3 × 1020 n cm−2, while they are only beginning to develop in Cu-free steels. However, large mole fractions of these precipitates, far in excess of those found in previous studies, are observed at 1.1 × 1021 n cm−2 at all Cu contents. At the highest fluence, the precipitate mole fractions primarily depend on the alloy Ni, rather than Cu, content. The Mn–Ni–Si precipitates lead to very large increases in measured hardness, corresponding to yield strength elevations of up to almost 700 MPa.

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1. Introduction

Light water reactor (LWR) plant life extension to 80 years is needed to sustain the largest US carbon-free energy resource [1]. The major permanent and safety-critical LWR component is the massive reactor pressure vessel (RPV). Neutron irradiation of RPV steels results in embrittlement, manifested as upward brittle-to-ductile transition temperature shifts (TTSs). TTSs are primarily caused by the precipitation and defect hardening that occur under irradiation. Life extension requires demonstration that RPVs operate within safety margins, including ensuring that the effects of long-term irradiation on fracture toughness can be predicted and safely managed. The major RPV challenge for life extension is to develop robust predictive models of TTS in neutron flux and fluence regimes for which data largely do not currently exist. Here we verify the existence of a potentially severe precipitation hardening and embrittlement mechanism that emerges only at high fluence. Notably, this mechanism is not accounted for in current embrittlement prediction models. We also report on a number of new insights and related details regarding the nature and potential impact of the responsible precipitation hardening phases.

Current US TTS regulations derive from physically motivated models fitted to the in-service power reactor, engineering (surveillance) database [2–4]. These models
treat the accelerated formation of Cu-rich precipitates (CRPs), due to radiation-enhanced diffusion [5], as well as solute–defect cluster complexes, referred to here as matrix features, which form in steels both with and without significant Cu contents. Matrix features are believed to initially form in displacement cascades as defect–solute cluster complexes, or their defect-free remnants [2–4,6–9]. Both CRPs and matrix features also generally contain significant quantities of Mn, Ni and Si [6–27]. However, current models predict that the CRP contribution to hardening saturates when Cu is depleted from the matrix [2,3]. Additional hardening due to matrix features increases linearly with the square root of fluence at the same relatively slow rate in both the Cu-bearing and Cu-free steels, and does not saturate. The semi-empirical models were fitted to the surveillance database that contained little high fluence (>5 × 10¹⁹ n cm⁻²) TTS, pertinent to extended life. Thus extrapolations of TTS to 80-year operation may not be reliable [4].

Most notably, the potential for large mole fractions of Mn–Ni–Si (MNS) precipitates to form at high fluence is not included in the existing embrittlement models. This deficiency may be one source of the large underpredictions of TTSs observed in higher flux and fluence test reactor irradiations [4]. MNS phases are also of interest in their Cu and Ni contents. The effects of high flux hardening in these high to very high fluence test reactor irradiations would likely occur at much lower irradiation conditions. The CRP contribution to hardening, primarily by delaying precipitation to higher fluence [2,6–8,14,28,29]. This is illustrated in Fig. 1a and b for irradiation hardening, represented by an equivalent change in yield stress (Δσₚ) and precipitate volume fractions (f_p) in a high-Cu, medium-Ni content steel (LC), plotted as a function of the square root of fluence (ϕt), for low-flux (ϕ) irradiations in the previous UCSB Irradiation Variables (IVAR) Program and high-flux BR2 irradiations [29]. The increasing delay in both precipitation and hardening with increasing flux is obvious. These results are presented here simply to show that the precipitation hardening in these high to very high fluence test reactor irradiation conditions would likely occur at much lower flux than in low-flux power reactor conditions. The flux-adjusted power reactor equivalent fluences for these irradiations are yet to be verified, but based on our current best estimates, the BR2 irradiation would likely have an equivalent fluence that occurs before an 80-year end of vessel service life, while the corresponding ATR irradiation equivalent fluence would require more than 80 years [29]. However, the data from the ATR irradiation permit interpolation to an 80-year condition, and provide insight about

Here we focus on atom probe tomography (APT) studies of precipitates formed at two very high flux and high to very high fluence irradiation conditions. The experiments were carried out in the Belgian Reactor 2 (BR2) and the US Advanced Test Reactor (ATR), respectively. The test reactor fluxes range from 2500 (BR2) to 5800 (ATR) times higher than those in a vessel that reaches an end-of-life fluence of ~10²⁰ n cm⁻² in 80 years. The corresponding BR2 and ATR fluence levels range from ~1.3 × 10³⁰ n cm⁻² to a previously unexplored ~11 × 10³⁰ n cm⁻².

As shown below, and for the first time, the very high fluence condition in this study produces extremely large mole fractions of MNS phases in six steels with systematic variations in their Cu and Ni contents. The effects of high flux will be discussed in detail in future publications. We note, however, that it is well known that higher flux affects hardening and embrittlement, primarily by delaying precipitation to higher fluence [2,6–8,14,28,29]. This is illustrated in Fig. 1a and b for irradiation hardening, represented by an equivalent change in yield stress (Δσₚ) and precipitate volume fractions (f_p) in a high-Cu, medium-Ni content steel (LC), plotted as a function of the square root of fluence (ϕt), for low-flux (ϕ) irradiations in the previous UCSB Irradiation Variables (IVAR) Program and high-flux BR2 irradiations [29]. The increasing delay in both precipitation and hardening with increasing flux is obvious. These results are presented here simply to show that the precipitation hardening in these high to very high fluence test reactor irradiation conditions would likely occur at much lower fluence than in low-flux power reactor conditions. The flux-adjusted power reactor equivalent fluences for these irradiations are yet to be verified, but based on our current best estimates, the BR2 irradiation would likely have an equivalent fluence that occurs before an 80-year end of vessel service life, while the corresponding ATR irradiation equivalent fluence would require more than 80 years [29]. However, the data from the ATR irradiation permit interpolation to an 80-year condition, and provide insight about

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Fig. 1. (a) Δσₚ and (b) f_p in a high-Cu, medium-Ni content steel (LC) for various irradiation conditions as a function of square root of the fluence showing a delay in both hardening and precipitate f_p with increasing flux.
the detailed nature of MNS precipitates, as well as how and why they form.

A description of the materials and methods is followed by a section that first summarizes data from the high-fluence BR2 irradiation, followed by the corresponding data for the very high-fluence ATR condition. Assessing similarities and differences between these two irradiation conditions provides insight, not only on MNS precipitation kinetics, but also on the sequence of events leading to the formation of large mole fractions of precipitates. Further, the very high-fluence ATR irradiation produces precipitates that are well developed, at both larger sizes and mole fractions than have been previously observed. Thus these data are analyzed in great detail, since the larger MNS precipitates are more amenable to detailed characterization by APT. The paper concludes with a brief discussion of some of the implication of our observations, a summary of the main conclusions and a few comments on future work.

2. Experimental

2.1. Materials and irradiation conditions

A large number of RPV split melt pressure vessel steels were irradiated to a wide range of irradiation conditions in IVAR, BR2 and the ATR. This paper will present data for only six steels in two of the irradiation conditions, which are shown in Table 1. The first irradiation was carried out at a flux of $\sim 1.0 \times 10^{14}$ n cm$^{-2}$ s$^{-1}$ to a high fluence of $\sim 1.3 \times 10^{20}$ n cm$^{-2}$ in BR2 at $\sim 300$ °C. The second irradiation was carried out at a flux of $\sim 2.3 \times 10^{14}$ n cm$^{-2}$ s$^{-1}$ to a very high fluence of $\sim 1.1 \times 10^{21}$ n cm$^{-2}$ in ATR at $\sim 290$ °C. The high-fluence BR2 specimens were in the form of 23 mm $\times$ 3 mm $\times$ 0.5 mm coupons. The very high-fluence specimens in the ATR irradiation were in the form of 8 mm $\times$ 0.5 mm discs. Four steels with similar Ni ($\sim 0.8$ wt.%) and Mn ($\sim 1.4$ wt.%) contents had systematic variations in their bulk Cu content from 0.01 to 0.41 wt.% (LG, LH, LI, LC). One high-Cu content steel (LD) had a larger 1.25 wt.% Ni, while another, that was essentially Cu-free, contained the highest 1.68 wt.% Ni along with 1.50 wt.% Mn and lower 0.17% Si (CM6). The steel compositions and heat treatments are summarized in Table 2. As a terminology guide, alloys that contain $\sim 0.8$% Ni (LG, LH, LI, LC) are referred to as medium-Ni content steels, the alloy with 1.25% Ni and 0.38% Cu (LD) is referred to as the high-Ni-Cu content steel, and the Cu-free alloy with 1.68% Ni (CM6) is referred to as the highest-Ni content, Cu-free steel.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Nominal steel compositions (wt.%).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
<td>Cu</td>
</tr>
<tr>
<td>LC</td>
<td>0.41</td>
</tr>
<tr>
<td>LD</td>
<td>0.38</td>
</tr>
<tr>
<td>LG</td>
<td>0.01</td>
</tr>
<tr>
<td>LH</td>
<td>0.11</td>
</tr>
<tr>
<td>LI</td>
<td>0.20</td>
</tr>
<tr>
<td>CM6</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Also contains some Cr, S and other trace elements. L-series heat treatment: austenitized at 900 °C for 1 h, air cooled, tempered at 664 °C for 4 h, air cooled, stress relieved at 600 °C for 40 h, followed by a furnace cooling to 300 °C, then air cooled to room temperature CM heat treatment: tempered at 660 °C for 4 h, air cooled, then stress relieved at 607 °C for 24 h followed by a slow cool at 8 °C h$^{-1}$ to 300 °C, then air cooled.

2.2. Characterization techniques

A wide variety of microstructural and mechanical property characterization methods are applied for post-irradiation evaluations of these high- to very high-fluence irradiation conditions. As dictated by the specimen size, microhardness was used to measure strength increases, and APT was used to characterize the precipitates. The discussion, which follows, focuses on APT methods and issues.

2.2.1. Atom probe tomography

APT on the high-fluence BR2 steels was carried out at the University of California, Santa Barbara (UCSB) on a Cameca LEAP 3000× HR, while the very high-fluence ATR steels were examined using a Cameca LEAP 4000× HR at the Idaho Center for Advanced Energy Studies (CAES). Both instruments are equipped with an energy-compensating reflectron, which improves mass resolution. APT tips were fabricated by focused ion beam milling (FIBing) at CAES and the University of California, Berkeley. A low-energy cleanup at 2 kV was used to reduce the Ga damage and contamination of the tips.

A complete discussion of APT procedures and issues is beyond the scope of this paper. More detailed coverage of these topics can partly be found in Refs. [30,31]. The main APT analysis parameters and improvements with respect to typical practice are summarized below.

All samples were run in voltage mode at a temperature of 50 K with a pulse fraction of 20%, a pulse repetition rate of 200 kHz and target evaporation rate between 0.5% and 1% per pulse. Mass to charge state ratio peak deconvolution was performed on overlapping element peaks, using the natural abundances of the various isotopes for individual elements with non-overlapping peaks [30]. The tip radius as a function of depth was estimated using SEM images taken after the final FIB milling step. This information was used in the tip profile reconstruction method, included in the Cameca Integrated Visualization and Analysis (IVAS) commercial software, instead of estimating the radius from the voltage evolution and $k$ factor. The first
several hundred thousand atoms were typically excluded from the reconstruction because these ions evaporated as the tip was being aligned and had a higher Ga concentration than is preferred. Excluding these atoms meant that the initial tip radius for the reconstruction was selected based on enforcing plane spacing criteria for low-index poles [(1 1 0), (2 0 0) or both].

The cluster analysis was performed using a modified version of the maximum separation method, also referred to as the density-based clustering algorithm; here, instead of finding the distance (d) between a solute, defined as Cu, Ni, Mn and Si, and its nearest solute neighbor, the corresponding distance between a solute and its fifth nearest solute neighbor is found [32]. If d is less than a defined distance (d_max), the solute is considered to be a core atom. After all core atoms have been found, any solute atom within d_max of a core atom is considered to be in the same cluster. Any cluster with less than N_min atoms is excluded from the analysis. We used d_max = 0.50–0.60 nm and N_min = 15–30 in our analysis.

APT results must be interpreted cautiously in the face of a number of potential artifacts of the technique. Lower evaporation fields, associated with more weakly bound precipitate atoms, result in flattening, or even dimpling, of the region in the vicinity of the feature. This, in turn, produces tip topology-induced ion trajectory aberrations and changes in the local magnification factors, specifying the separations and densities of atoms at the detector vs. the actual physical tip. In this case, artifact matrix atoms are focused into the precipitate region of the detector along with the solute atoms [33]. These so-called trajectory aberrations result in artifacts in the apparent composition of the precipitates, and are signaled by higher-than-physical local atom densities. Further, coupled with assumptions used in the reconstruction algorithms, in some cases spatially inhomogeneous evaporation sequences may also lead to distortion of the shapes of reconstructed precipitates (flattening or elongation), as well as features with chemically segregated tops and/or bottoms (when there are no physical tops and bottoms along the APT analysis z-direction) [33–35].

These APT issues have long been recognized, but have not yet been resolved. However, they are of current intense interest, and recent research is leading to much better understanding of APT artifacts; for example, electrostatic simulations of field emission from a tip containing small features with a range of evaporation fields have been combined with experimental observations of spatial–temporal correlations in atom emission sequence [35]. The most relevant conclusion is that excess Fe in precipitates is almost certainly largely an APT artifact, if only because the atom densities in the precipitates are 2–3 times higher than is physical. This conclusion is reinforced by the fact that high Fe content is inconsistent with other techniques, such as small-angle neutron scattering (SANS), as only one of several examples, as well as with thermodynamic considerations [8,16]. Thus our analysis assumes the precipitates found in this study do not contain a significant amount of Fe. However, the nominal Fe contents are included in the tables summarizing the precipitate compositions for those that choose to interpret the data differently.

The precipitate sizes were calculated by determining the spherical radius, r_p, of the volume of the total number of solute atoms in a cluster, corrected for the detection efficiency, assuming the solute atomic volume is the same as for Fe, as r_p = 3/4 π N_sol / η g_s X_p. Here N_sol is the number of Cu, Ni, Mn and Si atoms in a given cluster, Ω is the atomic volume of Fe, and η is the efficiency of the LEAP (0.37 in the case of a reflectron-equipped instrument). The possible intermetallic phases that exist in these steels have atom densities that vary from those of Fe within ±10%, so the corresponding effect on r_p is less than ~±3%. Given the various uncertainties in the APT reconstructions, we believe that this method of estimating r_p is more physically justified and systematic compared to other common approaches, such as multi-axis Guiner radius-based estimates, especially since the artifacts discussed above leave the precipitates with distorted shapes, length scales and atomic densities [20,33,35]. The corresponding cluster mole fraction, f, is estimated by dividing the total number of solutes in the precipitates by the total number of atoms in the sample.

Precipitates on the edge of the reconstruction are not used in calculating the size distributions. However, edge precipitates are counted as one half in determining their total number density, N. The N is calculated by dividing the total number of clusters by the total reconstruction volume, which is determined by multiplying the total number of atoms in the reconstruction, corrected for the efficiency, by the atomic volume of Fe. There is also a possibility of overestimating the residual solutes left in the matrix due to the presence of trajectory aberrations [35,36,37]. To account for this, the matrix atoms immediately surrounding the clusters are excluded from the matrix composition.

Multiple APT measurements were carried out on each alloy, except in two cases where only one tip was available. The mean bulk, matrix and precipitate compositions, as well as precipitate ⟨ρ⟩, N and f were determined for each tip for a given alloy nominal condition. The ion-weighted mean and standard deviation of the measurements were calculated for a given alloy from the means of all runs. The expression for the weighted mean and weighted standard deviation are given by:

\[ \bar{x} = \frac{\sum_{i=1}^{n} w_i x_i}{\sum_{i=1}^{n} w_i} \]

\[ S = \sqrt{\frac{n}{(n-1)}} \cdot \sqrt{\frac{\sum_{i=1}^{n} w_i (x_i - \bar{x})^2}{\sum_{i=1}^{n} w_i}} \]

Here \( \bar{x} \) is the mean value for a set of given alloy condition runs, \( x_i \) is the calculated value for the \( i \)th run for a single alloy condition, \( S \) is the standard deviation of the mean for the alloy, \( w_i \) is the total number of atoms for the \( i \)th measurement, and \( n \) is the total number of measurements
on a single alloy condition. The mean value uncertainties were taken as the standard error of a given quantity as $SE = \frac{s}{\sqrt{n}}$.

In two cases at high fluence, the medium-Ni, high-Cu content (LC) and highest-Ni content, Cu-free (CM6) alloys, when only one APT tip was available, the uncertainty was estimated using the uncertainty for other alloys with similar compositions, but increased by a factor of two. These estimated uncertainties are flagged in the tables with an asterisk.

The main source of analysis uncertainty in calculating $f$ for a single run is the selection of $d_{\text{max}}$ and $N_{\text{min}}$. A parametric study was performed varying $d_{\text{max}}$ by $\pm10\%$. The corresponding $f$ varied by $\sim\pm5\%$ of the total and the individual Ni, Mn and Si varied by $\sim\pm6\%$, while the Cu showed very little variation. These uncertainties in $f$ for single tips were used in the scatter plots of $f$ vs. bulk composition for individual runs.

Finally, a major general limitation of APT is the very small volumes of material that are probed, typically of the order of $10^{-16}$ cm$^3$. This is a critical issue for heterogeneously distributed features, especially if their number densities are low. While the precipitates in these steels are not completely homogeneously distributed, the results show very similar high number densities in all the steels with similar Ni content. Additionally, APT samples were made from two separate liftout locations for three of the steels (LC, LD and CM6) in the very high-dose condition; both locations showed consistent precipitate sizes and number densities for a given steel. This relatively uniform distribution of precipitates allowed us to use compositional heterogeneities to advantage. Specifically, tip-to-tip variations in the overall local bulk solute compositions, which were significant in some cases, can be directly correlated with the corresponding compositions and $f$ of the precipitates on a nearly one-to-one basis. We show below that the effects of tip-to-tip bulk composition variations for the same alloy condition are generally consistent with larger alloy-to-alloy bulk compositional variations with respect to their effects on the precipitate parameters. Consequently, all of the APT bulk compositions that follow are specified as either the actual measured values in at.\% for a given tip, or the average measured value for a given alloy condition.

In closing this section we note that APT reconstructions contain a great amount of detailed information that is generally not available using other techniques. This includes associations between different features, core-shell structures, co-formation of different precipitates, relations between precipitate size and composition, etc. The results described below give some examples of how such information can be exploited, but many additional opportunities can, and should be, explored in the future.

### 2.2.2. Microhardness

Microhardness tests were performed at UCSB on a Leco M400 hardness tester with at least 10 indents per sample at a load of 500 g. A common calibration block was used in all cases to ensure the accuracy of the test. The mean and standard error were calculated for the hardness of each alloy in both the baseline and irradiated conditions. For the high-flux irradiations, the as-irradiated hardness was taken both before and after a mild post-irradiation anneal at 350 °C for 5 h to remove the thermally unstable damage that is likely associated only with high flux [4,14,38]. The yield stress increase was estimated using the relation $\Delta\sigma_y \approx 3.3\Delta H_v$ [39]. The uncertainty in the $\Delta\sigma_y$ was calculated from the root mean square of the standard errors of the baseline and as-irradiated measurements.

### 3. Results and discussion

We first describe the APT measurements of the total solute contents of the alloys in this study, and how they vary from nominal “bulk” chemistry values. These measurements show that the total APT and nominal bulk values are relatively consistent, differing only in ways that are expected. Next, we summarize the results for the high-fluence irradiation condition where MNS precipitates are just beginning to be observed in the Cu-free steels (LG and CM6), likely representing a continued evolution of matrix feature clusters that are continuously formed in displacement cascades. Data from the other steels clearly show that Cu catalyzes MNS precipitate formation. We next show that this initial phase formation is followed by continued precipitation of the MNS solutes up to a large fraction of the alloy contents of these elements. The large precipitate mole fractions observed at very high fluence range from 1.3% to 2.8%, and lead to correspondingly large equivalent $\Delta\sigma_y$. Note that at very high fluence, the Cu fraction in the MNS-dominated precipitates ranges from $\sim$0 to $\sim$15%, in rough proportion to the alloy content of this element. At very high fluence, the Cu is nearly fully depleted from the matrix. The well-established precipitates at very high fluence provide a basis for more detailed characterization and analysis of their dependence on the local alloy composition and various morphological details, which are the major focus of this work. Structural studies are ongoing and will be reported in the future.

#### 3.1. Alloy compositions and composition variations

The average APT bulk and matrix solute compositions, in at.\%, are given in Tables 3 and 4 for the high- and very high-fluence conditions, respectively. The nominal bulk chemical values are given in parenthesis. Observed differences between the measured total and nominal values are largely expected. For example, the alloys that nominally contain $\sim$0.34% Cu have a lower average total APT content of $\sim$0.25%. This value is consistent with previous observations of lower residual amounts in solution due to coarse-scale pre-precipitation during tempering and stress-relief heat treatments, when the total Cu is beyond the solubility limit [2,3,7,40]. Likewise the Mn contents are lower than the nominal value since this element is
Table 3
Bulk, nominal and matrix APT compositions for the high-fluence condition (G1) (at.%).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Bulk and nominal (in parenthesis) composition (at.%)</th>
<th>Matrix composition (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu ± Ni ± Mn ± Si ±</td>
<td>Cu ± Ni ± Mn ± Si ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LC*</td>
<td>0.21 (0.36) 0.02 0.91 (0.81) 0.10 0.97 (1.46) 0.20 0.53 (0.46) 0.06</td>
<td>0.06 0.01 0.70 0.08 0.84 0.18 0.43 0.06</td>
</tr>
<tr>
<td>LD</td>
<td>0.21 (0.33) 0.01 1.00 (1.16) 0.01 1.08 (1.37) 0.10 0.52 (0.45) 0.03</td>
<td>0.06 0.00 0.74 0.02 0.91 0.08 0.41 0.03</td>
</tr>
<tr>
<td>LG</td>
<td>0.01 (0.01) 0.00 0.86 (0.69) 0.05 1.09 (1.36) 0.09 0.49 (0.43) 0.02</td>
<td>0.01 0.00 0.81 0.04 1.07 0.09 0.46 0.02</td>
</tr>
<tr>
<td>LH</td>
<td>0.08 (0.09) 0.01 0.72 (0.69) 0.01 0.97 (1.38) 0.03 0.45 (0.47) 0.02</td>
<td>0.01 0.06 0.66 0.01 0.93 0.03 0.41 0.01</td>
</tr>
<tr>
<td>LI</td>
<td>0.15 (0.17) 0.01 0.72 (0.69) 0.01 1.21 (1.36) 0.03 0.43 (0.46) 0.01</td>
<td>0.06 0.00 0.59 0.00 1.11 0.02 0.37 0.01</td>
</tr>
<tr>
<td>CM6†</td>
<td>0.00 (0.02) 0.01 1.34 (1.57) 0.10 1.09 (1.50) 0.20 0.33 (0.33) 0.06</td>
<td>0.00 0.01 1.27 0.08 1.05 0.18 0.31 0.06</td>
</tr>
</tbody>
</table>

* Note that measurements for LC and CM6 from this irradiation condition came from a single APT run of LC and CM6. The uncertainty given for these alloys is twice the largest uncertainty of the other alloys.

Table 4
Bulk, nominal and matrix APT compositions for the very high-fluence condition (ATR1) (at.%).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Bulk and nominal (in parenthesis) composition (at.%)</th>
<th>Matrix composition (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu ± Ni ± Mn ± Si ±</td>
<td>Cu ± Ni ± Mn ± Si ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LC</td>
<td>0.28 (0.36) 0.01 0.80 (0.81) 0.03 1.16 (1.46) 0.01 0.43 (0.46) 0.02</td>
<td>0.02 0.01 0.11 0.01 0.47 0.02 0.10 0.01</td>
</tr>
<tr>
<td>LD</td>
<td>0.25 (0.33) 0.02 1.18 (1.16) 0.05 1.08 (1.37) 0.08 0.54 (0.45) 0.02</td>
<td>0.02 0.03 0.18 0.01 0.57 0.07 0.08 0.01</td>
</tr>
<tr>
<td>LG</td>
<td>0.00 (0.01) 0.01 0.71 (0.69) 0.01 0.87 (1.36) 0.08 0.43 (0.43) 0.01</td>
<td>0.00 0.00 0.08 0.01 0.37 0.06 0.10 0.01</td>
</tr>
<tr>
<td>LH</td>
<td>0.08 (0.09) 0.01 0.73 (0.69) 0.02 1.19 (1.38) 0.06 0.42 (0.47) 0.02</td>
<td>0.01 0.02 0.11 0.01 0.57 0.04 0.11 0.01</td>
</tr>
<tr>
<td>LI</td>
<td>0.15 (0.17) 0.01 0.70 (0.69) 0.01 0.97 (1.36) 0.10 0.42 (0.46) 0.01</td>
<td>0.02 0.01 0.11 0.01 0.41 0.05 0.11 0.01</td>
</tr>
<tr>
<td>CM6</td>
<td>0.00 (0.02) 0.01 1.69 (1.57) 0.04 1.42 (1.50) 0.03 0.39 (0.33) 0.01</td>
<td>0.00 0.00 0.17 0.01 0.32 0.01 0.04 0.01</td>
</tr>
</tbody>
</table>

partially sequestered in coarse Mn₀.₈Fe₂₄C carbides. The quantitative differences between the nominal and measured bulk compositions are shown in Tables 3 and 4.

These overall composition averages do not reflect the tip-to-tip variations in individual alloys, which are significant in some cases. For example, the standard error for the bulk Mn measurements of a given alloy is as large as 0.20%. While seemingly an esoteric detail, we show below that the effects of the tip-to-tip composition variations in a given alloy are directly reflected in the precipitates, and are also consistent with observed alloy-to-alloy trends. A corollary is that it is important to use the actual local compositions in analyzing the APT precipitate data.

3.2. High-fluence condition

Fig. 2 shows atom maps for the highest-Ni content, Cu-free steel (CM6) and the high-Ni–Cu content steel (LD) in the high-fluence condition. The precipitates are numerous and well defined in the Cu-bearing steel, but are not as easy to observe in the Cu-free alloy; however, they are readily characterized by the cluster search algorithm. Table 5 summarizes the corresponding APT measurements. The left portion of the table gives the Cu–Mn–Ni–Si compositions of the precipitates. The uncertainty is the standard error of the mean of the various measurements. The nominal precipitate Fe content is also shown to the right of the precipitate compositions. While we believe that the Fe is largely an APT artifact, it is included for those who might seek an alternative analysis. The right portion of Table 5 gives the average radius (\( r \)), number density (\( N \)) and mole fraction (\( f \)) of the MNS precipitates, as well as the standard error uncertainties in the measurements. The bar chart in Fig. 3a summarizes the precipitate \( f \) and corresponding compositions. We will later show that the \( f \) directly scales with the individual tip solute contents. Thus Fig. 3a shows the mole fraction for individual tips with bulk compositions close to the average values of the alloy. The trends for Ni content in Cu-free steels, Cu content at medium Ni content, and Cu content at both the higher and the highest Ni content, are individually highlighted in the three sections. The corresponding \( r \) and \( N \) are plotted in Fig. 3b. The major observed trends are as follows:

- The highest-Ni content, Cu-free steel has only a slightly larger \( f \) than the Cu-free, medium-Ni content alloy (Fig. 3a, left). The Cu–Mn–Ni–Si contents of the precipitates, hence the total \( f \), increase with increasing Cu content in the medium-Ni content steels (Fig. 3a, center). The mole fraction of Cu in the precipitates increases from ~0, in the Cu-free steel, to 0.15% in the highest-Cu content steel. The average residual matrix Cu content is 0.06% in the Cu-bearing steels, indicating incomplete phase separation for this highly insoluble element.
- The increase in \( f \) with higher Ni content in the 0.21% Cu steels is due to higher contents of Ni, Mn and Si in the precipitates (Fig. 3a, center and right). These results clearly demonstrate the thermodynamically driven synergisms between these elements, and the very important role played by Ni. The corresponding effect of increasing Ni content on \( f \) in the Cu-free and high-Cu content steels is minimal in this case (Fig. 3a, right) because \( f \) is so strongly dependent on Cu.
– Both $N$ and $\langle r \rangle$ increase with Cu content (Fig. 3b). $N$ also increases with Ni content, except in the Cu-free steels. It should be noted that at these small $f$ and $\langle r \rangle$, the uncertainties in $N$ are larger.

– The MNS cluster compositions are generally similar in the medium- and high-Ni content steels (LG, LH, LI, LC, LD) with fractional averages and standard deviations of: 0.31 ± 0.04 Mn, 0.47 ± 0.01 Ni and 0.22 ± 0.03 Si. The precipitate Ni fraction is higher and the Si is lower in the highest-Ni content, Cu-free steel (CM6) averaging 0.26 Mn, 0.59 Ni and 0.15 Si.

The most important observation for the high-fluence condition is that Cu and Ni play a combined role in mediating $f$, although Cu seems to have a stronger influence over the range of Ni compositions studied here. While

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Table 5
Precipitate compositions and $\langle r \rangle$, $N$ and $f$ at high fluence (G1).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Precipitate relative compositions (at.%</th>
<th>Nominal Fe**</th>
<th>$\langle r \rangle$ (nm), $N$ (m$^{-3}$), $f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Ni</td>
<td>Mn</td>
<td>Si</td>
</tr>
<tr>
<td>LC</td>
<td>25.7</td>
<td>1.4</td>
<td>35.1</td>
</tr>
<tr>
<td>LD</td>
<td>22.2</td>
<td>0.7</td>
<td>37.8</td>
</tr>
<tr>
<td>LG</td>
<td>0.5</td>
<td>0.1</td>
<td>46.8</td>
</tr>
<tr>
<td>LH</td>
<td>14.8</td>
<td>0.9</td>
<td>39.8</td>
</tr>
<tr>
<td>LI</td>
<td>24.2</td>
<td>1.0</td>
<td>34.2</td>
</tr>
<tr>
<td>CM6</td>
<td>0.1</td>
<td>0.1</td>
<td>58.9</td>
</tr>
</tbody>
</table>

* Note that measurements for LC and CM6 from this irradiation condition came from a single APT run of LC and CM6. The uncertainty given for these alloys is twice the largest uncertainty of the other alloys. The CM6 mole fraction uncertainty was twice the uncertainty of the LG volume fraction as they had similar measured $f$.

** Assumed to be an artifact, but provided for alternative interpretations.
the features in the Cu-bearing steels contain >75% MNS, the total mole fraction of these elements roughly scales with the alloy Cu content. Thus higher Cu and Ni content lead to larger \( f \). These trends are consistent with previous lower-flux-fluence SANS studies. However, the latter results will be described and analyzed in detail elsewhere. The most plausible hypothesis for explaining these observations is that in the Cu-free steels, the clusters are still predominantly matrix features. However, the presence of Cu catalyzes the formation of MNS precipitates. The Cu is highly supersaturated, thus precipitates quickly, while simultaneously being enriched in the other solutes. In the presence of Cu, the difficult nucleation step for nearly pure MNS phases is largely avoided by co-precipitation, and these solutes subsequently flow to the Cu-catalyzed precipitates starting at relatively low fluence.

3.3. Very high-fluence condition

Atom maps, for the same alloys as Fig. 2, but at the very high-fluence condition are shown in Fig. 4. They clearly demonstrate the large changes that occur between the high-fluence vs. very high-fluence conditions. The changes in the precipitates are particularly notable in both the highest-Ni content, Cu-free (CM6) and the high-Ni–Cu content (LD) steels. The average precipitate parameters are summarized in Table 6. These large changes are not surprising, since the fluence increased by a factor of \( \sim 8 \) between the high- and very high-fluence conditions. The major observations can be summarized as follows.

- There is a large increase in \( f \) between the high- and very high-fluence conditions. The histograms in Fig. 5a, again for individual tips with bulk compositions close to the average values, show both the total \( f \) and precipitate composition for each alloy. These results demonstrate that the effect of Cu is not nearly as significant at very high vs. high fluence, and that Ni plays a much stronger role in the ATR case. At very high fluence, the MNS precipitates no longer need Cu to form. The precipitate \( f \) more than doubles in the Cu-free steels with increasing bulk Ni from \( \sim 0.7\% \) to 1.6% (Fig. 5a, left). In contrast, at medium-Ni contents, increasing the bulk Cu only slightly increases \( f \) (Fig. 5a, center); this increase is almost entirely caused by the higher amount of co-precipitate Cu itself. Notably, the highest \( \sim 1.6\% \) Ni, Cu-free steel (CM6) has a larger \( f \) than in the high 1.2% Ni, 0.25% Cu (LD) alloy (Fig. 5a, right).

- The effects of Cu at both high and very high fluence are more clearly seen in the \( f \) for MNS only vs. bulk Cu plots shown in Fig. 5b. At high fluence (bottom, black dashed line), the MNS \( f \) is minimal at \( \sim 0.1\% \) in the Cu-free steels, but increases rapidly with larger alloy Cu contents. These results clearly show, as discussed previously, that Cu catalyzes the precipitation of the other MNS solutes. In contrast at very high fluence (top), the MNS \( f \) only increases slightly with higher bulk Cu content in the medium-Ni content steels (purple dashed line). This is because the very high fluence is well beyond the range for which Cu is needed to catalyze MNS precipitation. Indeed, the small increase in the MNS \( f \) is largely due to the fact that slightly higher bulk Ni content happens to accompany the increase of bulk Cu in this case. In contrast to the effect of Cu, higher Ni contents cause a significant increase in MNS \( f \) in the high-Ni–Cu content alloy (LD, the red dotted line) and a much larger corresponding increase in the highest-Ni content, Cu-free steel (cyan data points).

- Fig. 5c shows that \( \langle r \rangle \) modestly increases with Cu in both medium- and higher-Ni content steels. In contrast, the corresponding \( N \) decreases with Cu. In the case of the high-Ni–Cu content steel (LD), the very high-fluence \( N \) is lower than for the high-fluence condition, perhaps suggesting that the precipitates have begun to coarsen.

- Table 6 shows that at the very high fluence, the nominally Cu-free steel precipitates contain <0.01 fraction of this element. In the medium-Ni content steels, the precipitate Cu composition increases (LH, LI, LC) with
this element up to \( \sim 15\% \) (LC). Fig. 6 shows that the relative precipitate MNS compositions do not change much between high and very high fluences. For example, the average fractional compositional difference for the medium-Ni content steels (LG, LH, LI, LC) is 0.02 Mn, –0.01 Ni and –0.01 Si in going from high to very high fluence. Further, the MNS precipitate compositions are generally similar in the medium-Ni content steels at very high fluence (LG, LH, LI, LC) with fractional averages and standard deviations of: 0.35 ± 0.03 Mn, 0.44 ± 0.02 Ni and 0.20 ± 0.02 Si. The precipitate Mn fraction is lower and Ni is higher in the high-Ni–Cu content steel (LD) at 0.25 Mn, 0.52 Ni, and 0.23 Si. The corresponding composition of the highest-Ni content steels is provided in Table 6.

**Table 6**
Precipitate compositions and \( \langle r \rangle \), \( N \) and \( f \) at very high fluence (ATR1).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Precipitate relative compositions (at.%)</th>
<th>Nominal Fe*</th>
<th>( \langle r \rangle ) (nm), ( N ) (m(^{-3})), ( f ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu ± Ni ± Mn ± Si</td>
<td>( \langle r \rangle ) ± N ± f</td>
<td></td>
</tr>
<tr>
<td>LC</td>
<td>14.8 ± 2.5 ± 1.8 ± 1.2 ± 1.4</td>
<td>62.0 ± 1.44 ± 0.07 ± 14.1 ± 2.6 ± 1.81 ± 0.19</td>
<td></td>
</tr>
<tr>
<td>LD</td>
<td>10.3 ± 2.4 ± 3.6 ± 2.5 ± 1.8</td>
<td>55.4 ± 1.96 ± 0.14 ± 7.3 ± 1.0 ± 2.1 ± 0.23</td>
<td></td>
</tr>
<tr>
<td>LG</td>
<td>0.2 ± 0.1 ± 1.5 ± 2.8 ± 1.6</td>
<td>63.5 ± 1.25 ± 0.04 ± 16.3 ± 1.6 ± 1.3 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>LH</td>
<td>5.0 ± 0.2 ± 1.5 ± 2.4 ± 1.1</td>
<td>64.9 ± 1.33 ± 0.05 ± 15.2 ± 2.4 ± 1.4 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>LI</td>
<td>9.5 ± 0.5 ± 2.5 ± 4.2 ± 1.9</td>
<td>62.7 ± 1.34 ± 0.06 ± 14.6 ± 1.4 ± 1.4 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>CM6</td>
<td>0.1 ± 0.0 ± 1.2 ± 1.9 ± 0.5</td>
<td>58.9 ± 1.52 ± 0.06 ± 19.5 ± 1.5 ± 2.8 ± 0.14</td>
<td></td>
</tr>
</tbody>
</table>

* Assumed to be an artifact, but provided for alternative interpretations.

Fig. 4. Atom maps for the highest-Ni content, Cu-free (top) and high-Ni–Cu content (bottom) alloys irradiated to very high fluence.
Cu-free steel (CM6) is 0.36 Mn, 0.52 Ni and 0.12 Si. Thus the precipitate compositions clearly reflect changes in the bulk alloy Ni and Si chemistry.

– Cu approaches full depletion at very high fluence, at a matrix level of \(0.03\%\), while there is still a modest fraction of the other elements left in solution. Fig. 7 shows that \(f\) approximately scales linearly with the total alloy Cu–Mn–Ni–Si solute content, above an extrapolated minimum of \(0.78\%\) with a slope of \(0.98\).

– Fig. 8 illustrates the evolution of the morphology of precipitates with increasing fluence in the high-Ni–Cu content (LD) steel. Fig. 8a shows a cross-section of a precipitate at high fluence, where there appears to be a MNS shell surrounding a Cu-rich core, consistent with previous experimental results and lattice Monte Carlo simulations [15,17,18,24]. Fig. 8b shows a precipitate at very high fluence, where there is a Cu-rich core–shell structure, similar to that at high fluence, but this feature is associated with a nearly “pure” MNS co-precipitate appendage. Such appendages have also been seen in irradiated surveillance steels [27].

In summary, the evolution between high and very high fluence is dominated by the continued flow of MNS to the precipitates. In Cu-free steels it is likely that the precipitates evolve from matrix feature solute–defect clusters initially formed in displacement cascades. At higher

Fig. 5. The Cu dependence of: (a) \(f\) showing the constituent elements for individual runs of each alloy, (b) Mn–Ni–Si \(f\) at both high and very high fluence, and (c) \(\langle r\rangle\) and \(N\) at very high fluence. Note that in some cases, the error bars were smaller than the size of the symbols.

Fig. 6. The average precipitate Mn–Ni–Si compositions at high and very high fluence.

Fig. 7. The precipitate \(f\) as a function of the bulk Cu + Ni + Mn + Si alloy content for individual tips at very high fluence.
supersaturated Cu contents, Cu–Mn–Ni–Si precipitates form rapidly and the MNS co-precipitate appendages continue to grow after matrix Cu is depleted at higher fluence.

3.4. Comparison of APT precipitate compositions with potential MNS intermetallic phases

The Mn–Ni–Si compositions of the precipitates in Cu-free steels are similar to those in the co-precipitates formed in Cu-bearing steels at very high fluence. These compositions can be compared to known intermetallic phases in the corresponding Mn–Ni–Si ternary and Mn–Ni–Si–Fe quaternary systems. As described in detail in a companion paper under submission, recent CALPHAD/Thermocalc computational modeling studies carried out at the University of Wisconsin (UW) have shown there are a variety of equilibrium MNS intermetallic phases in the Fe–Mn–Ni–Si quaternary system at low RPV operating temperatures [41]. Briefly, these models were based on two different thermodynamic databases, including both “in-house” and commercial versions. The in-house database, assembled from literature, predicts formation of the \( \Gamma_2 (\text{Mn}_2\text{Ni}_3\text{Si}, \text{T6}) \) phase in all alloys at \( \sim 290 \) °C, while the commercial database predicts varying fractions of \( \Gamma_2 \) and \( G (\text{Mn}_6\text{Ni}_{16}\text{Si}_7, \text{T3}) \) phases, depending on the alloy MNS composition, determined from the average APT values measured in this study.

Fig. 9 shows the APT MNS precipitate compositions (filled symbols) plotted on the MNS ternary phase diagram for both the medium-Ni (circles) and high-Ni (squares) content steels compared to the predicted average compositions for the commercial (open symbols) database. The commercial database predicts 100% \( \Gamma_2 \) (T6) (open cyan square) for the highest Ni content, Cu-free (CM6) steel, which is very consistent with the APT data (filled cyan square). The commercial database predicts \( \sim73\% \ G \) (T3) and \( \sim27\% \ \Gamma_2 \) (T6) phases (open red square) for the high-Ni–Cu content (LD) steel, again very close to the measured value (filled red square). The medium-Ni content alloys cluster around the Si-rich end of the \( \Gamma_2 \) phase field (filled circles), shown by the heavy green line at approximately constant Mn, while the commercial database predicts the presence of either \( G \) or \( \Gamma_2 \) phases (open circles).

The precipitates in the Cu-free, medium-Ni content steel (LG) have slightly less Mn and higher Ni than the other three medium-Ni content steels that contain various amounts of Cu. This might be interpreted to suggest that there is some effect of Cu on the dominant MNS phases. However, these differences are actually highly consistent with variations in the bulk alloy Ni contents, that trade off with Mn in the precipitates, at approximately constant Si. For example, the medium Ni content alloy with the greatest fraction of Mn in the precipitates (LH), which is furthest to the right of the \( \Gamma_2 \) line in the MNS ternary (filled green circle), has a bulk Mn/Ni of 1.6. On the other hand, the alloy furthest to the left of the \( \Gamma_2 \) line (LG, filled blue circle) has much less bulk Mn, with a bulk Mn/Ni of 1.2.

While the relatively good agreement between Thermocalc average composition predictions and the APT measurements is encouraging, there are also important
differences that should be noted. In particular, the commercial database predicts the presence of multiple near-stoichiometric phases in some alloys. In contrast, the APT measurements show that there is a unimodal distribution of MNS precipitate compositions that decreases in extent with increasing precipitate size, converging to a relatively narrow range of MNS at the largest \( r_p \). The corresponding average compositions also appear to vary somewhat with \( r_p \). The variation and spread in compositions with \( r_p \) is an example of the additional insight available from APT measurements. However, this will require more detailed analysis, since, for example, nominal precipitate compositions and the spread in the measured compositions are affected by counting statistics, especially at small sizes. However, further discussion of this topic, and other opportunities, are beyond the scope of this paper.

As noted previously, the total APT local chemistries vary from tip to tip, allowing characterization of the effects of both smaller single-alloy and larger alloy-to-alloy changes in composition. Fig. 10 shows the precipitate individual solute \( f \) as a function of local composition for Cu (a), Ni (b), Mn (c) and Si (d). The plots of \( f \) vs. bulk solute for Cu and Ni form a tight band in both cases, with least-square fit slopes of 0.95 and 0.89, combined with thresholds of \( \sim 0.01\% \) Cu and \( \sim 0.05\% \) Ni, respectively (Fig. 10a and b). In the case of Mn, all the alloys fall into one tight band, except for the highest-Ni content, Cu-free (CM6) steel (Fig. 10c). The least-square fit slope for the 0.8–1.2\% Ni steels is 0.36 with an intercept of Mn \( \sim -0.32\% \). The corresponding least-squares fit Mn slope for the highest-Ni content, Cu-free alloy is 0.80 with an intercept of Mn \( \approx 0.17\% \). There are also two bands for the effect of Si on \( f \). The medium-Ni content steels with varying Cu content (LG, LH, LI, LC) fall along with a least-squares fit slope of 0.80 and a threshold of Si \( \approx 0.07\% \), while the least-squares fit slope is 0.63 with an intercept of Si \( \approx -0.14\% \), for the highest-Ni content, Cu-free and high-Ni–Cu content steels (CM6 and LD). Note the high-Ni content fits are less reliable in the cases of Mn and Si since they are for only one and two alloys, respectively.

The very systematic behavior in precipitate \( f \) as a function of alloy composition will be used to develop physically based chemistry factors for advanced TTS embrittlement models. The most significant observation is that the precipitation behavior is consistent with two MNS intermetallic phases at \( \sim 550 \) K that are found in Thermocalc evaluations. Further, at high fluence, Ni has a dominant role in precipitation, compared to Mn and Si, in terms of both the strength of the effect itself, and the wider range of Ni content in the steels studied here. These results are also very consistent with previous observations on the effect of Ni and Mn on both the precipitates and hardening and also help clarify the role of Si [6–9,13–23]. However, since developing robust physically based chemistry factor will require evaluation of a wider range of alloy compositions and irradiation conditions, this will not be discussed further in this paper.
3.5. Consequences of MNS precipitates: irradiation hardening and embrittlement

While not the focus of the current study, it is useful to consider the consequences of the very large mole fractions of MNS precipitates for hardening and embrittlement, including at very high fluence. Fig. 11 shows the predicted vs. measured values up to very large equivalent $\Delta \sigma_y \approx 700$ MPa. The fact that these steels studied are small, split-melt heats is sometimes raised as a concern. Thus it is important to emphasize that these “model” steels have normal contents of all key alloying elements and embrittlement related solutes, and were processed with conventional heat-treatment schedules. Their microstructures and irradiation responses are virtually identical to those observed in actual service pressure vessel alloys, with the exception that they are perhaps cleaner, and do not contain coarse-scale impurity phases such as MnS and CuS.

Thus the $\Delta \sigma_y$ can be used to estimate the TTS. Of course such property–property transfers carry some degree of uncertainty. However, they are based on a solid physical foundation, derived from finite-element simulations of the various tests using the same true stress-strain constitutive law [39,43]. The corresponding estimated TTS in the toughness–temperature master curve 100 MPa/$^\circ$C reference temperature (TTS = $\Delta T_u$) at the very high-fluence and $\Delta \sigma_y$ condition is $\Delta T_u \approx 0.7 \Delta \sigma_y$, or up to a remarkable $\sim 500$ $^\circ$C [44]. For any reasonable flux adjusted effective fluence, the power reactor end-of-life TTS would be lower. Based on our best estimate interpolation, this TTS would be $\sim 210$ $^\circ$C in the highest-Ni content, Cu-free steel (CM6) and $\sim 330$ $^\circ$C in the high-Ni–Cu content steel (LD). However, we acknowledge that these estimates are uncertain and more research is needed to quantify the flux effect.

4. Summary, conclusions and future work

Large mole fractions of MNS-dominated precipitates form in both Cu-free and Cu-bearing RPV steels at very high fluence. Consistent with long-standing predictions:

- In Cu-free steels the MNS precipitates likely evolve from defect–solute cluster matrix feature precursors that constitute only a small $f \approx 0.1\%$ at high fluence, but subsequently grow to much larger mole fractions at very high fluence.
- Cu catalyzes the initial formation of MNS precipitates. This is especially the case of rapidly forming precipitates at the high supersaturations of Cu. Thus at the high-flux/high-fluence condition in this study, Cu and Ni are the primary compositional variables leading to large mole fractions of MNS.
- However, since the precipitates are dominated by MNS, Cu has a much weaker effect at very high fluence, while Ni has the major influence on the $f$. 

![Fig. 11. Predicted vs. measured yield stress increases from the various previous UCSB irradiations, including the two conditions presented in this study.](image-url)
The precipitate Si in the highest-Ni content, Cu-free (CM6) steel is significantly lower, in part due to the corresponding lower bulk Si content in this alloy. However, lower Si trades off with higher Mn and Ni so the net f is relatively unaffected. Indeed, we will show elsewhere that there is a close correlation between a simple alloy chemistry factor $2Ni + Cu$ and $f$.

The increase in precipitate mole fractions leads to correspondingly large increases in hardness, and hence also leads to severe embrittlement.

The experimental results in this study compare favorably to calculations using CALPHAD/Thermocale models and associated databases. The precipitates in the high-Ni–Cu content (LD) steel are close to $G$ phase ($Mn_6Ni_{16}Si_3$), while they are close to the $G_2$ phase ($Mn_2NiSi$) in the highest-Ni content, Cu-free (CM6) steel. The precipitate compositions in the other medium-Ni content alloys were in reasonably good agreement with the $Si$-rich end of the $G_2$ phase field, although the Thermocale predictions vary somewhat from these compositions in this case.

There is a significant amount of additional detailed information and that can be derived from the APT studies. Further, future work will include other alloys and irradiation–annealing conditions. The resulting APT database will also be complimented by measurements based on other techniques, such as transmission electron microscopy and X-ray diffraction, as well as neutron and X-ray scattering. These tools will be important to characterizing the actual structure of the MNS phases that appear to be diffracting in preliminary TEM studies. Coupled with mechanical property data, this experimental knowledge base will be used to develop new physically based models of high-fluence/low flux irradiation hardening and embrittlement.

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