Small-Angle Neutron Scattering Study of Phase Decomposition in Fe-Cu Binary Alloy

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Small-angle neutron scattering (SANS) measurements were carried out in order to investigate the structure change during early stage of phase decomposition in an Fe-1.17 at% Cu alloy. The integrated intensity first increased and then saturated beyond $2 \cdot 10^4$ s aging at 773 K, while the Guinier radius increased with the time exponent of $1/3$, emphasizing the coarsening process of precipitates. The peak hardness was observed, when the Guinier radius reached 2.8 nm. The intensity ratio of magnetic scattering component to nuclear one has been analyzed in terms of chemical composition and internal structure of precipitates. Its change during aging was concluded to relate that bcc copper-rich clusters decomposed from the supersaturated α Fe phase transform mainly to the ϵ Cu phase.

(Received August 27, 1992)

Keywords: small-angle neutron scattering, iron-copper alloy, copper-rich cluster, 9R phase, ϵ phase, coarsening process

I. Introduction

The precipitation phenomenon in the Fe-Cu alloy was firstly reported by Wasserman and Wincierz⁽¹⁾, where the precipitation of the ϵ -Cu(fcc) phase from the supersaturated α -Fe(bcc) solid solution was measured by means of X-ray diffraction technique. Rickett and Leslie⁽²⁾ observed the shape change of the ϵ -Cu phase from sphere to rod during long-time aging at high temperatures by using the extraction replica technique. Hornbogen and Glenn⁽³⁾ carried out also microstructure observation and made clear that a spherical ϵ -Cu phase precipitates preferentially in the matrix. Based on the classical nucleation theory⁽⁴⁾, the contribution of interfacial energy to the driving force is relatively important in comparison with the elastic strain energy, because the ratio of atomic radius between Fe and Cu is as small as 1.03. Consequently, the precipitates have a spherical shape at the early stage, but the shape changes to rod due to the strain energy term, when they grow beyond a critical size, which was estimated to be about 30 nm diameter. Hornbogen and Glenn⁽³⁾ suggested that the metastable phase which first precipitates is composed of coherent bcc copper-rich clusters, which transform to fcc ϵ -copper precipitates upon reaching a critical size. Its value has been reported by several authors as experimentally 9 nm⁽³⁾ or 5 nm⁽⁵⁾ and theoretically 4 nm⁽⁶⁾. From Mössbauer effect study, Lahiri *et al.*⁽⁷⁾ supported the hypothesis that Cu-rich clusters with bcc structure form

prior to the precipitation of the ϵ -Cu phase.

Hornbogen⁽⁴⁾ claimed that the chemical composition of the ϵ -Cu phase is almost 100% Cu and tried to prove it by the diffraction study. However, the determination has not been succeeded, because the atomic scattering factors of Fe and Cu are nearly the same each other. Early work on the atom probe by Goodman, Brenner and Low⁽⁵⁾⁽⁶⁾ suggested that the particle composition remains nearly constant at about 50 at%Cu in the beginning of aging up to 11 ks at 773 K. Then it increased and approached 100 at%Cu after 430 ks aging. On the other hand, SANS experiment by Lucas and Odette⁽⁸⁾ made clear that the Cu content in the precipitates was much larger than that indicated by the atom probe.

Controversial research subjects in the present alloy have bearings on the chemical composition of coherent bcc clusters, the transformation of bcc cluster to ϵ -phase and the shape change of precipitates due to elastic strain. In order to elucidate the structure change during the early stage of phase decomposition, SANS measurements have been carried out in the present study.

II. Experimental Procedure

The chemical composition of Fe-Cu binary alloy was 1.17 at%Cu with impurities of 0.019C, 0.002Si, 0.01Mn, 0.014S, 0.015Al, 0.01O and 0.005N in units of at%. After forging and hot-rolling, small pieces with the dimensions of $2.7 \times 10 \times 30$ mm were prepared for SANS measurements. The specimen was sealed in evacuated silica ampoule and solution-treated at 1123 K for 10.8 ks in the α primary phase region. The ampoule was quenched and broken in ice water. It was again sealed in the ampoule and then isothermally aged at 773 K. SANS measure-

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ments were performed using the KENS-SAN facilities of the National Laboratory for High Energy Physics, KEK. The details have been reported elsewhere⁽⁹⁾. Scattering intensities were measured by the two-dimensional position sensitive detector in the scattering vector ($|Q| = 4\pi \sin \theta / \lambda$) range from 0.06 to 3 nm⁻¹. In general, the scattering intensity is composed of both magnetic and nuclear components for the ferromagnetic material. In order to separate both contribution, the external magnetic field was applied in the horizontal direction perpendicular to the incident neutron beam. The SANS measurements were carried out at room temperature. By using the same specimen, Vickers hardness was measured.

III. Experimental Results and Discussion

Figure 1 shows the change of two-dimensional scattering intensity as a function of external magnetic field for the Fe-Cu alloy aged at 773 K for 360 ks. Here the

magnetic field was applied parallel to the horizontal axis in the figure. The equi-intensities are depicted by the contour lines around the center. From the preliminary magnetization measurement, the saturation magnetization (M_0) was found to be 2.4×10^{-4} Wb·m/kg at the internal magnetic field ($H_{o,eff}$) of 240 kA/m and more for the present Fe-Cu alloy. Therefore in order to realize the magnetically saturated state, the external magnetic field is required, minimumly above 430 kA/m. As seen in Fig. 1(a), the contour lines are elongated towards the vertical direction and narrowed in the horizontal direction. When the strength of external magnetic field increased, the intensity distribution was more narrowed in the horizontal direction as seen in Fig. 1(a) to (c). However, the scattering intensities did not change, when the external magnetic field exceeded 600 kA/m as seen in Fig. 1(c) and (d). This means that the specimen is magnetically saturated above 430 kA/m as mentioned above. Thus the SANS measurements were carried out hereafter under

Fig. 1 Two-dimensional contour map of SANS intensity under different external magnetic fields for Fe-1.17 at%Cu alloy aged at 773 K for 360 ks.

external magnetic field of 780 kA/m.

Figure 2 shows the change of two-dimensional scattering intensity during isothermal aging at 773 K for Fe-Cu binary alloy. Figure 2(a) corresponds to the data for the as-quenched specimen. The strong intensity around the center is due to the parasitic scattering oozed out from the beam stopper. Otherwise weak scattering spreads over the whole Q -region. After 0.72 ks aging at 773 K (Fig. 2(b)), a diffuse scattering intensity elongated towards the Q_y direction appeared. This asymmetric scattering intensity became clearer with increasing aging time as seen in Fig. 2(c) and (d).

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. The SANS cross section (intensity) is given by the sum of both magnetic and nuclear scattering components as follows:

$$\frac{d\Sigma}{d\Omega} = \left(\frac{d\Sigma}{d\Omega}\right)_{\text{NUC}} + \left(\frac{d\Sigma}{d\Omega}\right)_{\text{MAG}} \sin^2 \alpha, \quad (1)$$

where α is the angle between the magnetization of the specimen and the direction of scattering vector Q . When the scattering intensity in a special direction of $\alpha=0$ or 90° is expressed as $(d\Sigma/d\Omega)_{H//Q}$ or $(d\Sigma/d\Omega)_{H\perp Q}$, respectively, each scattering component is given as follows:

$$\left(\frac{d\Sigma}{d\Omega}\right)_{\text{NUC}} = \left(\frac{d\Sigma}{d\Omega}\right)_{H//Q}, \quad (2)$$

$$\left(\frac{d\Sigma}{d\Omega}\right)_{\text{MAG}} = \left(\frac{d\Sigma}{d\Omega}\right)_{H\perp Q} - \left(\frac{d\Sigma}{d\Omega}\right)_{H//Q}. \quad (3)$$

As we can get experimentally two-dimensional scattering data at once, it is easy to derive both magnetic and nuclear scattering components. Figure 3 shows the Q -dependence of the two components thus driven from the above equations for the specimen aged at 773 K for 36 ks. It is recognized that the Q -dependence is almost the

Fig. 2 Two-dimensional contour map of SANS intensity for Fe-1.17 at%Cu alloys as-quenched (a), aged at 773 K for 0.72 ks (b), 1.8 ks (c), and 3.6 ks (d).

Fig. 3 Change of magnetic and nuclear scattering components of SANS intensity as a function of scattering vector for Fe-1.17 at%Cu alloy aged at 773 K for 36 ks.

same for both components except the difference of absolute value.

As reported by several authors⁽⁴⁾⁽⁵⁾, the Cu-rich clusters are spherical at the early stage of precipitation. Here it is supposed that N_p spherical clusters per unit volume distribute randomly in the matrix. Then the nuclear scattering intensity is given by the equation:

$$\left(\frac{d\Sigma}{d\Omega}\right)_{\text{NUC}} = (\Delta\rho_{\text{NUC}})^2 N_p \int F(R) \left(\frac{4}{3}\pi R^3\right)^2 |\Phi(QR)|^2 dR, \quad (4)$$

where $\Delta\rho_{\text{NUC}}$ is the difference in the nuclear scattering length density between matrix and cluster, $F(R)$ is the size distribution function, R is the radius of cluster and $\Phi(QR)$ is the form factor for a cluster. When the magnetic scattering is attributed to the same origin as the nuclear one, the similar expression with eq. (4) holds for the magnetic scattering intensity.

Guinier radius can be estimated from the Q -dependence of SANS intensity, which is an average value of cluster radius. Figure 4 shows the aging time dependence of Guinier radius together with the integrated intensity for the specimens aged isothermally at 773 K, where the integrated intensity (Z_0) is obtained

Fig. 4 Aging time dependence of the integrated intensity and Guinier radius for Fe-1.17 at%Cu alloy during isothermal aging at 773 K, together with the reported data by Goodman *et al.*⁽⁵⁾

from the nuclear scattering cross section. As shown in Fig. 4, both values of Guinier radius determined from magnetic and nuclear scattering intensities are nearly the same each other. This fact approves that the magnetic domain size contributing to small-angle scattering coincides with the dimension of chemical cluster. Then the form factor in eq. (4) is the same for both scattering intensities, that is, $|\Phi(QR)|_{\text{NUC}}^2 = |\Phi(QR)|_{\text{MAG}}^2$. Therefore the ratio of the scattering intensities is expressed as

$$A = \frac{(d\Sigma/d\Omega)_{\text{MAG}}}{(d\Sigma/d\Omega)_{\text{NUC}}} = \frac{(\Delta\rho_{\text{MAG}})^2}{(\Delta\rho_{\text{NUC}})^2}. \quad (5)$$

As discussed above, the structure model for clusters is visualized in Fig. 5. 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 precipitates are paramagnetic, the magnetic component is zero, i.e., $p_p = 0$. Thus the magnetic scattering length density is given by the equation,

$$\Delta\rho_{\text{MAG}} = N_m p_{\text{Fe}}, \quad (6)$$

where N_m is the atomic number density of the matrix. As mentioned in Sec. I, the chemical composition in the precipitates may change depending on the progress of precipitation reaction, but it is reasonable to assume that the matrix is pure Fe. Then the nuclear scattering length density is given by

Fig. 5 A structure model of precipitates in Fe-Cu binary alloy explaining the SANS data.

$$\Delta\rho_{\text{NUC}} = N_m b_{\text{Fe}} - N_p \{ (1 - x_{\text{Cu}}) b_{\text{Fe}} + x_{\text{Cu}} b_{\text{Cu}} \}, \quad (7)$$

where b_i is the nuclear scattering length of element i , N_p the atomic number density and x_{Cu} the mole fraction of Cu in the clusters. The composition dependence of N_p is supposed to be given by the equation,

$$N_p = (1 - x_{\text{Cu}}) N_{p,\text{Fe}} + x_{\text{Cu}} N_{p,\text{Cu}}, \quad (8)$$

where $N_{p,\text{Fe}}$ and $N_{p,\text{Cu}}$ are the atomic number density of pure substance occupying the precipitates, respectively. As shown in Fig. 6, the ratio A changes as a function of Cu concentration. Here there are two possibilities depending on the crystal structure of clusters, whether it is bcc or fcc. In the case of $x_{\text{Cu}} = 1$, for instance, $\Delta\rho_{\text{NUC}}$ becomes 2.10 or $1.58 \times 10^{14} \text{ m}^{-2}$ for bcc or fcc, respectively, while $\Delta\rho_{\text{MAG}} = 4.92 \times 10^{14} \text{ m}^{-2}$. In such a way, the ratio is very sensitive on the structure of cluster. As seen in Fig. 6, it is also remarkable that the ratio decreases with increasing Cu concentration in the clusters.

The experimentally determined ratio A is shown in Fig. 7 as a function of aging time at 773 K for Fe-1.17 at%Cu alloy. The ratio tends to increase and saturate during isothermal aging. If it is assumed that the Cu concentration increases from about 50 to 100 at%Cu accompanying with increasing cluster size, the ratio A is expected to decrease as seen in Fig. 6. However, in order to explain the experimental fact, it is reasonable at least to take into account the structure change in the clusters. Homogeneous nucleation in the matrix is more favorable for bcc clusters as suggested by Hornbogen⁽⁴⁾. These bcc clusters grow in size and transform to fcc ϵ precipitates beyond a critical size, at which the loss of coherency will occur. As clusters have in fact a size distribution, a continuous increase of the ratio A will be observed. As seen in Fig. 7, the ratio A saturates at about $2 \cdot 10^4 \text{ s}$. This saturation indicates a completion of structure transformation. Therefore the mean critical

Fig. 6 Calculated value of ratio A as a function of Cu-concentration in the precipitates, of which crystal structure is assumed to be fcc or bcc.

Fig. 7 Aging time dependence of the ratio, A for Fe-1.17 at%Cu alloy aged at 773 K.

diameter is suggested to be $5.6 \text{ nm} (= 2 \cdot R_G)$, which is very similar to the experimental data⁽⁵⁾, but slightly larger than the theoretical prediction⁽⁶⁾.

Several attempts have been performed in order to determine the chemical composition in the clusters. Worrel *et al.*⁽¹⁰⁾ pointed out that the atom probe analysis generates a large statistical error, when particles are analysed relatively smaller than the probe hole size. In the over-aged specimen, they found that the precipitates contain less than a few at% iron. The SANS data of Kampmann and Wagner⁽¹¹⁾ suggested that all precipitates larger than 1 nm were pure copper. From the present SANS data, it is difficult to determine quantitatively the chemical composition of precipitates. The saturated value of the ratio A was found to be 8.4, which does not coincide with the fcc-value, but is present between the bcc and fcc ones. Recently, Othen *et al.*⁽¹²⁾ reported that a twinned 9R close-packed structure is generated initially by a martensitic transformation from the bcc clusters prior to the precipitation of ϵ -phase. They observed this metastable structure in the over-aged specimen, in which the particle diameter distributed between 6 and 15 nm. When the structure of precipitates in the present specimen over-aged beyond $2 \cdot 10^4 \text{ s}$ is this metastable phase, it is reasonable to observe the inconsistent value with the expected fcc-one. At present, however, we have no information about this metastable phase for the present specimens. A prompt confirmation should be required.

The change of mean particle radius for Fe-1.4 at%Cu alloy aged at 773 K, reported by Goodman *et al.*⁽⁵⁾ is plotted in Fig. 4. They claimed the $t^{1/2}$ dependence and therefore suggested the growth stage of copper particles in the same region of aging condition with the present experiment. As seen in Fig. 4, the integrated intensity became constant beyond $2 \cdot 10^4 \text{ s}$ aging. This means that the volume fraction reached an equilibrium value. On the other hand, the Guinier radius increased still with increasing time. The time dependence is expressed as $t^{1/3}$. This behavior of phase decomposition kinetics is well characterized by the coarsening process mentioned

theoretically⁽¹³⁾⁽¹⁴⁾.

It is interesting to know the change of size distribution during the progress of phase decomposition. Worrel *et al.*⁽¹⁰⁾ suggested the bimodal size distributions due to two groups of bcc and fcc precipitates for the Fe-1.14 at%Cu alloy aged at 823 K for 36 ks, but a single size distribution for the specimen aged for 7.2 ks. Here we examine the relative change of size distribution by using the following scaled function:

$$\frac{R_G Q^4 \left(\frac{d\Sigma}{d\Omega} \right)_{\text{NUC}}}{Z_0} = \frac{4}{3} \pi (R_G Q)^4 \int F(R) \left(\frac{R}{R_G} \right)^6 \times |\Phi(RQ)|^2 dR, \quad (9)$$

where the integrated intensity is assumed as the equation,

$$Z_0 = (\Delta\rho)_{\text{NUC}}^2 N_p \frac{4}{3} \pi R_G^3. \quad (10)$$

As seen in the right hand side of eq. (9), the function shows exactly the same dependence on the scaled scattering vector, $R_G Q$, when the size distribution function $F(R)$ is the same. Figure 8 shows the $R_G Q$ -dependence of the above defined scaled scattering function for three specimens aged for different times. Those three scaled values are well overlapped each other. This fact indicates that the normalized size distribution by the average radius becomes the same over the whole aging time at least from 18 to 360 ks at 773 K.

The hardness was measured for the alloy aged at 773 K. The result is shown in Fig. 9 together with the data reported by Hornbogen and Glenn⁽³⁾. The aging time dependence is almost the same for both data. The maximum appears at around $2 \cdot 10^4$ s, when the corresponding Guinier radius is found to be 2.8 nm and the ratio A became constant as shown in Fig. 7. This behavior might be explained based on the mechanism on precipitation hardening. The interaction between cluster and dislocation is typically classified in two regimes⁽¹⁵⁾. One is the so-called cut-through mechanism. Another is the Orowan mechanism. When clusters are small and coherent with the matrix, the former mechanism will operate. On the other hand, the Orowan mechanism takes place, when the cluster size is enough large and if it is plausible, incoherent with the matrix. As mentioned above, during

Fig. 8 Change of the scaled scattering function as a function of scaled scattering vector for three Fe-Cu alloys aged at 773 for various times.

Fig. 9 Aging time dependence of Vickers hardness for Fe-Cu alloy aged at 773 K, together with the reported data by Hornbogen and Glenn⁽³⁾.

the coarsening process, the cluster size increases, but the number density decreases. Therefore the first increase of hardness as seen in Fig. 9 is attributed to the growth of coherent bcc clusters and the decrease of hardness is mainly caused from the decrease of number density of precipitates. Furthermore, in the present Fe-Cu system, the structure of precipitates changes from bcc to a more stable phase or equilibrium fcc phase during the process. The disappearance of coherency with the matrix enhances the operation of Orowan mechanism. Youle and Ralph⁽¹⁶⁾ observed peak hardness at 21.6 ks for the Fe-1.5 at%Cu alloy aged at 743 K, where they estimated an average diameter of 3.6 nm. Also Goodman *et al.*⁽⁵⁾ reported that the mean diameter at maximum strength is about 2.4 nm. Buswell *et al.*⁽¹⁷⁾ found the mean diameter of 4 nm for peak hardness, when the Fe-1.14 at%Cu alloy was aged at 823 K. Therefore the present experimental value is suggested to be reasonably in agreements with the reported ones.

IV. Conclusion

The structure change during early stage of phase decomposition in Fe-1.17 at%Cu alloy has been investigated by means of SANS technique. The integrated intensity increased firstly and saturated beyond $2 \cdot 10^4$ s aging at 773 K, while Guinier radius increased monotonically with aging time, suggesting the coarsening process of precipitates. The size distribution normalized by the average radius remains constant during the phase decomposition process. It was made clear that the intensity ratio of magnetic scattering component to nuclear one depends on chemical composition and internal structure of precipitates. From the change of the ratio, it was concluded that Cu-rich precipitates with bcc structure are decomposed from the supersaturated α Fe phase and transform mainly to the ϵ Cu phase with fcc structure during isothermal aging. The change of hardness could be qualitatively explained in terms of the structure change during the phase decomposition.

Acknowledgment

The authors wish to express their gratitude to Mr. H. Suzuki of Kawasaki Steel Co. for the sample preparation, and to Prof. H. Wada, Kyoto University for the magnetization measurements. Also they thank Drs. F. Kurosawa and K. Kishida, Nippon Steel Co. for their valuable discussions.

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