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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 5.8×10^{23} 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 1.7×10^{23} n.m^{-3}, this copper level was below the solubility limit. A number density of 2×10^{22} 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 3.6×10^{23} n.m^{-3}) and 0.09± <0.01 at.% Cu (fluence of 5.8×10^{23} 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.

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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

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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 5.8×10^{23} $n.m^{-2}$ (E > 1 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 Ref. [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 5.8×10^{23} $n.m^{-2}$. 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 5.8×10^{23} $n.m^{-2}$ (E > 1 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 285–289 °C (545–552 °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

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