Cu precipitation behaviour in long-term thermally aged, high-copper model reactor pressure vessel steels

Xiangbing Liu*, Yuanfei Li‡, Chaoliang Xu§, Fei Xue†, Wangjie Qian#,
Ping Huang∗

Life Management Technology Center, Suzhou Nuclear Power Research Institute, Suzhou, China

*Corresponding author e-mail: xiangbing_liu@yahoo.com, ‡P193258@cgnpc.com.cn, §xuchaoliang@cgnpc.com.cn, †xuefei@cgnpc.com.cn, #qianwangjie@cgnpc.com.cn, ∗huangping@cgnpc.com.cn

Abstract. Nanoscale Cu-rich precipitates that were formed in Cu-containing reactor pressure vessel (RPV) steels during service have a deleterious effect on mechanical properties, which can result in RPV embrittlement and limit reactor operation life. To understand the nanoscale precipitation mechanism, thermal aging at 370°C for up to 13200 h of high-copper RPV model steels was performed to produce nanosized Cu-rich precipitates. Then the Cu-rich precipitates were systematically investigated by atom probe tomography (APT). The changes in the mechanical properties of the steels were characterized by Vickers hardness test. The results show that the Cu-rich precipitates as determined by APT construction analysis have a spatial core-shell structure. The core is enriched with Cu atoms, and the region near the precipitate/matrix interface is enriched with Mn, Ni, Mo, and Si and C atoms. Cu-rich precipitates lead to precipitation strengthening and hardening/embrittlement effects. Using the Russell-Brown model, we estimated the hardening due to Cu-rich precipitates in the matrix and observed that the measured hardness and the estimated changes in hardness were in good agreement.

1. Introduction

License renewal of current nuclear fission power plants is becoming a new trend for meeting the world’s growing demand for nuclear energy. However, irradiation hardening/embrittlement in reactor pressure vessel (RPV) steels, which is mainly caused by the formation of ultrafine Cu-rich precipitates (CRPs), is one of the factors limiting the lifetime of PWR power plants [1]. From this perspective, the copper precipitation behavior in iron and steels has been extensively studied using atom probe tomography (APT) [2], positron annihilation spectroscopy (PAS) [3], small angle neutron scattering (SANS) [4] and transmission electron microscopy (TEM) [5] over the past decades. However, the formation behavior of CRPs as a function of materials and service environmental parameters is only partially understood.

Performing experiments in a real reactor neutron irradiation environment is expensive and materials-activated. There has been renewed interest in analyzing thermally aged RPV steels to develop an improved mechanistic understanding of the precipitation process [6-8]. Although much research has been performed to elucidate the atomic structure of Cu-enriched precipitates in ferritic steels containing copper, a thorough experimental investigation of the correlation between microstructural features and...
mechanical properties such as size, number density, composition, and hardness/strength has not yet been undertaken. Furthermore, newly developed high-strength steels, such as the high-strength low-carbon (HSLC) NUCu-140 [9, 10], tend to be designed with a Cu alloying element to achieve a suitable combination of high strength and toughness. Therefore, a detailed understanding of nanoscale precipitation behavior will provide a design baseline for developing advanced high-strength steels.

In this study, the APT was firstly used to characterize CRPs in high-copper RPV model steels aged at 370°C for up to 13200 h. Then the effect of CRPs on changes in mechanical properties was investigated.

2. Materials and Experimental Methods

2.1. Model steels
The preparation of model steels was described in our previous paper [11]. Chemical compositions of the steels are shown in Table 1. The Cu content was increased to up to 0.50 wt. % (0.43 at. %) to accelerate the formation of CRPs. Thermal aging was conducted at 370°C for different times of 1150 h, 3000 h and 13200 h.

2.2. APT observation
The APT experiment was performed using a LEAP 3000XHR by Cameca at a residual pressure of 3 Pa, a specimen base temperature of 50 K and a pulse repetition frequency of 200 kV. The tip specimens for APT were prepared by a standard two-step electro polishing method at room temperature. Data analysis was performed using the Imago Visualization and Analysis Software (IVAS) program.

2.3. Hardness test
To study the effect of CRPs on changes in mechanical properties of the steel samples, hardness measurements were also carried out using a Leica VMHT30 instrument under a load of 0.1 kg of force.

3. Results and discussion

3.1. Microstructural evolution of Cu-rich precipitates
Fig. 1(a) shows Cu atom maps of the steels aged for 13200 h. Using equation (1), the diameter was calculated to 5.04 nm, and the number density of Cu-rich clusters was on the order of $10^{22}$ m$^{-3}$.

$$D = \sqrt[3]{\frac{6n\Omega}{\pi f}}$$ (1)

where the atomic volume, $\Omega$, was equal to $1.178 \times 10^{-2}$ nm$^3$ for bcc Fe, and the overall detection and reconstruction efficiency, $f$, was estimated to be 0.37. The number of solute atoms, $n$, was determined by the envelope method [12] based on clusters with more than 20 (N=20) Cu atoms separated not farther than a maximum separation distance of 0.5 nm and employing an envelope grid spacing of 0.3 nm (L=0.3 nm). Table 2 presents the statistic average precipitate size, number density and calculated volume fraction for RPV model steels aged at 370°C for 1150 h, 3000 h and 13200 h. The results show that there was a slight increase in the Cu-rich precipitate size, number density and volume fraction with increasing
aging time. After 1150 h of aging, no Cu precipitate was detected. This result is consistent with the TEM results. The fact that no precipitate was observed was mostly due to the long impregnation time for the Cu-rich precipitates at 370°C. Our results also show that aging for 13200 h at 370°C is not sufficient to attain equilibrium Cu solubility. In other words, the steels remained underaged even after undergoing 13200 h of aging due to the limited Cu solubility at low temperature. This result agrees well with the findings reported by Miller et al. [13].

Table 2. Average precipitate size, number density and calculated volume fraction for RPV model steels aged at 370°C for 1150 h, 3000 h and 13200 h.

| Aging time (h) | Detected size (nm³) | Numbers of precipitates (pcs) | Average diameter (nm) | Number density (×10²²m⁻³) | Calculated volume fraction (%) |
|---------------|---------------------|--------------------------------|----------------------|---------------------------|-------------------------------|
| 1150          | 90×89×42            | 0                              | /                    | /                         | /                             |
| 3000          | 57×57×440           | 24                             | 2.34                 | 1.68                      | 0.115                         |
| 13200         | 67×67×99            | 8                              | 3.38                 | 1.86                      | 0.181                         |

It is well known that Cu-rich precipitates are always accompanied by Ni, Mn and Si [14]. Fig. 1(b) demonstrates the synergistic effects of the atomic distributions of Cu and Ni. The figure shows that the Cu-rich precipitates had a core-shell structure. The core was mainly composed of Cu atoms, and the shell was composed of Ni atoms. This atomic distribution trend also applied to Mn, Ni, Si, etc. Therefore, we created the core-shell model shown in Fig. 1(c) to illustrate the atomic distribution of all alloy elements. A represents Cu atoms, and B represents Fe, Mn, Ni, Si, Mo, C and P.

Figure 1. (a) Positions of Cu atoms in an APT reconstruction, 27×65×64 nm³ in size, obtained from a steel aged at 370°C for 13200 h. (b) Cu and Ni atom distribution in a Cu-rich precipitate. (c) Schematic atom distribution in a Cu-rich precipitate with core-shell structure.

3.2. Changes of mechanical property
Irradiation embrittlement, which is considered to be associated with Cu-rich precipitates, is the most serious threat to serviced RPV steels. The mechanical degradation of RPV steels can be typically evaluated by hardness test. To extend the correlation from macro mechanical changes to microstructure...
evolution, particularly Cu precipitation behavior, the dependence of the Vickers hardness (Hv) on aging time is plotted in Fig. 2. With the increase in aging time, the Hv increased due to the strengthening of nanosized Cu-rich precipitates.

The hardening due to Cu-rich precipitates was estimated using the Russell-Brown (RB) model based on the measured Cu-rich precipitate features listed in Table 2. This model assumes a random distribution of spherical precipitates that are elastically softer than the surrounding matrix, which is the case for Fe-Cu based alloys [15]. In the RB model, the strengthening is calculated as follows:

\[ \Delta \sigma = f_s \left( G_m b / L \right) \left\{ 1 - \left( \frac{E_p}{E_m} \right)^2 \right\}^{3/4} \sin^{-1} \left( \frac{E_p}{E_m} \right) \geq 50^\circ \]  

\[ \frac{E_p}{E_m} = \frac{E_p^\infty \log \frac{r}{r_0} + \frac{\log \frac{R}{r_0}}{\log \frac{R}{r}}}{E_m^\infty} \]  

\[ L = 1.77 \frac{r}{V_f^{1/2}} \]  

Where \( f_s \) is the Schmid factor; \( G_m \) is the shear modulus in the matrix; \( b \) is the Burgers vector; \( E_p \) is the dislocation energy in the precipitate and \( E_m \) is the dislocation energy in the matrix; \( E_p^\infty, \ E_m^\infty \) refer to the energy per unit length of a dislocation in an infinite precipitate and matrix; \( r \) is the average radius of precipitates; \( r_0 \) is the inner cut-off radius; \( R \) is the outer cut-off radius, which is \( 1000r_0 \); and \( L \) is the inter-particle spacing. We referred to the studies of several research groups in determining these variables, which are shown in Table 3. Using the APT data in Table 2 and \( \Delta HV = 0.41 \Delta \sigma \) for low-alloy steels [16], the predicted and the measured hardness increment plotted in Fig. 3 show that they are in good agreement for the 3700 h and 13200 h samples. These results suggest that the changes of hardness are attributed to the size, number density and distribution of the nanoscale Cu-rich precipitates.

**Table 3.** Variable selection in Russell-Brown model.

|                | \( G_m \) (GPa) | \( b \) (nm) | \( R \) (nm) | \( r_0 \) (nm) | \( f_s \) | Ref.  |
|----------------|----------------|-------------|-------------|---------------|---------|------|
| Russell et al. | 83             | 0.248       | 0.6         | 2500b         | 2.5b    | 2.5  |
| Nagai group    | 49             | 0.248       | 0.938       | 2500b         | 2.5b    | 2.5  |
| Seidman group  | 77             | 0.25        | 0.6         | 2500b         | 2.5b    | 2.5  |
| Fukuya et al.  | 49             | 2.5         | 0.6–0.8     | 2500b         | 2.5b    | 2.5  |
| Schmauder group| 83–86          | 0.248       | 0.6         | 2500b         | 2.5b    | 2.5  |
| Our group      | 83             | 0.248       | 0.6         | 2500b         | 2.5b    | 2.5  |
Figure 2. Hardness dependence on aging time for model steels.

Figure 3. The hardness change ($\Delta H_{\text{v,esti.}}$), estimated using Russell-Brown model, as a function of measured hardness change ($\Delta H_{\text{v,meas.}}$) for model steels.

4. Conclusion

Based on microstructural evolution of Cu precipitation behavior and changes of mechanical property during long-term thermal aging, the following conclusions are drawn:

The Cu-rich precipitates possess a core-shell structure, as determined by APT construction analysis. The depletion of Cu and the enrichment of Fe change monotonically toward the precipitate/matrix interface, whereas the concentrations of Mn, Ni, Mo, Si and C exhibit diffuse enrichment near the interface.

In the underaged condition, the size and number density of nanoscale Cu-rich precipitates increase with aging time, leading to precipitation strengthening and hardening embrittlement effects. Using the
Russell-Brown model, we estimated the hardening due to Cu-rich precipitates in the matrix. It was observed that the measured hardness and the estimated changes are in good agreement.

Acknowledgments

This work is supported by the National Key Research and Development Program of China under grants 2016YFB0700401, by the National Natural Science Foundation of China under grants 11675123 and 11775255. The authors would like to thank Prof. Wenqing Liu of Shanghai University for his supports in APT results discussion.

References

[1] W. J. Phythian, C.A. English, Microstructural evolution in reactor pressure vessel steels, J. Nucl. Mater. 205 (1993) 162 - 177.
[2] M. K. Miller, K.F. Russell, Embrittlement of RPV steels: An atom probe tomography perspective, J. Nucl. Mater. 371 (2007) 145 - 160.
[3] Y. Nagai, Z. Tang, M. Hassegawa, T. Kanai, M. Saneyasu, Irradiation-induced Cu aggregations in Fe: An origin of embrittlement of reactor pressure vessel steels, Phys. Rev. B, 63(2001) 134110 - 4.
[4] M. K. Miller, B.D. Wirth, G.R. Odette, Precipitation in neutron-irradiated Fe-Cu and Fe-Cu-Mn model alloys: a comparison of APT and SANS data, Mat. Sci. Eng. A, 353 (2003) 133 - 139.
[5] P. J. Othen, M.L. Jenkins, G.D.W. Smith, W.J. Phythian, Transmission electron microscope investigations of the structure of copper precipitates in thermally-aged Fe-Cu and Fe-Cu-Ni, Phil. Mag. Lett., 64 (1991) 383 - 391.
[6] L. W. Cao, S. J. Wu, B. Liu, On the Cu precipitation behavior in thermo-mechanically embrittlement processed low copper reactor pressure vessel model steel, Mater. Design, 47 (2013) 551 - 556.
[7] P. D. Styman, J.M. Hyde, K. Wilford, A. Morley, G.D.W. Smith, Precipitation in long term thermally aged high copper, high nickel model RPV steel welds, Prog. Nucl. Energ. 57 (2012) 86 - 92.
[8] P. Pareige, K. F. Russell, R.E. Stoller, M.K. Miller, Influence of long-term thermal aging on the microstructural evolution of nuclear reactor pressure vessel materials: an atom probe study, J. Nucl. Mater., 250 (1997) 176 - 183.
[9] M. D. Mulholland, D. N. Seidman, Nanoscale co-precipitation and mechanical properties of a high-strength low-carbon steel, Acta Mater. 59(2011) 1881 - 1897.
[10] J. D. Farren, A. N. Hunter, J.N. Dupont, D.N. Seidman, C.V. Robino, E. Kozesnich, Microstructural evolution and mechanical properties of fusion welds in an iron-copper-based multicomponent steel, Metall. Mater. Trans. A, 43 (2012) 4155 - 4170.
[11] Z. L. Chen, X. B. Liu, Y. C. Wu, R. S. Wang, F. Xue, P. Huang, C.L. Xu, W.J. Qian, Positron Annihilation and TEM Characterization of Cu-Enriched Clusters in the Ferritic Steels Containing Copper, Defect Diffus. Forum, 373 (2017) 150 - 154.
[12] M. K. Miller, Atom probe tomography, Kluwer Academic/Plenum, New York, 2000.
[13] M. K. Miller, K. F. Russell, P. Pareige, M. J. Starink, R.C. Thomson, Low temperature copper solubilities in Fe-Cu-Ni, Mat. Sci. Eng. A, 250(1998) 49 - 54.
[14] J. M. Hyde, G. Sha, E.A. Marquis, A. Morley, K.B. Wilford, T. J. Williams, A comparison of the structure of solute clusters formed during thermal ageing and irradiation, Ultramicroscopy, 111 (2011) 664 - 671.
[15] K. G. Russell, L. M. Brown, A dispersion strengthening model based on differing elastic moduli applied to the iron-copper system, Acta Metall., 20 (1972) 969 - 974.
[16] J. T. Buswell, W.J. Phythian, R. J. McElroy, S. Dumbill, P.H.N. Ray, J. Mace, R.N. Sinclair, Irradiation-induced microstructural changes, and hardening mechanisms, in model PWR reactor pressure vessel steels, J. Nucl. Mater., 225 (1995) 196 - 214.
[17] A. Kuramoto, T. Toyama, Y. Nagai, K. Inoue, Y. Nozawa, M. Hasegawa, M. Valo,
Microstructural changes in a Russian-type reactor weld material after neutron irradiation, post-irradiation annealing and re-irradiation studied by atom probe tomography and positron annihilation spectroscopy, Acta Mater., 61 (2013) 5236 - 5246.

[18] T. Takeuchi, A. Kuramoto, J. Kameda, T. Toyama, Y. Nagai, M. Hasegawa, T. Ohkubo, T. Yoshiie, Y. Nishiyama, K. Ohizawa, Effects of chemical composition and dose on microstructure evolution and hardening of neutron-irradiated reactor pressure vessel steels, J. Nucl. Mater., 402 (2010) 93 - 101.

[19] H. H. Wang, X. H. Yu, D. Isheim, D.N. Seidman, S.S. Babu, High strength weld metal design through nanoscale copper precipitation, Mater. Design, 50 (2013) 962 - 967.

[20] K. Fukuya, K. Ohno, H. Nakata, S. Dumbill, J.M. Hyde, Microstructural evolution in medium copper low alloy steels irradiated in a pressurized water reactor and a materials test reactor, J. Nucl. Mater., 312 (2003) 163 - 173.

[21] S. Schmauder, P. Binkele, Atomistic computer simulation of the formation of Cu-precipitates in steels, Comp. Mater. Sci. 24 (2002) 42 - 53.

[22] S. Nedelcu, P. Kizler, S. Schmauder, N. Moldovan, Atomic scale modelling of edge dislocation movement in the α-Fe-Cu system, Modelling Simul. Mater. Sci. Eng., 8 (2000) 181 - 191.