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Contribution of irradiation-induced defects to hardening of a low-copper reactor pressure vessel steel

Masaki Shimodaira [a, *], Takeshi Toyama [a], Kenta Yoshida [a], Koji Inoue [a], Naoki Ebisawa [a], Keiko Tomura [a], Toshimasa Yoshiie [b], Milan J. Konstantinović [c], Robert Gérard [d], Yasuyoshi Nagai [a]

[a] Institute for Materials Research, Tohoku University, Oarai, Ibaraki, 311-1313, Japan
[b] Research Reactor Institute, Kyoto University, Kumatori, Osaka, 590-0494, Japan
[c] SCK-CEN, Nuclear Materials Science Institute, Boeretang 200, 2400, Mol, Belgium
[d] Tractebel ENGIE, Avenue Ariane, 1200, Brussels, Belgium

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ABSTRACT

We investigated the fluence dependence of irradiation-induced solute cluster, dislocation loop, and very small defect to reveal the hardening mechanism in surveillance test specimens from a reactor pressure vessel steel with low-Cu content (0.04 wt%) using atom probe tomography (APT), weak-beam scanning transmission electron microscopy (WB-STEM), and positron annihilation spectroscopy. A high number density ($>10^{23}$ m^{-3}) of solute clusters mainly composed of Ni, Mn, and Si atoms were found in highly neutron irradiated specimens (~10^{24} neutrons m^{-2} ($E > 1$ MeV)) by APT. These solute clusters were one of the main sources of hardening as reported previously. On the other hand, it was also revealed that dislocation loops were formed with a number density of ~10^{22} m^{-3} in the high-fluence specimens by WB-STEM. The estimated hardening due to dislocation loops was more than half of the actual hardening, showing that dislocation loops are also main source of irradiation hardening at high neutron fluence with the solid experimental evidences. Regarding specimens subjected to a low neutron fluence (~10^{23} neutrons m^{-2}), very small defects, not detected by either WB-STEM or APT, were formed by positron annihilation spectroscopy. This result suggested that, at a low neutron fluence, the defects were the initial hardening source and they may grow the dislocation loops observed by WB-STEM at high fluence range.

1. Introduction

The irradiation-induced embrittlement of reactor pressure vessel (RPV) steel is a critical issue for ensuring the safe operation of light water reactors. A more precise understanding of the embrittlement mechanism is necessary in order to improve the reliability of irradiation-induced embrittlement predictions. The primary embrittlement mechanism is hardening of the steel due to irradiation-induced microstructural changes, such as nano-scale solute clusters (SCs) and matrix damage (MD) [1–4]. Typical SCs are Cu-rich clusters [5,6] and Ni-Mn-Si clusters [7,8]. MD is a concept that describes all induced features other than SCs, although its exact nature remains somewhat ambiguous [4].

The atom probe tomography (APT) has enabled us to quantitate SCs. In the high-Cu RPV steels of first-generation reactors, over-saturated Cu was found to rapidly form Cu-rich clusters with a high number density ($\geq 10^{23}$ m^{-3}) at a low neutron fluence (~10^{23} n m^{-2}) [5,6,9,10] (noted that unit 'n' means 'neutrons' in this paper). Even in relatively recently manufactured low-Cu RPV steel, high-number-density Ni-Mn-Si clusters were observed at neutron fluences greater than 3×10^{23} n m^{-2} [7–9,11]. Based on large amount studies on the relationship between the formation of SCs and hardening, it is widely accepted that SCs are one of main sources of hardening in RPV steels. For example, Soneda et al. [12] suggested that the hardening is proportional to the square root of the volume fraction of SC.

* Corresponding author. 2145-2 Narita-cho, 311-1313, Oarai, Ibaraki, Japan.
E-mail address: shimodaira.masaki@jaea.go.jp (M. Shimodaira).

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On the other hand, the contribution of MD to irradiation hardening is not yet fully understood. The candidates for irradiation-induced MD are dislocation loops, vacancy clusters, and point defect-solute atom complexes [12]. In particular, irradiation-induced dislocation loops are considered to be the primary MD candidate [4]. Commonly, the number density and size of irradiation-induced dislocation loops have been measured by conventional weak-beam transmission electron microscopy (WB-TEM) [12–18]. At neutron fluences below 10^{24} n m^{-2}, the number density of dislocation loop in RPV steels has been typically reported as 10^{21} - 10^{22} m^{-3} [12,15,16], which is one or two orders of magnitude smaller than the number density of SCs. This relatively small number density qualitatively suggests that dislocation loops might make a smaller contribution to irradiation hardening compared to SCs. However, the quantitative investigation of the contribution of dislocation loops to hardening is still insufficient. Since the size of irradiation-induced dislocation loops in RPV steels is typically 2–7 nm [12,15,16], it is difficult to quantify such nano-scale dislocation loops using conventional WB-TEM due to strong interference effects, such as Fresnel fringes, thickness, and bend contours, especially in real steels with an inhomogeneous microstructure. Kuramoto et al. [19] performed post-irradiation annealing combined with APT and positron annihilation spectroscopy to examine RPV steel irradiated in a materials testing reactor up to a neutron fluence of 3.9×10^{23} n m^{-2}, and found that approximately half of the hardening originated from features other than SCs, suggesting a large MD contribution. Bergner et al. [16] suggested that dislocation loops are stronger obstacles for dislocation glide than SCs (Cu-rich clusters). Therefore, the contribution of dislocation loops to irradiation hardening might be large, although the number density of dislocation loops is smaller than that of SCs.

Most recently, Yoshida et al. [20] developed weak-beam scanning transmission electron microscopy (WB-STEM), which can reduce the effect of the interference. This advantage achieves a large field-of-view with sufficient spatial resolution to analyze nano-scale defects, and enables to more accurately quantify dislocations in real steels with an inhomogeneous microstructure. In this WB-STEM study [20], quantification of nano-scale dislocation loops was demonstrated using a highly irradiated RPV steel (~10^{24} n m^{-2}). As a result, the number density of dislocation loops was estimated to be 3.4×10^{22} m^{-3}. The systematic analysis for dislocation loops in RPV steels would achieve us a more precise understanding of the contribution of dislocation loops to hardening.

In this work, the fluence dependence of the number density and size of dislocation loops and SCs in surveillance test specimens from a European pressurized water reactor (PWR) were investigated using WB-STEM and APT. As a result, it was found that dislocation loops and SCs were densely formed at high neutron fluence (~10^{24} n m^{-2}). In addition, irradiation-induced defects in low-fluence specimens (~10^{23} n m^{-2}), in which WB-STEM and APT detected neither dislocation loops nor SCs, were analyzed by positron annihilation spectroscopy. In addition to these microstructural analyses, the hardening was evaluated by Vickers micro hardness test. We discuss the sources of hardening in the surveillance test specimens, and show that the contribution of MD to the irradiation hardening is enough large to be one of the main source at high fluence range.

2. Experimental method

2.1. Specimens

The surveillance test specimens were A508 class 3 weld materials with a low-Cu content (0.04 wt%), as shown in Table 1. We also included an un-irradiated specimen, designated T0; the other four irradiated specimens, T1, T2, T3, and T4, were irradiated in a commercial PWR at temperature of 283–289 °C with different neutron fluences. These fluences were 1.3×10^{23} n m^{-2} ($E > 1$ MeV) for T1, 3.4×10^{23} n m^{-2} for T2, 8.2×10^{23} n m^{-2} for T3, and 1.2×10^{24} n m^{-2} for T4; the flux was 1.3×10^{15} n m^{-2} s^{-1}. The increase of the ductile-brittle transition temperature (*ΔDBTT*), were 33 °C, 48 °C, 81 °C, and 137 °C for the T1 − T4 specimens, respectively (*DBTT* was defined as the temperature at which $E = 41$ J in Charpy test). Note that the neutron fluence at the end-of-life for this reactor was 6.1×10^{23} n m^{-2}, thus the last surveillance data has no impact on operation. Microstructural changes in the specimens were analyzed by APT, WB-STEM and positron annihilation spectroscopy. Specimens for each experiment were cut from used Charpy impact test specimens by an electrical discharge cutter to minimize the processing strain. The surface of each cut specimen was polished by chemical etching with a solution of 5% hydrofluoric acid, 85% hydrogen peroxide, and 10% distilled water to remove the damaged layer formed during cutting.

2.2. Atom probe tomography

Needle specimens for APT measurements were prepared from rod-shaped specimens with dimensions of $0.5 \times 0.5 \times 10$ mm by electro-polishing at a DC voltage of 15 V. The polishing solution was 5% perchloric acid in 2-butoxyethanol. The needle specimens were measured by a local electrode atom probe (LEAP4000X HR, CAMECA) at pulse rate of 200 kHz, a pulse fraction of 20%, a DC voltage of 3–8 kV, and a specimen temperature of 50 K. Three-dimensional atom maps were reconstructed by dedicated software (IVAS-3.6.6, AMETEK-CAMECA). All APT datasets were analyzed using a cluster analysis algorithm based on the maximum separation and erosion method [21,22] to estimate the number density, size, and solute atom concentrations for SCs. Parameters for cluster analysis, such as the maximum separation between Ni, Mn, and Si atoms, $d_{max} = 0.55$ nm, and the minimum number of Ni, Mn, and Si atoms, $N_{min} = 70$, were carefully chosen. No SCs were found in the un-irradiated specimen T0 using the above analysis parameters. The number density was estimated by dividing the number of SCs by the measured volume. The SC size was defined as the Guinier diameter, d_G, using the following equation [23]:

$$d_G = 2\sqrt{\frac{5}{3}} \times \sqrt{\frac{\sum_{i=1}^{n} (x_i - x_c)^2 + (y_i - y_c)^2 + (z_i - z_c)^2}{n}} \quad (1)$$

where x_i, y_i, and z_i are the spatial coordinates of each atom in a

Table 1
Chemical composition of surveillance test specimens (wt%).

C	S	P	Si	Mn	Ni	Cr	Cu	Mo	V	Al	N	Fe
0.05	0.01	0.02	0.13	1.13	0.94	0.04	0.05	0.54	0.01	0.02	0.02	Bal.