The distribution of nano size clusters in deformed Fe-Cu alloy by small angle neutron scattering

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ABSTRACT

The behavior of copper precipitations in the Fe-Cu alloy which is used as a simulation of radiation damage was investigated using a small angle neutron scattering (SANS). The alloy was made through a melting with pure Fe and pure Cu. Initially, the alloy is 10% cold rolled, and isothermally aged at 753 K for 20, 200 and 1800 min. The CRPs sizes, volume fractions and A-ratio of Fe-Cu alloy with aging time are obtained from the SANS data analysis. The sizes of Cu precipitates nearly constant up to aging time of 200 min and fast increased, but the volume fraction of Cu precipitates linearly increased with aging time.

Keywords: Fe-Cu alloy, small angle neutron scattering, Copper precipitates, A-ratio, volume distribution,

1 INTRODUCTION

The reactor pressure vessel (RPV) steel of nuclear power plant is degraded and embrittled by the neutron irradiation. The main cause of these degradation is known as the copper precipitates, which is enhanced by the neutron irradiation of RPV steel. Fe-Cu alloys are commonly used for a simulation of radiation damage of RPV steel because a neutron irradiation enhances the copper precipitates which is known as the primary reason of a RPV embrittlement. An investigation of thermal aged Fe-Cu model alloy has been a common and adequate alloy for a study of this purpose. For this purpose the selected annealing temperature is sufficiently low (753K) compare with the solubility limit (e.g. 1023K for Fe-1wt%Cu)[1,2]. The precipitation of copper from super saturated Fe-Cu alloys has been investigated extensively, both experimentally and teoretically. Indeed, copper induces: (i) grain refinement by lowering the α -γ transformation temperature and (ii) precipitation hardening after rapid cooling and tempering [3]. When these clusters which have a metastable bcc structure coherent with an iron matrix reach a critical size (order of 4 to 6 nm), then the coherent strain energy become to large and change to an incoherent fcc structure via a 9R structure at the aging temperature of 823K[4]. The sizes of copper precipitates is known to be a few nanometers. In order to characterize the defects several methods were used, i.e. transmission electron microscopy (TEM)[5], positron annihilation spectroscopy (PAS)[6], Mossbauer spectroscopy(MB)[7], and small angle neutron scattering (SANS)[8]. Among these, the SANS technique is known as the best technique to characterize the nano sized inhomogeneities in bulk samples, which gives the role of copper precipitates and the influence of thermomechanical processing on on the defect-induced precipitation, responsible for radiation hardening. The precipitation of copper from supersaturated Fe-Cu alloys has been investigated extensively, both experimentally[9, 10] and theoretically[11, 12]. Although the copper precipitatation kinetics of Fe-Cu alloy has been investigated in earlier SANS[13, 14] and small angle x-ray scattering (SAXS) experiments[15, 16], limitated information is available on the precipitation behavior before peak aging.

The investigation is focused on the behavior of copper precipitates with aging time in the 10% cold rolled Fe-Cu alloy. The objective is to identify the aging time dependence of precipitates evolution such as volume fraction and size distribution.

2 EXPERIMENTAL

The starting material for this study was a binary Fe-1.0%Cu alloy. The alloy was made through a melting with pure Fe and pure Cu. After the samples were solution-treated at 1123 K for 5 hrs in a vacuum condition, they were water-quenched. Initially, the alloy is 10% cold rolled, and isothermally aged at 753 K for 20, 200 and 1800 min. The SANS experiments were performed at the the HANARO reactor in the KAERI [17]. The experimental set-ups included a wavelength of 6 Å, and the sample to detector distance was 2.5 m and 11 mm. The scattering vector ranged between between 0.012 $Å^{-1}$ and 0.2 $Å^{-1}$. In order to separate the magnetic and nuclear scattering intensities, the sample was placed in a saturating magnetic field of 1.1 T perpendicular to the neutron beam direction. SANS data was obtained as a 2-dimentional array. The data perpendicular and parallel to the magnetic field were collected separately with the angular width of 20 degree from the 2-dimentional SANS data in order to divide the magnetic and nuclear scattering cross section.

3. RESULT AND DISCUSSION

By applying a transverse magnetic field of $\mu_0 H = 1.1T$, the magnetization of the ferromagnetic Fe-Cu alloy containing nonmagnetic Cu clusters (fcc copper is weakly diamagnetic) is nearly saturated with the spins in the ferromagnetic matrix aligned along the magnetic field (x-axis) perpendicular to the incident neutron beam (z-axis). Fig.1 shows the two-dimensional SANS patterns obtained for Fe-Cu alloy with 10% prestrain before and after isothermal aging for 1800 min at 753K. As shown in Fig. 1(a), few anisotropic scattering pattern is observed before aging with a dominant scattering contribution perpendicular to the applied magnetic field. This anisotropy of the scattered intensity becomes more pronounced with increasing aging time, increased with increasing aging time. As shown in Fig. 1(b), a clear anisotropic scattering pattern has formed after 1800 min aging at 753K. From the two-dimensional patterns the measured differential cross section $\left(\frac{d\Sigma(Q)}{d\Omega}\right)_{meas}$ is the sum of the differential cross section of the nuclear and magnetic scattering components,

$$\left(\frac{d\Sigma(Q)}{d\Omega}\right)_{meas} = \left(\frac{d\Sigma(Q)}{d\Omega}\right)_{nuc} + \left(\frac{d\Sigma(Q)}{d\Omega}\right)_{mag} \sin^2\alpha \qquad (1)$$

With $\left(\frac{d\Sigma(Q)}{d\Omega}\right)(\alpha = 0)_{meas} = \left(\frac{d\Sigma(Q)}{d\Omega}\right)_{nuc}$

$$\left(\frac{d\Sigma(Q)}{d\Omega}\right)(\alpha = \pi/2)_{meas} = \left(\frac{d\Sigma(Q)}{d\Omega}\right)_{nuc} + \left(\frac{d\Sigma(Q)}{d\Omega}\right)_{mag} \qquad (2)$$

Where α is the angle between applied magnetic field H (orientation of the magnetization of the specimen M) and the scattering vector Q. When the scattering vector is parallel to the applied magnetic field (α =0), and perpendicular(=$\pi/\alpha 2$). Since the complete two-dimensional scattering pattern is measured, the magnetic and nuclear scattering components can be obtained simultaneously from a fit of the full scattering pattering with Eq. (1). For the two-phase approach (homogeneous matrix and copper precipitates) and under the condition of magnetic saturation, the nuclear and magnetic SANS contribution can be described by Eq (2). The magnetic scattering originates from a difference in magnetization and nuclear scattering from a difference chemical composition (copper precipitates). By applying a strong magnetic field to the specimen, these two components could be separated [18, 19] .

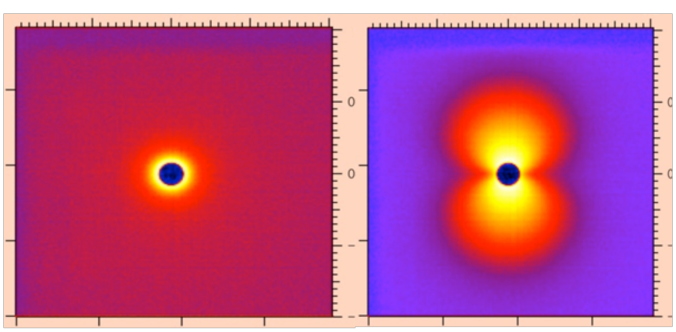

Fig. 1. Small angle neutron scattering patterns of Fe-Cu alloy with 10% prestrain (a) before and (b) after 1800 min of aging at 753K. A magnetic field of 1.1 T was applied horizontally.

Fig. 2 shows the Q dependence of the nuclear and magnetic scattering components for the Fe-Cu alloy with 10% prestrain with different aging time at 753K. The SANS signal at Fig. 2 roughly follows a power-law behavior with a constant background for both the nuclear and magnetic contributions. The scattering intensities by nuclear component in the sample with aging time of 20 min. are similar to those for as-annealed sample. The substantial difference of the scattering intensity created from the scattering vector of 0.02 Å. The additional contribution of the nuclear and magnetic scattering caused by aging has roughly the same Q dependence in the range 0.02<Q<0.2 Å^{-1} , reflecting the formation of nanoscale copper precipitation. The data indicate that especially the magnetic scattering is strongly enhanced by aging. The magnetic scattering intensity in the 1800 min aged sample begins from the scattering vector of 0.01, and slowly decrease up to 0.06 and sharply decreased, which means large copper precipitates are created at higher temperature. This complementary nuclear contribution, observed for the long time aged sample, reflects additional scattering from copper precipitation at more extended objects (dislocations or interfaces).

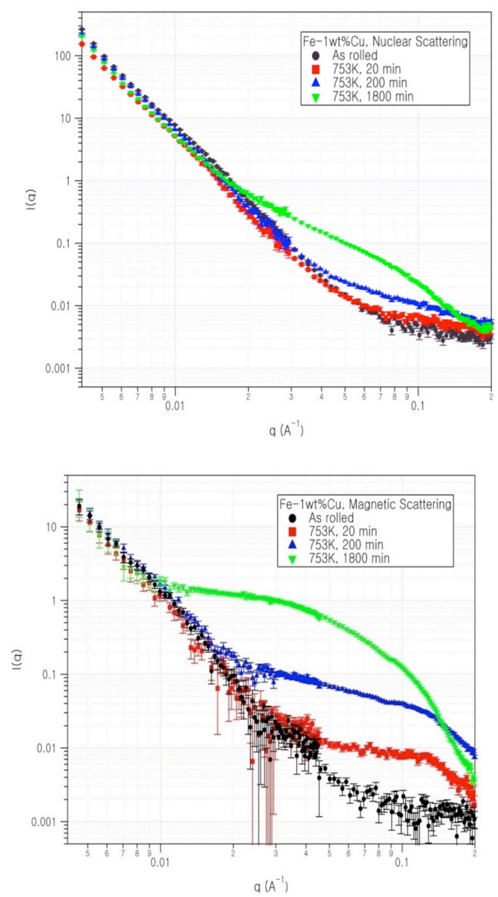

Fig. 2. Nuclear and magnetic SANS components as a function of wave-vector transfer Q for the Fe-Cu alloy with

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10% pre-strained measured at room temperature with different aging time at 753K.

For a dilute system of particle of particles embedded in a homogeneous matrix, the macroscopic differential scattering cross section ($^{d\Sigma}/_{d\Omega}$) characterizes the scattering power by [20]

$$\left(\frac{d\Sigma}{d\Omega}\right) = (\Delta\rho)^2 \int D_N(R)V(R)^2|F(Q,R)|^2 dR \qquad (3)$$

Where $\Delta\rho=\rho_p - \rho_m$ is the difference in the scattering length density of the precipitate ρ_p and the matrix ρ_m. The strength of the magnetic and nuclear scattering is directly proportional to the magnetic and nuclear contrast $(\Delta\rho)^2$. For spherical precipitates with a radius R, the particle volume is $V(R) = 4\pi R^3/3$ and the form factor is $F(Q,R) = 3[\sin(QR) - (QR)\cos(QR)]/(QR)^3$. $D_N(R)$ is the size distribution function for the number of precipitates per unit volume. This number distribution $D_N(R)$ is directly related to the volume distribution $D_V(R) = V(R)\,D_N(R)$. Integration of $D_N(R)$ gives the number of precipitates per unit volume N_p while integration $D_v(R)$ results in the volume phase fraction of the precipitates f_v. In order to relate the scattering curves of the SANS experiments to the size distribution of the precipitates, some model assumptions have to be made. From previous TEM observations, we know that the spherical Cu precipitates approximately show a log-normal size distribution $D_N(R)$ which is described by

$$D_N(R) = \frac{N_p}{R\sigma\sqrt{2\pi}} \exp\left\{-\frac{[\ln(R)-\ln(R_m)]^2}{2\sigma^2}\right\}, \qquad (4)$$

Where N_p is the number density of precipitates, R_m is the median radius, and σ the standard deviation.

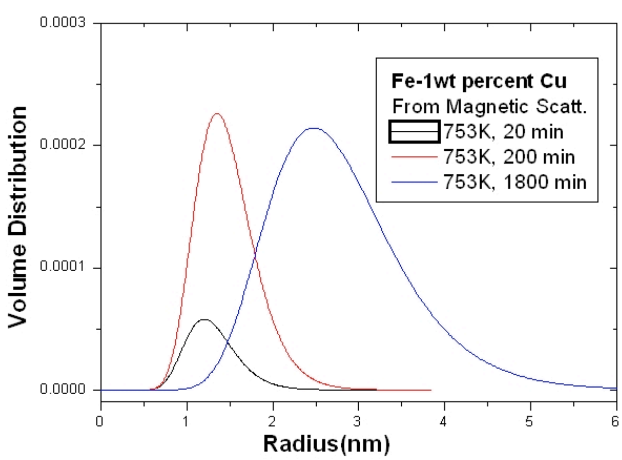

Fig. 3. Volume distribution of spherical Cu prcipitates in the 10% cold rolled Fe-Cu alloy with aging time of 20, 200 and 1800 min aging at 753K.

Fig. 3 shows the log-normal volume distribution D_V of spherical copper precipitates with precipitate radius R as a function of the aging time at a temperature 753K for the Fe-Cu alloy. The particle size distributions were obtained by a fit of the magnetic SANS component with a log-normal distribution using the SASFIT [21]. For relatively short aging time less than 200 min, the peak height of the volume distribution increases with the aging time without changing the peak position, indicating that nucleation is the dominant process in the early aging stage. For the aging time of 1800 min, the volume distribution of the Cu precipitates broadens, the peak height slightly reduces and the peak position increases with aging time, suggesting that the growth of precipitates is the dominant process. In the case of early aging stage, narrow volume distributions compared to long aging time reflect the relatively homogeneous precipitates distributions.

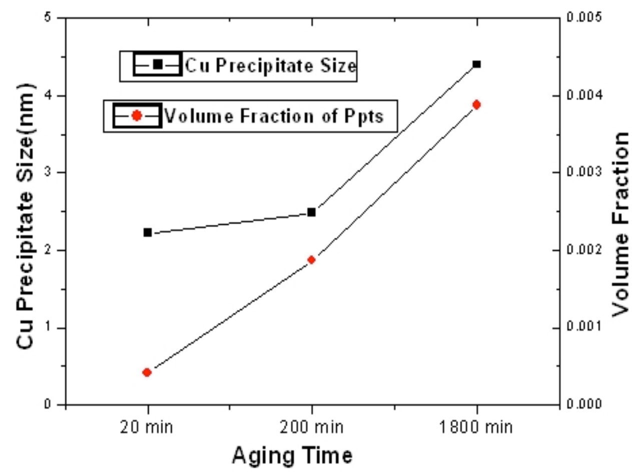

Fig. 4. Time evolution of the median radius and the volume fraction of Cu precipitates in the Fe-Cu alloy during aging at 753K.

Fig. 4 shows the sizes and volume fraction of Cu precipitates as a function of aging time. The sizes of Cu precipitates nearly constant up to aging time of 200 min and fast increased, but the volume fraction of copper precipitates linearly increased with aging time.

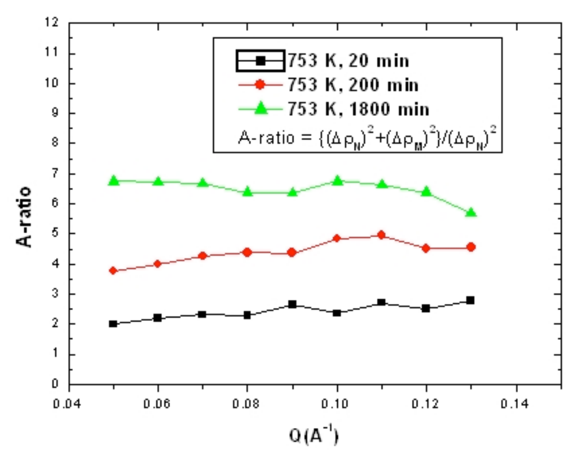

Fig. 5. Dependence of the A-ratio on the scattering vector Q with aging time.

Fig. 5 shows the dependence of the A-ratio on the scattering vector Q with aging time. The ratio between the nuclear+magnetic and nuclear scattering, the so-called A-ratio is a function of Q which does not provide information about the nature of the scattering inhomogenities. However, information can be gained by transformation of dependence of A on the scattering vector Q into a dependence of A on the size R of the inhomogenities. This can be done using the indirect transformation method [22]. The A-ratio estimated from absolute scattering intensity of the more than 5 hours aged samples scattered region are represented about 7~8. An A-ratio >3 was reported for irradiated RPV steel, containing over 0.1 wt% Cu[23, 24]. The A-ratio of Cu precipitates having bcc structure in an iron matrix is estimated 7.0[25]. The aging curve of A-ratio for the aging time are different each other, and the 1800 min aged exhibits the highest A value at all scattering vector Q. The aging response of A originates from a full decoration of dislocation and interfaces by mobile atoms before the less mobile Cu atom have had the enhance to precipitates at these site. As the magnetic scattering from the copper precipitates is dominant $[(\Delta\rho_{MAG})^2 > 2\pi^2(\Delta\rho_{NUC})^2]$, we have used the magnetic component to estimate the phase fraction. The size of Cu precipitates for the two sample aging time 20 and 200 min are close to each other but the A value for these two sample shows the difference about factor of two.

4 CONCLUSION

SANS results were analyzed in the 10% cold rolled Fe-Cu alloy with aging time, volume fractions, size distribution, and A-ratio were obtained. For relatively short aging time less than 200 min, the peak height of the volume distribution increases with the aging time without changing the peak position, indicating that nucleation is the dominant process in the early aging stage. The SANS signal of Fe-Cu alloy indicate that the precipitation of copper in the form of spherical nanoscale precipitates and decoration of dislocations and/or interfaces. Both contributions were monitored independently as a function of aging time.

REFERENCES

[1] M. Perez, F. Perrard, V. massardier, X. Kleber, A. Deschamps, H. De Monestrol, P. Pareige and G. Covarel, Philosophical Magazine. 85, 2197, 2005.

[2] A. Deschamps, M. Militzer and W.J. Poole: ISIJ International. 41, 196, 2001.

[3] M. Charleux, F. Livet, F. Bley, F. Louchet and Y. Breechet: Philosophical Magazine. A 73, 883, 1996.

[4] R. Monzen, M.L. Jenkins and A.P. Sutton, Philosophical Magazine. A, 80, 711, 2000.

[5] J. Kocik, E. Keilova, J. Cizek and I. Prochazka: J. Nucl. Mater. 303, 52, 2002.

[6] V. Slugen: Nucl. Eng. Des. *235*, 1961, 2005.

[7] V. Sluge, J. Lipka, I. Toth and J. Hasick: NDT&E International 35, 511, 2002.

[8] M. Grosse, A. Gokhman and J. Bohmert: Nucl. Instrum. And Meth. In Phy. Res., B 160, 515, 2000.

[9]U. Dahmen, P. Ferguson, and K.H. Westmacott, Acta Metall. 32, 803, 1984

[10] m.K. Miller, P. Pareige, and M.G. Burke, Mater. Charact. 44, 235, 2000.

[11] J.J. Blackstock and G.J. Ackland, Philos. Mag. A 81, 2187, 2001.

[12] Y. Le Bouar, Acta Mater. 49, 2661, 2001.

[13] K. Osamura, H. Okuda, S. Ochiai, M. Takashima, K. Asano, and M. Furusaka, Mater. Trans. JIM 34, 305, 1993

[14] K. Osamura, H. Okuda, S. Ochiai, M. Takashima, K. Asano, and M. Furusaka, and F. Kurosawa, ISIJ Int. 34, 359, 1994.

[15] A. Deschamps, M. Militzer, and W.J. Poole, ISIJ Int. 41, 196, 2001.

[16] A. Deschamps, M. Militzer, and W.J. Poole, ISIJ Int. 43, 1826, 2003.

[17] B.S. seong, Y.S. Han, C.H. Lee, J.S. Lee, K.P. Hong, K.N. Park and H.J. Kim, Appl. Phys. A, 74, S201, 2002.

[18] [K. Osamura, H. Okuda, M. Takashima, K. Asano, and M. Furusaka, Mater. Trans., JIM 34, 305, 1993.

[19] K. Osamura, H. Okuda, S. Ochida I, M. Takashima, K. Asano, and M. Furusaka, and F. Kurosawa, ISIJ Int. 34, 359, 1994.

[20] [N. H.van Dijk, W.G. Bouwman, S.E. Offerman, M. Th. Rekveldt, J. Sietsma, S. van der Zwaag, A. Bodin, and R.K. Heenan, Metall. Mater. Trans. A33, 1833, 2002.

[21] J. Kohlbrecher and I. Bressler, SASFIT: software package for fitting small-angle scattering curves, http://kur.web.psi.ch/sans1/SANSSoft/sasfit.html.

[22] O. Glatter, J. Appl. Cryst. 10, 415, 1977

[23] A. Ulbricht, J. Bohmert, M. Grosse and P. Strunz: Physica B Vol. 276-278, 936, 2000.

[24] A. Ulbricht, J. Bohmert: Physica B, 350, e483, 2004.

[25] M. Grosse, A. Gokhman, J. Bohmert, Nucl. Inst. Method in ZPhys. Res. B 160, 515, 2000.