Intergranular Segregation in the Pressure Vessel Steel of a Commercial Nuclear Reactor Studied by Atom Probe Tomography

Takeshi Toyama1, Yasuyoshi Nagai1, Abderrahim Al Mazouzi2*, Masahiko Hatakeyama1, Masayuki Hasegawa1, Tadakatsu Ohkubo3, Eric Van Walle2 and Robert Gerard4

1International Research Center for Nuclear Materials Science, Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan
2SCK-CEN, Nuclear Materials Science Institute, Boeretang 200, 2400 Mol, Belgium
3National Institute for Materials Science, Tsukuba 305-0047, Japan
4Tractebel Engineering, Avenue Ariane, 1200 Brussels, Belgium

Solute/impurity segregation and precipitation at grain boundaries (GBs) in a nuclear reactor pressure vessel (RPV) steel were investigated using laser-assisted atom probe tomography (APT): RPV surveillance test specimens irradiated in a commercial nuclear reactor to neutron doses of \(0.83 \times 10^{19} \text{n cm}^{-2}\) (low-dose) and \(5.1 \times 10^{19} \text{n cm}^{-2}\) (high-dose), corresponding to in-service exposure of \(\approx 5\) and \(\approx 30\) years, respectively. The segregation of C, P and Mo was found on GBs after the low-dose irradiation. The segregation of Si and Mn as well as C, P and Mo was observed after the high-dose irradiation. The monolayer coverage of P is estimated to be less than a suggested level for intergranular embrittlement. The segregation of C, P and Mo was also observed along parallel array of dislocation lines in small-angle grain boundaries. However, no segregation of Si and Mn was detected there. Copper-nano precipitates (CNPs) were observed on the GBs, along the dislocation lines and in the matrix. The sizes and the solute-impurity enrichment in these CNPs are compared.

Keywords: grain boundary segregation, atom probe tomography, reactor pressure vessel steel, irradiation effect

1. Introduction

The reactor pressure vessel (RPV) of a nuclear power plant contains the nuclear fuel rods and the moderator/coolant water. Since it is irreplaceable and a primary safety boundary, the RPV is one of the essential components that limits the life of light water reactors. A second-generation reactor will soon exceed their designed operational lifetimes, extensive studies are being conducted worldwide to clarify the mechanisms of irradiation-induced embrittlement of the RPV steel. It is widely accepted that the embrittlement of RPV steel can be caused by two major mechanisms:1-5 the first mechanism is associated with irradiation-induced hardening of the matrix, and the second mechanism is associated with grain boundary (GB) weakening, mainly due to segregation of P impurities.3,4

Hardening embrittlement originates from irradiation-induced/enhanced features in the matrix: solute/impurity precipitates, such as Cu nano-precipitates (CNPs) and so-called matrix defects (MDs), such as interstitial loops and nanovoids.1,2,5 We have reported the evolution of these features in surveillance test specimens of commercial reactors, Doel-1 and -2 in Belgium, irradiated up to a neutron dose of \(\approx 6 \times 10^{19} \text{n cm}^{-2}\), corresponding to an in-service period of \(\approx 30\) years in the previous paper.6 In this paper, we report the GB segregation of impurity/solute atoms in the same specimens. Such observation for dislocations/GBs are expected to contribute significantly to the understanding of non-hardening embrittlement, which is increasingly important, especially in the case of higher neutron doses for prolonged irradiation periods in aged nuclear reactors.

Irradiation-induced GB segregation of P in RPV steel has been investigated by Auger electron spectroscopy,7-9 field-emission gun scanning transmission electron microscopy,10 and atom probe tomography (APT).11-13 APT enables the observation of direct, three-dimensional (3D) features. The recent development of a local-electrode atom probe (AP) has enabled the analysis of much larger volumes and higher data acquisition rates than previously possible.12 Furthermore, recent incorporation of laser-pulse assistance provides a higher yield to observe brittle specimens, such as irradiated RPV steels containing GBs, which are one of the main origins of specimen fracture during APT measurements.

In this study, GBs in the surveillance test specimens of the Doel-2 reactor were investigated with laser-assisted, local-electrode APT. We observed GB segregation of solute/impurity elements and investigated the morphology of CNPs formed on the GBs.

2. Materials and Experiments

The specimens were obtained from the capsule V of the surveillance program of the Doel-2 reactor in Belgium, which has been in operation since 1975. The RPV was made by welding forged rings of A508 cl.3 (Soudotenax 56) steel using the submerged arc welding process, Unionmelt 40 wire and Unionmelt 89 flux, as described in a previous report.13 The final post-weld heat treatment of the vessel was carried out for 8 h at 600°C, leading to a bainitic structure with a substantial amount of carbides and siliconides. The chemical composition of the specimens is listed in Table 1. The high concentration of Cu is mainly attributable to the welding fluxes of the early 1970s, which contained rather high Cu concentrations. Furthermore, the Ni content is relatively low compared to other standard materials, such as A533B, whereas C and P concentrations are similar. The specimens
were subjected to neutron irradiation doses of either 0.83 × 10¹⁹ n·cm⁻² (low dose) or 5.1 × 10¹⁹ n·cm⁻² (high dose) with a flux of 8.5 × 10¹⁰ n·cm⁻²·s⁻¹ at 304°C. These doses correspond to in-service irradiation periods of about 5 and 30 years, respectively. Unfortunately, no unirradiated archive material has been preserved; examination of unirradiated specimens for comparison is thus impossible.

The specimens for APT measurements were prepared from the surveillance test specimens for tensile test. Specimens were cut into 0.4 mm × 0.4 mm × 10 mm rods using an electrodischarge cutter to minimize cutting-induced surface damage; cutting was followed by electropolishing to make needle-shaped tips with a solution of 2% perchloric acid in 2-butoxyethanol. Next, the tips were milled using a focused ion beam (FIB) to locate a GB within about a few micrometers of the top of the needle tip, as shown in Fig. 1(a). Finally, electropolishing was repeated several times to remove the damaged layer caused by FIB milling and to set the GB just below the top of the tip, as shown in Figs. 1(b) and 1(c).

3D-AP analysis was carried out with a laser-assisted, local-electrode APT (LEAP-3000X) from IMAGO Scientific Instruments. Conditions included a laser power of 0.5 nJ, a laser repetition rate of 250 kHz, a DC voltage in the range of 5 to 10 kV and a temperature of about −240°C (30 K).

3. Results and Discussion

Figure 2 shows representative examples of atom maps near a GB in (a) the low-dose and (b) the high-dose specimens, respectively: observations was made for four GBs in total for the low-dose specimens and three for the high-dose specimens. The plane of the GB in the low-dose specimen is nearly parallel to the view direction (y). At the GBs of both dose specimens, C, P and Mo segregation and CNPs were...
observed. In the high-dose specimen, the segregation was enhanced and furthermore Si and Mn segregation was also observed. All of the segregating elements, except for Cu, were distributed almost homogeneously on the GB plane in both the low- and high-dose specimens. On the other hand, neither segregation nor depletion at GBs occurred for Ni and Cr, even in the high-dose specimen.

Figure 3 shows the concentration profiles of each element in the GBs from Fig. 2. The results shown in Fig. 3 were obtained from a rectangular parallelepiped region with area $5 \times 5 \text{ nm}^2$ from a cross-section perpendicular to the GBs shown in Fig. 2 using a bin width of 0.2 nm. The moving averages on 3 adjoining bins are indicated by dashed (0.85 $\times 10^{19} \text{ n cm}^{-2}$) and solid (5.1 $\times 10^{19} \text{ n cm}^{-2}$) lines.

Here we focus on P segregation because of its importance in the embrittlement of low alloy ferritic steels. To estimate the monolayer coverage of P at the GBs, a method based on simple geometrical models for all boundary orientations and on the Gibbsonian interfacial excess$^{14-17}$ was employed. In this method, the Gibbsonian interfacial excess of the solute element, $\Gamma$, is estimated by $\Gamma = N/A (c_{\text{GB}} - c_{\text{matrix}})$, where $N$ is the total number of atoms contained in the analyzed volume, $A$ is the cross section of the analyzed volume, $c_{\text{GB}}$ is the composition of the solute element in the entire analyzed volume and $c_{\text{matrix}}$ is the composition of the solute element in the matrix. The monolayer coverage, $\Phi$, is given by $\Phi = \Gamma / \rho w$, where $\rho$ is the atomic density and $w$ is the width of the GB plane. In this study, the atomic density for body-centered cubic (bcc) Fe, $8.49 \times 10^{22}$ atoms/cm$^3$, was used for $\rho$ and the interatomic distance of the closest packed plane in bcc Fe, $d_{110} = 0.20 \text{ nm}$, was used for $w$. The obtained $\Phi$ values were $\sim 0.04$ and $\sim 0.09$ for the low- and high-dose specimens, respectively.

These values for the monolayer coverage of P do not exceed the suggested trigger level of P segregation for intergranular embrittlement for a commercial RPV steel, 0.1–0.15$^{18}$ even in the high-dose specimen ($5.1 \times 10^{19} \text{ n cm}^{-2}$). This result is consistent with our observation that no intergranular fracture occurred in the surveillance test specimen of the Doel-2 reactor irradiated to a dose of $3.7 \times 10^{19} \text{ n cm}^{-2}$.13

We also analyzed another GB in the high-dose specimen. Figure 4(a) shows atom maps near a GB as a projection onto the $x-z$ plane, in which the view direction $(y)$ is parallel to the GB; the GB plane is perpendicular to the picture plane. A high level of C, P and Mo segregation at the GB was evident, as shown by the arrows in the figure; this result is similar to that observed in the case of Fig. 2(b). However, no segregation was observed for Si and Mn, in contrast to Fig. 2(b). The other orientation projection onto the $y-z$ plane as shown in Fig. 4(b), C, P and Mo segregation occurred along the different segments of the striped line series. The separation between the neighboring striped lines was similar to be about 12 nm. Furthermore, a high number density of CNPs was observed along the striped lines of the P segregation, as well as in the matrix.

For a small-angle GB, the angle of the neighboring grains, $\theta$, can be related to the spacing between the neighboring dislocations on the small-angle GB, $h_{12}^{19}$ $\tan(\theta/2) = b/2h$, where $b$ is the Burgers vector, is defined as $b = \sqrt{3}/2 \times 0.2866 \text{ nm}$ for bcc Fe. This formula yields a $\theta$ value of $\sim 1$ degree using $h \sim 12 \text{ nm}$ for the GB shown in Fig. 4(b), implying that the preferential segregation of the solute/impurity elements occurs along each segment of a parallel array of dislocations on a small-angle GB. Furthermore, CNPs form on (within or in the vicinity of) the dislocation lines on the small-angle GB.

P segregation in the small-angle GB was inhomogeneous along dislocations as shown in Fig. 4(b). A possible reason of this is the GB structure; it is believed that solute/impurity segregation at GBs changes with the GB structure, such as misorientation angle, GB width, open-space distribution and so on.$^{19}$ In addition, segregation or precipitation of other solutes, such as CNPs on dislocations, could have an influence on the P distribution.

As stated above, no segregation of Si and Mn was observed at the small-angle GB as shown in Fig. 4(a), in contrast to the case of large-angle GB as shown in Fig. 2(b). This difference might be due to the GB structure, i.e., the difference between large and small-angle GBs may affect the
observed Si and Mn segregation. To clarify this, further observation of various kinds of GBs are necessary in future studies.

The average P concentration on the dislocations at the small-angle GB was estimated using the tracer method proposed by Miller\textsuperscript{20,21)} to be about 2 mol\% with local maxima of up to \(\sim 5\) mol\%. These P concentrations at the dislocations are about 20 times higher than those in the matrix. Segregation of P to dislocations other than GBs, has been reported in several RPV steels containing lower P concentrations than the present specimen.\textsuperscript{11)} For weld materials with 0.014–0.022 mass\% P at a neutron dose of \(3.4 \times 10^{19}\) n cm\(^{-2}\), the average P concentration at dislocations is estimated by the tracer method to be 1–2 mol\%, with local maxima of up to 3–4 mol\%. The observed P concentration at the dislocation in the present study is similar to those reported previously, implying that the P segregation level at dislocations might saturate at an average of around 2 mol\%.

We are much concerned with the chemical compositions of the three types of CNPs observed in the high-dose specimen: (1) CNPs in the matrix, (2) on the dislocations and (3) on GBs. The CNPs of similar size (\(\sim 3\) nm in diameter) were selected from the matrix (as indicated by the arrow [D] in Fig. 4(b), the dislocation at the small GB (the arrow [C] in Fig. 4(b)) and the GB (the arrows [A] and [B] in Fig. 2(b)). The enlarged atom maps of these CNPs are shown in Figs. 5(a), 5(b) and 5(c), respectively. (1) At the CNPs in the matrix, marked enrichment of Mn and slight enrichment of P, Ni and Si were seen (Fig. 5(a)). It should be noted that some of the CNPs are enriched with these solute/impurities but the other are not (Fig. 4). These results are in agreement with the many studies using APT on irradiation-induced CNPs in the matrix of RPV steels reporting that CNPs are enriched with other solute elements, such as Si, Mn, P and Ni.\textsuperscript{6,11,22–24)} (2) In contrast, at the CNPs on dislocation lines in the small angle GB, no enrichment of Si and Ni was evident and only slight enrichment of P, Ni and Si were seen (Fig. 5(a)). (3) Moreover, at the CNPs on the GB, almost no Si, Mn, P and Ni enrichment was observed (Fig. 5(c)). Thus, enrichment of the solute/impurity elements differs substantially between CNPs formed in the matrix, on the dislocations and on GBs.

The size of CNPs was analyzed in the high-dose specimen using the maximum separation algorithm.\textsuperscript{20)} The clustering atoms selected were Cu, Si, Mn, Ni and P, and a maximum

![Fig. 4 Atom maps near a GB in a Doel-2 RPV surveillance test specimen irradiated to a neutron dose of \(5.1 \times 10^{19}\) n cm\(^{-2}\).](image-url)
separation distance, $d_{\text{max}}$, of 0.7 nm and a minimum number of atoms, $N_{\text{min}}$, of 30 atoms were employed. The average radius (Guinier radius) was obtained as $2.9 \pm 0.5$ nm for CNPs in the matrix, $2.1 \pm 0.7$ nm for the CNPs on the dislocation at the small-angle GB and $2.3 \pm 0.9$ nm for CNPs on the large-angle GBs, respectively. It is found that the size of CNPs on the dislocation and on large-angle GBs was slightly smaller than that of CNPs in the matrix.

Fig. 5 Enlarged atom maps of Cu nano-precipitates (CNPs) in a Doel-2 RPV surveillance test specimen irradiated to a neutron dose of $5.1 \times 10^{19}$ n·cm$^{-2}$. (a): The CNP in the matrix indicated by the arrow [D] in Fig. 4(b). (b): The CNP on the dislocation in the small-angle GB indicated by the arrow [C] in Fig. 4(b). The view direction is perpendicular to the GB plane as in Fig. 4(b). (c): The CNPs on the GB indicated by the arrows [A] and [B] in Fig. 2. The view direction is perpendicular to the GB plane as in Fig. 2(b).
In contrast to the results in the present study, Miller et al. observed no appreciable differences between the chemical compositions and sizes of CNPs in the matrix and on the dislocations in the welded RPV steels. A possible reason for this discrepancy is that the enrichment of the solute/impurity in CNPs might be sensitive to the type of dislocations. We have observed CNPs on the array of dislocation lines in the present study, whereas Miller et al. observed CNPs on a single dislocation. This discrepancy can influence the sink strength and/or strain fields of dislocations. These characteristics might change the kinetics of CNP formation and/or the stability of CNPs on dislocations; the migration of solute/impurity atoms could be affected as well. Further studies are necessary to reveal this.

4. Conclusions

We used APT to observe GBs in surveillance test specimens of the Doel-2 reactor irradiated to neutron doses of 0.83 × 10¹⁹ and 5.1 × 10¹⁹ n·cm⁻². C, P and Mo segregation at the low dose and C, Si, Mn, P and Mo segregation at the high dose were observed, indicating that solute/impurity segregation at the GBs is substantially enhanced by further irradiation. However, P segregation did not exceed the suggested trigger level for intergranular embrittlement for RPV steels, even at the high irradiation dose. On a GB in the high-dose specimen, marked segregation of C, P and Mo, as well as precipitation of CNPs, along the striped line series was also observed, implying segregation and precipitation along the parallel array of dislocation lines in the small-angle GB. Almost no enrichment of solute/impurity elements was observed in the CNPs on dislocations or in the CNPs at GBs, while enrichment was common in CNPs formed in the matrix.

Acknowledgements

The authors would like to thank Dr. L. Malerba and Dr. Y. Matsukawa for useful discussions, M. Narui and M. Yamazaki for their support of hot laboratory work and the Utility Electrabel for permission to publish the present results on the surveillance test specimens. This work was partially supported by Grants-in-Aid for Scientific Research of the Ministry of Education, Culture, Sports, Science and Technology, Japan (Nos. 17002009, 1776076, 18686077 and 23760822), a research program of the Japan Nuclear Energy Safety Organization and Nuclear Research of the Ministry of Education, Culture, Sports, Science and Technology, based on screening and counseling by the Atomic Energy Commission.

REFERENCES