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SANS study of phase decomposition in Fe-Cu alloy added by Ni and Mn

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abstract

Small-angle neutron scattering (SANS) measurements were mainly carried out in order to investigate the structure change during early stage of phase decomposition in Fe-Cu-Ni-Mn quaternary alloy. The fact that the nuclear Guinier radius becomes larger than the magnetic one beyond about 2 nm is attributed to the formation of segregated layer enriched by Ni and Mn around fcc copper-rich precipitate. The calculated SANS intensities have been well fitted simultaneously with both experimental data of magnetic and nuclear components. Addition of Ni and Mn in Fe-Cu binary alloy was suggested to promote the precipitation reaction of ϵ -Cu phase.

Introduction

The Fe-Cu alloy is known to be an age-hardenable material. From the supersaturated solid solution with bcc structure, coherent bcc copper-rich clusters are decomposed, which transform to fcc ϵ -copper precipitates upon reaching a critical size. Precipitates have spherical shape at the early stage, but their shape changes to rod due to the strain energy term. In order to improve the properties of this alloy, an addition of third elements has been investigated till now, when it is used as the pressure vessel of a pressurized water reactor¹⁾ and the line pipe steel for low temperature service²⁾. A characteristic behavior has been recognized to appear in microstructure evolution by addition of Ni and/or other third elements in age-hardenable Fe-Cu alloys. However its mechanism is not yet fully understood. In order to elucidate the effect of additional elements, especially Ni and Mn on the kinetics and structure change during phase decomposition, SANS measurements have been mainly carried out in the present study.

Experimental Procedure

The chemical composition of Fe-Cu alloy used here was 1.41 at%Cu, 0.27at% Ni and 0.25at% Mn. The specimen with dimensions of 2.7x10x30 mm³ was sealed in evacuated silica ampoule and solution-treated at 1123 K for 10.8 ks. The ampoule was quenched and broken in ice water. It was again sealed in the ampoule and then isothermally aged at 773 and 823 K. SANS measurements were performed using the KENS-SAN facilities of National Laboratory for High Energy Physics, KEK. The details have been reported elsewhere³⁾. Scattering intensities were measured by the two-dimensional position sensitive detector under magnetic field of 0.98 T.

Experimental Results and Discussion

By applying a strong magnetic field to a ferromagnetic specimen containing paramagnetic particles, the magnetization is saturated, where all spins are aligned in one direction perpendicular to the incident neutron beam. Two dimensional SANS cross section (intensity) is shown in Fig. 1. As two-dimensional scattering data can be obtained at once, it is easy to derive both magnetic and nuclear scattering components, $(\frac{d\Sigma}{d\Omega})_{NUC}$ and $(\frac{d\Sigma}{d\Omega})_{MAG}$. Figure 2 shows the Q-dependence of two components for the specimen aged at 773 K for 18 ks. It is found that the magnetic scattering intensity is larger than the nuclear one.

Fig. 1 Two-dimensional contour map of SANS intensity for the specimen aged at 823 K for 0.18 ks (a) and 1.8 ks (b).

Guinier radius is estimated from the Q-dependence of SANS intensity, which is an average value of particle radius. Figure 3 shows the aging time dependence of Guinier radius for the specimens aged isothermally at 773 and 823 K. Both values of Guinier radius determined from magnetic and nuclear scattering intensities are different each other, especially the difference became larger for the longer aging time. This fact approves that the magnetic domain size contributing to small-angle scattering are smaller than the dimension of chemical cluster. As seen in Fig. 3, the growth rate of particle size was found to be much enhanced in the present alloy added by Ni and Mn.

Fig. 2 Change of magnetic and nuclear scattering components of SANS intensity as a function of scattering vector for the specimen aged at 773 K for 18 ks. The solid and dotted curves are the calculated results mentioned in the text.

As shown in Fig. 3, $R_{G,NUC}$ is always larger than $R_{G,MAG}$, when the radius exceeds about 2.1 nm. In the Fe-Cu binary system, however, both radii were essentially the same each other as reported in our recent paper³⁾. Therefore this size difference is caused from the addition of thirds elements, Ni and Mn, which are remarkable to be magnetic element. The magnetic scattering is very sensitive on the spatial configuration of spins, because it changes easily due to low energy excitation. From the preliminary result of AP-FIM study, Cu rich precipitates are surrounded by a segregated layer,

where Cu is depleted and third elements of Al, Ni and Mn are enriched, approximately 2 times of Ni, 10 times of Mn and 15 times of Al comparing with the average values in the matrix. On the other hand, the chemical composition in the core was found to be almost 100%Cu. The SANS data of Kampmann and Wagner⁴⁾ suggested that all precipitates larger than 1 nm were pure copper. Such an interfacial segregation has been reported in the irradiated A533B steel, where considerable enrichments of Ni and Mn were measured within 2 nm of the Cu-Mn precipitates/ferrite interface by means of AP-FIM⁵⁾.

Fig. 3 Aging time dependence of Guinier radius for the specimens during isothermal aging at 773 and 823 K, together with the data for Fe-1.17at%Cu alloy³⁾

Fig. 4 Schematic illustration of three phase model for Cu rich clusters in the quaternary Fe-Cu alloy.

In order to explain the experimental facts, we propose a three phase model as shown in Fig. 4. As the matrix consists of almost pure Fe and is in the ferromagnetic state at room temperature, the magnetic scattering length, p_m of the matrix is approximately equal to p_{Fe} . When the core of precipitates consists of pure copper and is paramagnetic, the magnetic scattering length is zero, i.e., $p_p = 0$. Thus the relative magnetic scattering length density of the core (1) is given by the equation, $\Delta\rho_{p,1} = N_m p_{Fe}$, where N_m is the atomic number density of the matrix. At the segregated layer (2), there exist typically three magnetic elements of Fe, Ni and Mn. When each concentration is given as $x_{Fe,2}$, $x_{Ni,2}$ and $x_{Mn,2}$, respectively, the relative scattering length density of the segregated layer is expressed by the equation, $\Delta\rho_{p,2} = N_m p_{Fe} - N_2(x_{Fe,2}p_{Fe} + x_{Ni,2}p_{Ni} + x_{Mn,2}p_{Mn})$, where N_2 is the atomic number density of the segregated layer. The exact value of chemical composition, however, is difficult to estimate. For the purpose of computer simulation, an adjustable parameter X_{MAG} is introduced as defined by the equation, $\Delta\rho_{p,2} = X_{MAG}\Delta\rho_{p,1}$. Nuclear scattering components are driven in the same manner as mentioned above. The relative scattering length density of the core is given by the equation, $\Delta\rho_{b,1} = N_m b_{Fe} - N_1 b_{Cu}$, where N_1 is the atomic number density of the core. As the chemical composition in the segregated layer is not fixed at present, the nuclear scattering length density is expressed by using an adjustable parameter, $\Delta\rho_{b,2} = X_{NUC}\Delta\rho_{b,1}$.

The scattering intensity is theoretically reproduced by using the structure model proposed here. The following informations are needed for numerical calculation. The precipitates are assumed to consist of spherical core surrounded by the segregated layer as shown in Fig. 4. In such a case, the analytical expression of form factor is so complicated, but it is easy to be evaluated numerically by the computer. With respect to the segregated layer, it is assumed to be in ferromagnetic state as

same as in the matrix, that is, X_{MAG} is put to be zero. At least three third elements are enriched, but it is difficult to determine apriori the chemical composition. Therefore, X_{NUC} is changed to fit the calculated result to the experimental data. The size distribution on the outer radius R_2 is proposed to obey the log-normal size distribution function.

The following relation is assumed $\frac{R_2}{R_1} \cong 1.51 - \frac{1}{R_1}$. When the volume fraction, V_f of the precipitated ϵ phase is given from the phase diagram, the number density of precipitates, N_p is determined from the equation,

$$N_p = V_f / \int \frac{4}{3} \pi R^3 F(R) dR. \quad (1)$$

By changing three variables of X_{NUC} , μ_2 and σ_2 , the scattering intensity has been calculated for fitting with experimental data. An example of calculated results is shown in Fig. 2, where experimental data for the specimen aged at 773 K for 18 ks are plotted. The calculated results are well fitted simultaneously with both experimental data of magnetic and nuclear components. A following set of parameters were used; $R_{G,1}=5.5\text{nm}$, $R_{G,2}=6.6\text{nm}$, $\mu_2=3.0\text{nm}$ and $\sigma_2=1.6$.

The present computer simulation suggested that X_{NUC} is 0.72. It has been also made clear that Ni, Mn and Al are enriched in the segregated layer. Among scattering lengths of these elements, there is a relation of $b_{Mn} = -3.70 \ll b_{Al} = 3.45 \ll b_{Cu} = 7.63 < b_{Fe} = 9.51 < b_{Ni} = 10.3$. Therefore small amounts of Al and Mn are very effective to get a reasonable quantity of X_{NUC} . For instance, an enrichment of 10at%Mn corresponds to $X_{NUC}=0.72$. Here the computer simulation has been performed for other aging conditions. We have obtained similar results mentioned here, where qualitative agreements with experimental data have been confirmed.

Conclusion

The structure change during early stage of phase decomposition in Fe-Cu alloy added by Ni and Mn has been investigated by means of SANS technique. The fact that $R_{G,NUC}$ differs from $R_{G,MAG}$ beyond about 2 nm is attributed to the formation of segregated layer enriched by Ni and Mn around the fcc ϵ phase. Based on the present structure model, the SANS intensity has been theoretically reproduced. The calculated results are well fitted simultaneously with both experimental data of magnetic and nuclear components.

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