Atom Probe Tomography Characterization of Neutron Irradiated Surveillance Samples from the R. E. Ginna Reactor Pressure Vessel

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Abstract

Surveillance samples of a low copper (nominally 0.05 wt.% Cu) forging and a higher copper (0.23 wt.% Cu) submerged arc weld from the R. E. Ginna reactor pressure vessel have been characterized by atom probe tomography (APT) after exposure to three levels of neutron irradiation, i.e., fluences of 1.7, 3.6 and 5.8 X 10²³ n.m⁻² (E > 1 MeV), and inlet temperatures of ~289 °C (~552 °F). As no copper-enriched precipitates were observed in the low copper forging, and the measured copper content in the ferrite matrix was 0.04± <0.01 at.% Cu, after neutron irradiation to a fluence of 1.7x10²³ n.m⁻³, this copper level was below the solubility limit. A number density of 2x10²² m⁻³ of Ni-, Mn- Si-enriched precipitates with an equivalent radius of gyration of 1.7±0.4 nm were detected in the sample. However, Cu-, Ni-, Mn-enriched precipitates were observed in specimens cut from different surveillance specimens from the same forging material in which the overall measured copper level was 0.08± <0.01 at.% (fluence of 3.6x10²³ n.m⁻³) and 0.09± <0.01 at.% Cu (fluence of 5.8x10²³ n.m⁻³). Therefore, these slightly higher copper contents were above the solubility limit of Cu under these irradiation conditions. A best fit of all the composition data indicated that the size and number density of the Cu-enriched precipitates increased slightly in both size and number density by additional exposure to neutron

irradiation. High number densities of Cu-enriched precipitates were observed in the higher Cu submerged arc weld for all irradiated conditions. The size and number density of the precipitates in the welds were higher than in the same fluence forgings. Some Cu-enriched precipitates were found to have Ni-, Mn-, Si-, and P-enriched regions on their surfaces suggesting a preferential nucleation site. Atom maps revealed P, Ni, and Mn segregation to, and preferential precipitation of, Cu-enriched precipitates over the surface of a grain boundary in the low fluence weld.

Keywords: Reactor pressure vessel steel; atom probe tomography; ductile-brittle transition temperature; Charpy impact energy; segregation to dislocations; weld metal; heat-affected zone.

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1. INTRODUCTION

The Nuclear Plant Life Extension Demonstration (NPLED) Project is a partnership between the Department of Energy (DOE), the Electric Power Research Institute (EPRI), and Constellation Energy, owner of the R. E. Ginna Nuclear Plant (also referred to as Ginna). The NPLED is investigating various technical issues and analysis methods to enable nuclear plant life extension to 80 years. Many issues have been identified that are of mutual interest within the partnership, and specific methods to investigate the issues are determined through the DOE Light-Water Reactor Sustainability (LWRS) Program and the EPRI Long Term Operation (LTO) Project. Constellation Energy's R. E. Ginna and Nine Mile Point nuclear power stations are both used as pilot plant sites due to their age (>40 years) and representation of the PWR and BWR technologies, respectively. For the Reactor Pressure Vessel (RPV) task of the LWRSP, materials from the Ginna PWR RPV are of the highest interest due to their higher irradiation fluence and demonstrated irradiation-induced embrittlement from the RPV surveillance program.[1]

The Ginna reactor is a Westinghouse 2-loop PWR that began commercial operation in July 1970 and produces approximately 580 MWe. The Ginna RPV was fabricated with forgings of A508 class 2 steel and welded with Linde 80 weld metals; these materials were included in the surveillance program. Westinghouse retrieved previously tested surveillance specimens of one forging, one of the welds, and heat-affected-zones (HAZ) from their storage facility and shipped the specimens to Oak Ridge National Laboratory (ORNL) Irradiated Materials Examination and Testing Laboratory (IMET) hot cells where cutting of thin slices was performed. The slices were transported to the ORNL Materials Science and Technology Division's Low Activation Materials Development and Analysis (LAMDA) Laboratory for preparation of atom probe tomography (APT) [2, 3] and small-angle scattering (SANS) samples. This paper reports the

results of APT examinations, while the SANS results are reported separately.

Although copper-enriched precipitates (CRPs), primarily responsible for the changes in mechanical properties, were conclusively detected by atom probe field ion microscopy (APFIM) [4] in an Fe-1.4 at.% Cu binary alloy as early as 1973 [5], and by field ion microscopy in a neutron irradiated Fe-0.34 wt.% (0.30 at.%) Cu binary alloy in 1978 [6], the first microstructural characterization of a surveillance specimen from a nuclear reactor – an A302B steel containing 0.17 at.% Cu – by APFIM was performed in 1981.[7, 8] The presence of copper-enriched precipitates that were also enriched in nickel, manganese, silicon and phosphorus after neutron irradiation was subsequently confirmed in several other APFIM and APT studies of RPV steels and related model alloys.[9-11] The majority of these investigations were performed on high copper variants in test reactors in order to accelerate the time scale. An APT study of a high copper (0.24 wt.% (0.21 at.%%)) weld from the Midland reactor revealed that 0.05 ± 0.01 at.% Cu remained in solid solution in the ferrite matrix after neutron irradiation to a fluence of 1.1×10^{23} n.m⁻² (E > 1 MeV) at a temperature of 288 °C.[12] Therefore, alloys with copper contents lower than 0.05 at.% Cu would not be expected to exhibit any copper-enriched precipitates under these irradiation conditions. However, few APT studies have focused on surveillance specimens nor Western RPV steels with low copper contents, as opposed to Russian low copper steels.

Thermodynamic-kinetic models have predicted the formation of manganese-nickel phases in copper-free steels, although at lower nucleation rates than for CRPs, as it was thought that relatively high incubation fluences are required for their formation. [13-15][16] In a neutron irradiated low copper, high nickel VVER-1000 (15Kh2NMFAA) base metal (1.19 at.% Ni, 0.46 Mn, 0.59 Si, and 0.04 Cu), and a low copper, high nickel (12Kh2N2MAA) weld metal (1.69 at.% Ni, 0.81 Mn, 0.65 Si, and 0.06 Cu), high number densities of ~2 nm-diameter Ni-Mn-Si-enriched

precipitates were observed by APT.[17] Similar precipitates were also observed in a neutron irradiated, copper-free Fe-1.1 at.% Mn, 0.7% Ni model alloys and a French 16MND5 (<0.07 at.% Cu, 131-1.56% Mn, 0.47-0.75% Ni, 0.20-0.59% Si) RPV steel.[18, 19] These results are all consistent with other studies examining the formation of Ni-Mn-Si-rich precipitates containing Cu in low Cu content, neutron irradiated steels.[20-22]

In this study, surveillance samples of the low copper [nominally 0.05 wt.% (0.04 at.%) Cu] forging and submerged arc weld [nominally 0.23 wt.% (0.20 at.%) Cu] from the Ginna reactor have been characterized by APT. The samples were examined after neutron irradiation to fluences between 1.7 and $5.8 \times 10^{23} \text{ n.m}^{-2}$ ($E > 1 \text{ MeV}$) and at an inlet temperature of approximately 289°C . The results are compared to previous APT characterization of other neutron irradiated RPV steels.

2. MATERIALS AND METHODS

The following information regarding the materials and surveillance test results has been taken from [1]. The weld material from the Ginna surveillance program comes from the circumferential weld joining the intermediate shell forging (Heat 125S255) and the lower shell forging (Heat 125P666). The forging was austenitized at 843°C (1550°F), water-quenched, tempered at 660°C (1220°F) for 12 h, and air-cooled. The weld is heat number 61782 (weld wire heat number) and, with the flux lot 8350, is a Linde 80 weld designated SA-847. Following welding, the vessel (thus, the weld material and the forging) was post-weld treated at 593°C (1100°F) for 11.25 h and furnace-cooled. The HAZ specimens come from the heat-affected-zone between the circumferential weld and lower shell forging (Heat 125P666), thus, one Charpy specimen half should be weld metal and the other half forging. Five capsules have been removed and tested over the course of reactor operation with neutron fluences ranging from 0.58×10^{23} to

$5.8 \times 10^{23} \text{ n.m}^{-2}$. Forging specimens were tested in the LT orientation, whereas those from the weld were tested in the TL orientation.

The nominal bulk compositions of the RPV surveillance forging and weld specimens used in this study are given in Table 1. The forging was a SA-508 class 2 steel (Heat 125P666). The submerged arc weld (weld wire heat 61782) was produced with a Linde 80 flux. The low copper (0.04 at.% Cu) forging contained 0.65 at.% Ni and 0.68 at.% Mn, whereas the high copper (0.23 at.% Cu) weld had lower Ni, 0.50 at.%, and significantly higher Mn, 1.31 at.%, concentrations. Both alloys also had typical levels of Si, Mo, C and P; and residual levels of Al, Co and V. The weld also contained 0.015 wt.% (0.06 at.%) N. The reactor vessel Charpy surveillance specimens were exposed to three fluences for up to 30.5 effective full power years (EFPY). The irradiation conditions are summarized in Table 2. Three levels of fluence were studied: 1.7, 3.6 and $5.8 \times 10^{23} \text{ n.m}^{-2}$ ($E > 1 \text{ MeV}$), corresponding to 8.9, 18.9, and 30.5 EFPY respectively. The reactor coolant temperature (assumed to be the irradiation temperature for the surveillance specimens) is given as 285 to 289 °C (545 to 552 °F). The latest removal, Capsule N, was removed after 30.5 EFPY of plant operation.

Atom probe tomography needle-shaped specimens for this study were prepared by standard electropolishing methods from small blanks cut from standard Charpy specimens.[12] The electropolishing solution was 2% perchloric acid in 2-butoxyethanol at room temperature and 15 VDC. Atom probe tomography characterizations of these surveillance specimens were performed in a CAMECA Instruments Inc. LEAP® 4000X HR local electrode atom probe. This instrument features an energy-compensating reflectron lens in the time-of-flight mass spectrometer to improve the mass resolving power and enable the individual isobars of all the elements present to be distinguished. All APT analyses were performed in voltage mode with a

specimen temperature of 50 K, a pulse repetition rate of 200 kHz, an ion collection rate of between 0.5 and 2 ions per pulse, and a pulse fraction of 0.2. All isobar overlaps were deconvoluted by standard methods.[14] Hereafter, all estimated compositions are quoted in atomic percent except where noted. The matrix compositions were estimated from the peak deconvolution method in CAMECA Instruments Inc. IVAS 3.6.6 which deconvolutes the overlapping isobars from the different elements (with the same isotopic mass) and removes the background noise.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties

Selected Charpy specimens from each group in Table 3 were tested for microhardness in the hot cell as a first step to identify the materials in the HAZ specimens, i.e., to identify which broken Charpy half is weld, and which half is forging. Seven measurements were performed on each specimen in the region about 6 mm from the specimen fracture surface. Additional microhardness testing was performed in the LAMDA Laboratory for final validation and Table 3 shows the average microhardness for each specimen. The microhardness data were used to verify weld vs forging for the HAZ specimens by correlation with the tensile and Charpy impact shift information from [1] and shown in Table 3.

As expected, based on higher concentration of radiation-sensitive elements (i.e. Cu, Ni, Mn), the weld specimens showed much higher irradiation-induced Charpy impact 41-J shifts at $5.8 \times 10^{23} \text{ n.m}^{-2}$ ($E > 1 \text{ MeV}$) than the forging, 120 °C (217 °F) and 51 °C (91 °F), respectively. The mechanical properties are summarized in Table 3 (ΔT_{30} is shift at 30 ft-lbs as reported). The measured Charpy impact energy over a series of test temperatures for the forging and weld metal

are shown in Figure 1 and 2,[1] respectively. The errors in Figures 1 and 2, based upon the unirradiated data on which multiple Charpy tests were conducted, was found to be 10.5% and 8.1% respectively.

3.2. Microstructure

3.2.1. FORGING

No copper-enriched precipitates were observed in the volume sampled in the low copper (0.04 at.% Cu) forging irradiated to a fluence of $1.7 \times 10^{23} \text{ n.m}^{-2}$. The overall composition of the volume sampled by APT (i.e. matrix and all precipitates) was estimated by a peak deconvolution method to be Fe-0.04% Cu, 0.78% Ni, 0.67 % Mn, and 0.67% Si (errors are less than 0.01%). These results indicated that the copper content of this volume was in solid solution and, therefore, the estimated level of 0.04% Cu was below the solubility limit of Cu at these irradiation conditions. However, a number density of $0.2 \times 10^{23} \text{ m}^{-3}$ of Ni-, Mn-, and Si-enriched precipitates were detected, as shown in a selected volume atom map in Figure 3a. These precipitates did not exhibit any significant Cu enrichment, as shown in the Cu atom map from the same volume in Figure 3b. A proximity histogram [23] from all 17 precipitates and the adjacent matrix regions surrounding the precipitates in this volume is shown in Figure 4. The equivalent radius, $r = \sqrt[3]{3V/4\pi}$, of these spheroidal precipitates was estimated from the volume, V , enclosed by the Ni concentration isosurface, Figure 3c, to be $2.2 \pm 0.5 \text{ nm}$. Therefore the equivalent radius of gyration, l_g , was $1.7 \pm 0.4 \text{ nm}$.

In contrast, Cu-, Ni-, Mn-, and Si-enriched precipitates were observed in a specimen cut from a different surveillance specimen from the same forging material in the intermediate fluence condition of $3.6 \times 10^{23} \text{ n.m}^{-2}$, as shown in the atom maps in Figure 5. The overall composition of this sample was estimated to be Fe-0.08% Cu, 0.71% Ni, 0.40% Mn, and 0.56%

Si (errors less than 0.01%). Copper-enriched precipitates were also observed in the high fluence condition of $5.8 \times 10^{23} \text{ n.m}^{-2}$, as shown in Figure 6. The overall composition of this sample was estimated to be Fe-0.09% Cu, 0.93% Ni, 0.57% Mn, and 0.66% Si (errors less than 0.01%).

Therefore, these slightly higher copper contents were above the solubility limit of Cu under these irradiation conditions. The variations in the composition estimates also indicate some expected local variations in the alloy content from one region to another of this forging. The radii of gyration of the Cu precipitates were estimated from the maximum separation method [2, 3, 24] to be $0.52 \pm 0.11 \text{ nm}$ and $0.82 \pm 0.11 \text{ nm}$, respectively, with number densities of 0.2 and $0.7 \times 10^{23} \text{ m}^{-3}$, respectively, for the intermediate and high fluence conditions. These results indicate that size and number density of the Cu-enriched precipitates increased slightly by the additional exposure to neutron irradiation. The compositions of the precipitates in the forgings are summarized in Table 4. The P atom map in Figure 6 of the high fluence condition also revealed P segregation to, and preferential precipitation of, the Cu precipitates along a dislocation, as commonly observed in neutron-irradiated RPV steels.[19]

3.2.2. WELD

The higher copper welds also contained high number densities of Cu-enriched precipitates, as shown in the Cu concentration isosurfaces for the low fluence condition of $1.7 \times 10^{23} \text{ n.m}^{-2}$ in Figure 7a. The overall composition of this sample was estimated to be Fe-0.20% Cu, $0.56 \pm 0.003\%$ Ni, $1.27 \pm 0.004\%$ Mn, and $1.05 \pm 0.003\%$ Si (errors less than 0.01%). The solute partitioning of Ni, Mn, Si and P atoms to the surface of Cu-enriched precipitates is highlighted in the atom map of two precipitates in Figure 7b. The sizes and number densities of these precipitates in the low fluence condition were estimated from the maximum separation method to be $0.93 \pm 0.17 \text{ nm}$ and $2.8 \times 10^{23} \text{ m}^{-3}$, respectively. Similar precipitates were also observed in the

intermediate ($3.6 \times 10^{23} \text{ n.m}^{-2}$) and high fluence ($5.8 \times 10^{23} \text{ n.m}^{-2}$) conditions where the overall compositions of the intermediate and high fluence samples were similar to the low fluence sample: Fe-0.20at.% Cu, 0.55% Ni, 1.20% Mn, and 0.92% Si and Fe-0.20at.% Cu, 0.60% Ni, 1.36% Mn, and 0.95% Si (all errors were found to be less than 0.01%), respectively. The sizes and number densities of these precipitates in these conditions were estimated from the maximum separation method to be $1.12 \pm 0.31 \text{ nm}$ and $1.7 \times 10^{23} \text{ m}^{-3}$; and $0.98 \pm 0.32 \text{ nm}$ and $3.7 \times 10^{23} \text{ m}^{-3}$, respectively. Both the size and number density of the precipitates in the welds were greater than in the forging specimen at the same fluence due to the higher copper content of the material.

An example of preferential precipitation of Cu-enriched precipitates on, and P segregation along, a dislocation is shown in Figure 8 for the high fluence weld at $5.8 \times 10^{23} \text{ n.m}^{-2}$. The distribution of P atoms in the bulk and at precipitates is also included in Figure 7 for reference. The precipitates exhibit a localized enrichment of P on the surface of the Cu-enriched precipitates. This is revealed in the high-resolution atom maps of the low fluence, $5.8 \times 10^{23} \text{ n.m}^{-2}$, weld of the different solutes (Ni, Mn, Si, and P) in the near vicinity of a Cu-enriched precipitate (Figure 9). These Cu-enriched precipitates were found to have Ni-, Mn-, Si-, and P-enriched regions on their surfaces. This behaviour suggests that the surface of some of the Cu-enriched precipitates was a preferential nucleation site for the Ni-, Mn-, Si-, and P-enriched clusters.

Grain boundaries also act as highly efficient sinks for the precipitation of the Cu-enriched clusters, and solutes as shown in the atom maps in Figure 10. Here the grain boundary is highlighted in the individual atom maps by the arrows and significant Cu, Ni, Mn, and P segregation to the grain boundary can be seen.

3.2.3. LIMITS OF CU ON FORMATION OF ENRICHED PRECIPITATES

The difference between the absence and presence of the Cu-enriched precipitates in the 0.04% and 0.08% Cu forging also indicated that the solubility limit for Cu precipitation was crossed between these measured overall copper contents, for these irradiation conditions (i.e., temperature, time and fluence) and alloy composition. The number density of Cu-enriched precipitates as a function of the measured bulk copper contents of the samples, ignoring the different fluence levels and materials – the three higher values are from the weld, and the three lower values are from the forging – is shown in Figure 11. The intercept of this polynomial curve fit suggests that the minimum Cu level in the Ginna alloy for forming Cu-enriched precipitates is 0.046 at. % Cu. The measured copper contents of the matrices for the forging and weld specimens are summarized in Table 4, for all fluence conditions studied. However, it should be noted that this data is specifically for the material investigated in this study and it could be expected that other alloys (with different levels of the various solutes) may behave differently. More data is required to determine any relationship between the solute levels and Cu solubility.

4. SUMMARY

Atom probe tomography has been used to investigate the microstructure of irradiation-induced precipitates in forging (low copper) and weld (high copper) steel surveillance specimens, irradiated in the R. E. Ginna PWR reactor for 30.5 EFPY. In the low copper forging specimens irradiated to low fluence, Cu-enriched precipitates (CRPs) were observed to form in one sample, while no CRPs were observed in a sample prepared from a different surveillance specimen of the same material. This was found to be as a result of local variation in the Cu content, with the ferrite region in which the CRPs were observed having a greater Cu content.

The high Cu weld material was found to have a significant number of CRPs at all

irradiation fluences. Closer examination revealed that the solutes Ni, Mn, Si and P were also associated with the CRPs, lying at the surface of the precipitates indicating that the CRPs act as preferential nucleation sites for the Ni-Mn-Si precipitates. It is clear from these results that the higher number densities of precipitates, especially the Cu-enriched precipitates, in the weld metal compared with the forging leads to the significantly greater irradiation-induced Charpy shift for the weld than for the forging.

Inspection of the number density of CRPs as a function of the Cu content within the analysed volumes suggests that the solubility limit of Cu in these steels, and therefore, the lower limit for the formation of CRPs, irradiated under these conditions, is ~0.046 at. % Cu.

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Table 1: Nominal composition of the Ginna RPV surveillance specimens used in this study. The balance is Fe.

Weld	Cu	Ni	Mn	Mo	Cr	C	Si	P	S
wt. %	0.23	0.53	1.31	0.36	0.59	0.075	0.59	0.012	0.016
at. %	0.20	0.50	1.31	0.21	0.63	0.34	1.16	0.021	0.028
Forging	Cu	Ni	Mn	Mo	Cr	C	Si	P	S
wt. %	0.05	0.69	0.67	0.57	0.37	0.19	0.20	0.010	0.011
at. %	0.04	0.65	0.68	0.33	0.39	0.88	0.40	0.021	0.019

Table 2: Irradiation conditions for the forging and weld surveillance specimens. The irradiation temperature was 289 °C.

Location	Specimen ID	Fluence ($\times 10^{23}$ n.m ⁻² (E > 1 MeV))	Nominal Cu (wt.%)	Nominal Ni (wt.%)
Forging	P26	1.7	0.05	0.69
Forging	H39-B	3.6	0.05	0.69
Forging	H48-A	5.8	0.05	0.69
Weld	W30	1.7	0.23	0.53
Weld	H39-A	3.6	0.23	0.53
Weld	H48-B	5.8	0.23	0.53

Table 3: Mechanical properties of the forging and weld surveillance specimens.^a The equivalent dpa and dpa.s⁻¹ for the fluences and fluxes are included in parentheses.

Location	Specimen ID	Fluence, 10^{23} n.m^{-2} (dpa)	Flux, $10^{14} \text{ n.m}^{-2}.\text{s}^{-1}$ ($10^{-6} \text{ dpa.s}^{-1}$)	VPN	ΔYS , MPa	ΔT_{30} , °C
Forging	P26	1.7 (0.029)	8.12 (1.4)	224	~0	19
Forging	H39-B	3.6 (0.064)	6.62 (1.16)	256	20-62	25
Forging	H48-A	5.8 (0.104)	5.92 (1.06)	258	~90	51
Weld	W30	1.7 (0.029)	8.12 (1.4)	266	100	83
Weld	H39-A	3.6 (0.064)	6.62 (1.16)	285	103-138	118
Weld	H48-B	5.8 (0.104)	5.92 (1.06)	277	~207	120

^a Fluence, flux, yield strength, and Charpy impact data are from [1].

Table 4: Compositions of the analysed material in the forging and weld surveillance specimens as estimated by the peak deconvolution method.

Location	Fluence, $\times 10^{23} \text{ n.m}^{-2}$	Cu	Ni	Mn	Si
Forging	1.7	0.04	0.78	0.67	0.67
Forging	3.6	0.08	0.71	0.40	0.56
Forging	5.8	0.09	0.93	0.57	0.66
Weld	1.7	0.20	0.56	1.27	1.05
Weld	3.6	0.20	0.55	1.20	0.92
Weld	5.8	0.20	0.60	1.36	0.95

Figure 1: Charpy V-notch impact energy vs. test temperature for the R. E. Ginna reactor vessel lower shell forging (Heat 125P666) in the longitudinal (LT) orientation following irradiation to different neutron fluences.[1] Legend refers to neutron fluences of: 1- Unirradiated; 2- 0.587×10^{23} ; 3- 1.02×10^{23} ; 4- 1.69×10^{23} ; 5- 3.64×10^{23} ; and 6- 5.8×10^{23} n.m⁻².

Figure 2: Charpy V-notch impact energy vs. test temperature for the R. E. Ginna reactor vessel surveillance program weld metal (weld wire heat 61782).[1] Legend refers to neutron fluences of: 1- Unirradiated; 2- 0.587×10^{23} ; 3- 1.02×10^{23} ; 4- 1.69×10^{23} ; 5- 3.64×10^{23} ; and 6- 5.8×10^{23} n.m⁻²

Figure 3: a) Atom maps of Ni, Mn, and Si atoms in a selected volume from the low fluence $1.7 \times 10^{23} \text{ n.m}^{-2}$ forging; b) atom map of Cu atoms in the same selected volume; c) Ni concentration isosurface (15%) of the Ni-, Mn-, and Si-enriched precipitates in a larger volume.

The scale bars in all figures are 20 nm.

Figure 4: Proximity histograms of the precipitates and adjacent matrix regions in the low fluence, $1.7 \times 10^{23} \text{ n.m}^{-2}$, a) forging, and b) weld specimens showing the partitioning of the Cu, Ni, Mn, and Si.

Figure 5: Atom maps of Cu, Ni, Mn, and Si atoms for the intermediate fluence, $3.6 \times 10^{23} \text{ n.m}^{-2}$, forging showing ultrafine Cu-enriched precipitates.

Figure 6: Cu atom maps of copper-enriched precipitates in the high fluence condition of 5.8×10^{23} n.m^{-2} . P atom map is superimposed to show P segregation to a dislocation.

Figure 7: a) Cu concentration isosurfaces for the low fluence condition of $1.7 \times 10^{23} \text{ n.m}^{-2}$ showing the Cu precipitates in the submerged arc weld. b) High-resolution atom map showing solute partitioning of Cu, Ni, Mn, Si and P atoms to two Cu precipitates.

Figure 8: Segregation P to a dislocation in the high fluence, $5.8 \times 10^{23} \text{ n.m}^{-2}$, submerged arc weld.

Figure 9: High resolution atom map of the different solutes (Ni, Mn, Si and P) in the vicinity of a Cu-enriched precipitate which is delineated by a Cu concentration isosurface in the low fluence, $1.7 \times 10^{23} \text{ n.m}^{-2}$, submerged arc weld. (Isosurfaces rendered using values of 5% and 15% for the Cu and NiMnSiP, respectively).

Figure 10: Atom maps of Ni, Cu, P and Mn (including a Cu concentration isosurface) showing the distribution of clusters and solutes in the matrix and at a grain boundary in the submerged arc weld material.

Figure 11: The number density of Cu-enriched precipitates for the different estimated bulk copper concentrations in the materials.