Microstructural Evolution of Thermally Aged RPV Model Alloys by 3D Atom Probe

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ABSTRACT

The accurate understanding and prediction of neutron irradiation embrittlement of reactor pressure vessel (RPV) steels is a very important issue to ensure the safety and continued operation of nuclear power plant. High-density nano-scale Cu-rich precipitates, which are typically alloyed with Si, Ni or Mn, have been considered as the main contributor to the hardening embrittlement of RPV steels. In our work, four series of RPV model alloys, Fe-Cu, Fe-Cu-Si, Fe-Cu-Ni and Fe-Cu-Ni-Mn, are thermally aged at 450°C for up to 380 hours. The effects of Si, Ni and Mn on hardening are discussed. Furthermore, Atom Probe Tomography (APT) was used to study Cu-rich precipitates.

1. Introduction

Reactor pressure vessel (RPV) materials are exposed to a high energy neutron flux which results in irradiation embrittlement (increase in yield strength and brittle-ductile transition temperature, decrease in upper shelf energy and tensile elongation). Since RPV is considered as irreplaceable, these degradations in mechanical properties would definitely limit the lifetime of nuclear power plants. The accurate prediction embrittlement of RPV steels is very important to ensure the safety continued operation of NPPs [1-3]. In accordance with extensive studies, general consensus on embrittlement mechanisms has been identified as follows [4-6]: (1) The formation of Cu-rich precipitates (CRPs); (2) The formation of matrix damage features due to radiation produced point-defect clusters, such as vacancy clusters and /or self-interstitial atom clusters, and solute atoms-point-defect complexes; (3) The segregation of phosphorus atoms at grain boundaries.

The formation of CRPs and matrix damage features are regarded as the major factors that cause embrittlement. The irradiation-enhanced CRPs are clusters of solute atoms, which consist of Ni, Si, Mn and a spatial enrichment of copper atoms. Cu atoms tend to precipitate easily because of their low solubility in iron matrix. Due to their small size and coherency in crystal structure with the matrix, it is difficult to observe these clusters directly even using High-Resolution Transmission Electron Microscope (HRTEM). But thanks to the advances in Three-Dimensional Atom Probe microscopy (3D-AP), a tool to map out alloying elements in three-dimensional space with near atomic resolution, the characterization of detailed morphology of these clusters becomes practical [7-9]. APT shows that the mean diameter of such clusters is typically 2-3 nm. Segregation of Ni, Mn and Si is frequently observed in various RPVs, even in these RPVs that do not contain enough Cu to precipitate into

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clusters. Therefore, it is necessary to identify the effects of solute atoms such as Si, Ni and Mn on the formation of CRPs. Thermal ageing treatment of materials [10,11] only involves thermal dynamic mechanism, compared with a complicate process of neutron irradiation, which is the method we used in this study work.

This study is aimed to better understand the formation of Cu-rich precipitates. For the first stage of our research, we will focus on characterize CRPs formed in thermally aged RPV model alloys using 3D-AP. Irradiation experiment will be performed in the future study.

2. Experimental

2.1. Specimens

The model alloys used in this study were Fe-0.5 wt.% Cu, Fe-0.5 wt.% Cu-0.2 wt.% Si, Fe-0.5 wt.% Cu-0.8 wt.% Ni, and Fe-0.5 wt.% Cu-0.8 wt.% Ni-1.4 wt.% Mn. These alloys were heat-treated at 900°C for 30 min., followed by water quenching. These model alloys were annealed up to about 380 hours at temperature 450±20°C in vacuum (below 1×10^{-3} Pa).

2.2. Vickers Hardness Test

Vickers hardness test was carried out in this study. The test surface of samples is polished both mechanically and chemically before a 1 kgf load is applied for 15 seconds. A hardness value is averaged by 16 indentations. All the procedures are consistent with the JIS Z2244 standard.

2.3. Atom Probe Tomography

Samples that were annealed for different period of time were analyzed by CAMECA Local Electrode Atom Probe (LEAP) 3000XSi equipped at Central Research Institute of Electric Power Industry (CRIEPI) in Japan [9]. It is an efficient technique able to reconstruct the atomic-scale microstructure of a material in three dimensions with a very high mass resolution. The LEAP analysis is performed at voltage pulse mode, with pulse repetition rate of 200 kHz, pulse fraction of 15% and specimen temperature of 40K. The CRPs were sorted out from the matrix phase using Recursive Search Algorithm that tells matrix atoms and precipitate atoms apart based on their local environment. The parameter used to identify CRPs is maximum separation distance, d_{max} (0.40 nm) and minimum number of atoms, N_{min} (20 atoms). Besides, grain boundaries and dislocations are carefully excluded.

3. Results and Discussion

3.1. Effect of Solute Atoms on Hardening

Previous studies have revealed that high number density of nano-scale CRPs acts as obstacles to dislocation movement, which is the main cause of material hardening and embrittlement [12,13]. Here, in our work, at the result of the formation of CRPs, hardening is clearly observed in these RPV model alloys annealed at temperature 450°C. Effect of different solute atoms on hardening in these model alloys is explained. Fig. 1 shows the hardness change of these model alloys as a function of thermal ageing time. Addition of Mn to Fe-Cu-Ni alloy accelerates the hardening process drastically with shorter time to peak hardening. But the peak hardness change in Fe-Cu-Ni-Mn is lower than that in Fe-Cu-Ni. Addition of Si has basically no effect on hardening in terms of incubation time, hardening rate, time to peak hardening and peak hardness with comparison of hardness change results of Fe-Cu-Si and Fe-Cu. Effect of Ni on hardening seems not clear. The hardening of Fe-Cu-Ni tends to be a little bit slower than Fe-Cu after 100 ageing hours.
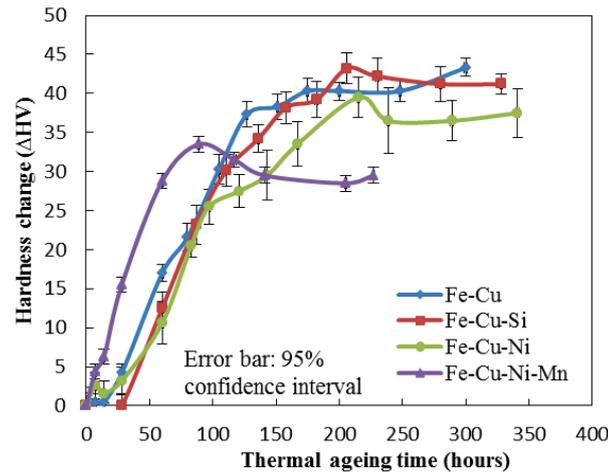
Fig. 1. Hardness change as a function of thermal ageing time

3.2. LEAP observation and Analysis

The LEAP analysis results of model alloys Fe-Cu-Ni-Mn which are thermally aged 14 hours and 62 hours, respectively, are illustrated in Fig. 2. The orange dots are Cu atoms. As can be seen clearly in the atom map, Cu atoms form precipitates. The cluster number density and cluster volume fraction in Fe-Cu-Ni-Mn thermally aged 14 hours, are 1.07×10^{23} m^{-3} and 4.14×10^{-4}, respectively. The cluster number density and cluster volume fraction in Fe-Cu-Ni-Mn thermally aged 62 hours, are 1.31×10^{23} m^{-3} and 1.75×10^{-3} respectively. Fig. 2 and Fig. 3 show cluster radius distribution in Fe-Cu-Ni-Mn aged 14 hours and 62 hours, respectively. Cluster radius 0.8nm has a high proportion when the alloy is aged for 14 hours, while cluster radius 1.6nm has a high percentage when the alloy is aged for 62 hours. In addition, there are still small size clusters formed in alloy aged 62 hours. It can be found it is a continuous formation process of clusters. Table 1 shows cluster composition. Cu, Ni and Mn atoms form clusters and Cu concentration increases with thermal ageing time increases.
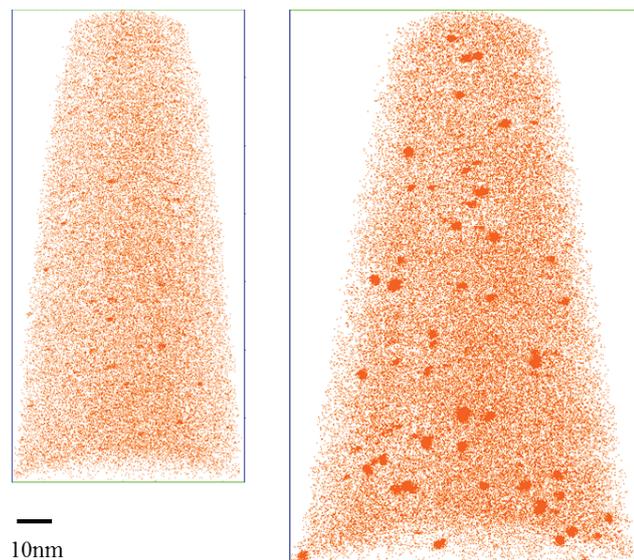

Fig. 2. Atom maps of Cu in Fe-Cu-Ni-Mn thermally aged 14 hours and 62 hours, respectively

It can be concluded that the cluster diameter, number density and volume faction increase as the thermal ageing time increases (before reaching hardness peak), which leads to the increasing hardness, as shown in Fig. 1. The characteristics of these clusters are just consistent with the general

consensus on copper-containing RPV materials.
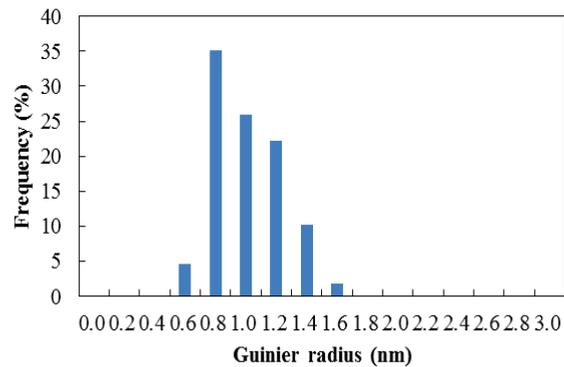
Fig. 3. Cluster radius size distribution in Fe-Cu-Ni-Mn thermally aged 14 hours
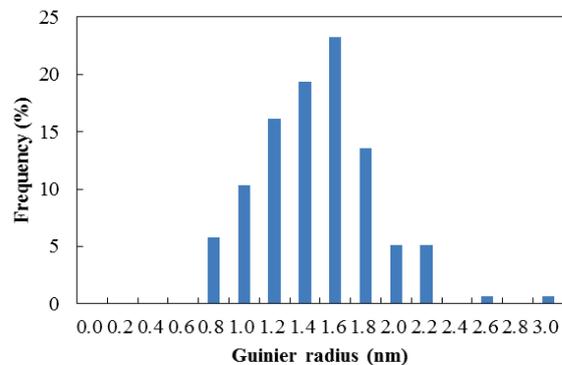
Fig. 4. Cluster radius size distribution in Fe-Cu-Ni-Mn thermally aged 62 hours

Table 1 Composition of clusters in Fe-Cu-Ni-Mn

	concentration in cluster (at.%)		
	Cu	Ni	Mn
14h aged	37	9	6
62h aged	43	6	5

4. Conclusion

The formation of CRPs results in hardness change in RPV model alloys after thermal ageing at 450ºC. The addition of Mn greatly accelerates hardening of the alloys. The formation of CRPs is observed by 3D-AP. The clusters are mainly formed by Cu atoms. A continuous formation process of clusters during thermal ageing is found. The cluster diameter, number density and volume faction increase as the thermal ageing time increases (before reaching hardness peak). More atom probe observation will be done. Effects of solute atoms on formation of clusters will be published in the near future.

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