Precipitation and Phase Transformation of Copper Particles in Low Alloy Ferritic and Martensitic Steels

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In order to make clear the influence of matrix microstructures on age-hardening behavior in copper containing steels, the precipitation and the phase transformation of copper particles during isothermal aging were investigated by differential scanning calorimetry (DSC), transmission electron microscopy (TEM) and atom-probe field ion microscopy (AP-FIM). In ferrite, it was found from the DSC analysis and the TEM observations that copper clusters, bcc and 9R structures exist prior to the formation of the stable fcc copper phase, and that the main structure of the particles in a maximum hardness specimen is a bcc structure. The bcc→9R transformation was found to occur during the particle coarsening by the qualitative analysis of the DSC curves and the kinetics was discussed by the free energy calculation in Fe-matrix/Cu-precipitate system. In martensite, most of the copper precipitated on laths and on dislocations during isothermal aging. This resulted in the decrease of the amount of bcc particles and the considerable decrease of maximum age-hardness of the specimen. On the other hand, the age-hardening behavior of 80%-deformed ferrite was almost the same as that of ferrite, although the dislocation density of the deformed ferrite was larger than that of ferrite. In this paper, the factors controlling the precipitation and the phase transformation of copper particles in association with the hardening behavior are discussed with focus on the effect of defects (dislocation, vacancy) in steels. Moreover, the effect of manganese addition on the precipitation of copper particles is discussed.

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I. Introduction

Low carbon steels containing 1–2% copper have been attracting an interest as structural steels ranging from thin sheets to thick plates due to their excellent strength/ductility balance⁽¹⁾⁽²⁾. This excellent balance derives from small copper particles which precipitate during aging or cooling. The small particles also play an important role in the embrittlement of thermally aged and irradiated ferritic alloys⁽³⁾. The early stage of precipitation of copper^{(4)–(15)} is thus of technical, as well as of scientific, interest.

In an early stage of precipitation of copper in aged ferritic steels and alloys, coherent bcc clusters nucleate and grow in the supersaturated bcc matrix, and lose the coherency after reaching certain critical size^{(4)–(8)}. It was initially thought that direct transformation to a twinned fcc structure having Kurdjumov-Sachs orientation relationship to the bcc matrix⁽⁸⁾ should take place. However, recent high resolution electron microscopic studies of copper precipitation in Fe–Cu alloys have shown that the transformation sequence with increasing aging time is bcc→9R→fcc⁽⁹⁾⁽¹⁰⁾⁽¹²⁾.

In order to apply copper-containing steels not only to ferritic steels but also to other steels such as martensitic and bainitic steels (that is, commercial steels), it is necessary to fully understand the effect of defects and

alloying elements on the precipitation and transformation of copper. Thompson *et al.*⁽¹⁴⁾⁽¹⁵⁾ has reported the copper precipitation at austenite/ferrite interfaces and within ferrite during continuous cooling of commercial low alloy steels. However, little detailed information exists regarding the copper precipitation and the transformation during thermal aging of these steels with high dislocation density, although many of the studies have been focused on carbon-free or ultra low carbon model alloys with low dislocation density^{(1)(3)–(10)(13)}.

The purpose of this study is to make clear the effect of matrix microstructure on the precipitation and isothermal age-hardening behavior of copper containing steels. In describing copper precipitation in the three types of microstructure of ultra-low carbon ferrite, low carbon martensite and highly deformed ferrite, the factors controlling precipitation and age-hardening behavior, especially, the role of dislocation, is discussed. A thermodynamic consideration is also made on the precipitation and bcc-9R transformation of copper particles in iron matrix in comparison with fcc-bcc transformation of iron particles in copper matrix which has been known as martensite transformation^{(16)–(20)}.

II. Experimental Procedures

Ultra-low carbon and low carbon steels with and without copper were melted in 25 kg vacuum furnace and

rolled to 20 mm thick plates. The chemical compositions of the steels are shown in **Table 1**. The plates were first reheated at 1523 K for 1.8 ks and subsequently quenched into water. By this treatment, two copper-supersaturated base specimens were obtained; a copper supersaturated ferrite matrix with low dislocation density, and a martensite matrix with high dislocation density. Moreover, the solution treated plate of ultra-low carbon steel was compressed at room temperature under the condition of

strain rate of 10 s^{-1} and reduction ratio of 80%. By this procedure, a ferrite matrix with high dislocation density was obtained. **Figure 1** shows the optical microstructure of the three base specimens.

For differential scanning calorimetry (DSC), discs of 4.8 mm in diameter and 1.7 mm in thickness, were cut out from these specimens. DSC was conducted with Rigaku TAS-200 with a qualitative analysis software. DSC measurements were carried out on these samples in air with a heat-up rate of 10 K/min from room temperature to 993 K to study precipitation and transformation of copper particles in steels.

Every specimen with copper supersaturated matrix was isothermally aged at various temperatures between 723 and 973 K for 1.8 ks. After aging, Vickers hardness test was done at room temperature under 98N load. The microscopy was also carried out by a high resolution transmission electron microscope (Hitachi HF2000, 200 kV) and atom probe field ion microscope (VG FIM100). Thin foil specimens for TEM observations were thinned by electro-polishing in an electrolyte containing 5% perchloric acid and 95% acetic acid held at 286 K, and subsequently repolished in a mixed solution of 135 mL of acetic acid, 25 g of chromic acid and 7 mL of water at room temperature with an applied potential of DC 30 V. For the FIM observation and atom probe analysis, needle-like specimens were prepared with electro-polishing in a supersaturated phosphoric acid solution of chromic acid. Ne gas was used as the imaging gas for the FIM observation. Atom probe analysis was performed at a pulse fraction of 24% and a pulse frequency of 250 Hz.

Table 1 Chemical compositions of steels (mass%).

Steels	C	Si	Mn	P	S	Cu	N
FBA	0.0013	0.006	0.024	<0.001	0.0001	—	0.0004
FCU	0.0011	0.005	0.014	<0.001	0.0001	1.57	0.0004
MBA	0.073	0.253	1.894	<0.001	0.0007	—	0.0044
MCU	0.072	0.256	1.900	<0.001	0.0006	1.52	0.0043

Fig. 1 Optical micrographs of Cu bearing base steels with (a) ferritic, (b) martensitic and (c) deformed ferritic microstructures.

III. Results

1. Hardness after isothermal aging

Figure 2 shows the hardness changes in ferrite, martensite and deformed ferrite matrices during isothermal aging for 1.8 ks at various temperatures. In the martensite and deformed ferrite, softening is pronounced at higher aging temperature where recovery takes place. **Figure 3** shows the net hardness increment due to copper addition after isothermal aging in these microstructures. All the three microstructures produce the hardening peak associated with copper precipitation as will be shown in TEM observations of Section III.2, but the hardness increment at the peak temperature in each microstructure looks different. Particularly in the martensite, considerably smaller hardness increment and the shifting of the first peak (775 K) in comparison with those in the ferrite and deformed ferrite are noticeable.

The hardness increment of the deformed ferrite is slightly larger than that of ferrite at all aging temperatures. Two possible reasons would be provided as the increase in the hardness increment; fine precipitation of copper particles, and retardation of softening due to solid solute copper and copper precipitates. However, the former reason is rejected because finer distribution of copper precipitates compared to that of ferrite is not

Fig. 2 Hardness variations with aging temperature in (a) ferrite, (b) martensite and (c) deformed ferrite.

Fig. 3 Hardness increment associated with copper addition in ferrite, martensite and deformed ferrite.

observed in a matrix of deformed ferrite as shown in TEM images (Figs. 4(d) and (f)). On the other hand, the latter reason is probable because a certain amount of

dislocations still exists even after the over-aging of deformed copper steel (for example, Fig. 4(f)) whereas a large part of dislocation disappears in the same aging condition of copper-free deformed steel.

In the hardness increment curve of martensite a hardness increase above 950 K is observed. Since α - γ transformation temperature (A_{c3}) of the sample MBA is about 1000 K and generally A_{c3} of ferrous alloys become lower with increasing copper content, the hardness increment is not responsible for the precipitation of copper but for the partial formation of martensite (α') during cooling.

2. Distribution and structure of precipitates after isothermal aging

Figure 4 shows TEM micrographs of ferrite, martensite and deformed ferrite containing 1.5 mass%-Cu, aged at 823 K ((a)–(c)) and at 923 K ((d)–(f)) for 1.8 ks. In the specimen of peak hardness in ferrite (Fig. 4(a)), a weak contrast which might be a strain contrast around copper particles is observed. However, micro diffraction of the weak contrast region only showed the same diffraction pattern as ferrite matrix with bcc structure,

Fig. 4 TEM micrographs of ferrite, martensite and deformed ferrite containing 1.5 mass%-Cu, aged at 823 K ((a)-(c)) and 923 K ((d)-(f)) for 1.8 ks.

Fig. 5 FIM image of Cu precipitate in ferrite aged at 823 K for 1.8 ks. Black region indicated by arrow correspond to the copper precipitate.

and also no stacking fault contrast and no twin contrast characteristics of twinned $9R$ structure⁽⁹⁾ are observed in the high resolution image. Since FIM micrograph of the same specimen clearly shows an existence of copper rich precipitates with 2–4 nm in diameter (Fig. 5), it is therefore concluded that the structure of precipitates existing in peak hardness is coherent bcc, which is consistent with

previous report⁽⁶⁾⁽⁷⁾.

In over-aged ferrite (Fig. 4(d)), copper precipitates with 10–15 nm in diameter are observed in matrix, and the copper precipitates are homogeneously distributed in matrix. Figure 6(a) shows a diffraction pattern of a copper precipitate taken along $\langle 111 \rangle$ direction of ferrite matrix, which is typically seen in the specimen aged at 923 K for 1.8 ks. The precipitate has a twinned $9R$ structure as indexed in Fig. 6(b), but could not be characterized by simple multiple-twinned fcc structure⁽⁸⁾. The orientation relationship between the $9R$ precipitate and α -iron matrix was as follows:

$$(11\bar{4})_{9R} // (110)_{\text{ferrite}}, \quad [1\bar{1}0]_{9R} // [\bar{1}\bar{1}1]_{\text{ferrite}}$$

which is in agreement with previous reports⁽⁹⁾⁽¹⁰⁾. Figure 7 shows the other type of a precipitate often seen in the same sample. The precipitate may be classified as a transition state from twinned $9R$ to twinned $3R$, because the stacking fault sequence is partially disappeared⁽¹²⁾.

In contrast with the ferrite, the dislocation density of martensite and deformed ferrite is higher than that of ferrite. From Fig. 8, the dislocation density of copper-containing deformed ferrite before aging is estimated to be an order of 10^9 – 10^{10} cm^{-2} and the density of martensite is higher than that of deformed ferrite by using the technique proposed by Ham⁽²¹⁾. In the martensite, a large amount of precipitates are located on internal dislocations in laths and on lath boundaries (Figs. 4(b) and 4(e)) where rapid particle coarsening occurs in association with pipe and boundary diffusions. The main structure of the precipitates on laths and dislocations after

Fig. 6 (a) Diffraction pattern of twinned $9R$ -Cu precipitate in copper-containing ferrite aged for 1.8 ks at 923 K, and (b) schematic representation of (a). The incident beam was aligned to $\langle 111 \rangle$ direction of ferrite matrix.

923 K aging is the fcc-type copper precipitate.

In deformed ferrite, the copper precipitates in contact with dislocations and not in contact with dislocations (that is, in matrix) are observed. The copper precipitates in contact with dislocation (Fig. 4(c)), the amount of which is smaller than that in matrix, have already transformed to $3R$ or fcc precipitates with an internal fringe⁽¹⁰⁾ even at 823 K aging. On the other hand, according to the high resolution TEM observation and the micro-diffraction analysis, the structure of the particles in matrix at 823 K aging and 923 K aging is similar to that observed in ferrite matrix, that is, bcc-Cu at 823 K aging and twinned $9R$ and its transition structure to $3R$ at 923 K aging.

3. DSC analysis of copper containing steels

Figure 9 shows DSC curves obtained from copper-supersaturated three base specimens. DSC curves are represented as a heat flow difference between copper containing steels and each base steel without containing copper to avoid a heat flow associated with oxidation and softening. In DSC curve of ferrite, three exothermic peaks at temperature around 600, 850 and 875 K, labeled A, B and C, respectively, are clearly observed. The activation energy of reaction associated with exothermic A and B are 60 and 230 kJ/mol, respectively, where the activation energy is calculated from the technique proposed by Luo *et al.*⁽²²⁾, which is based on Avrami-Johnson-Mehl equation⁽²³⁾ and requires only one heating rate to obtain the kinetic parameters. For peak A and B, the obtained activation energies are consistent well with the activation energy of nucleus formation of copper precipitate, 54.4 kJ/mol⁽⁶⁾, and activation energy of copper diffusion in α -iron, 244 kJ/mol⁽²⁴⁾, respectively. Since the clustering of copper atoms has been observed around 600 K aging⁽¹³⁾, it is probable that the exothermic A and B correspond to the clustering and coarsening stage of copper precipitation⁽¹³⁾, respectively. Peak C is probably associated with bcc $\rightarrow$ $9R$ transformation, not with a certain activation process in precipitation. We give a discussion of this point in Section IV.1.

In DSC curve of martensite (Fig. 9(b)), two exothermic peaks labeled A' and B' are observed. Peak B' would be the shifted peak of B and C because there are no other peaks considered as copper precipitation, but difficult to be discerned from two peaks of coarsening and transformation peak. That the transformation peak is not clearly distinguished from the coarsening peak implies a large part of the particles does not experience the phase transformation from bcc to $9R$, or bcc to fcc, and this implication seems to correspond with the results of TEM observation that bcc-Cu is hardly observed in the matrix of martensite. In DSC curve of deformed ferrite (Fig. 9(c)), three exothermic peaks are distinguished. The positions of these peaks are very similar to the positions of the ferrite, although the deformed ferrite is heavily dislocated like martensite. At present, the reason for the different feature in DSC curves between deformed ferrite and martensite is considered to be the difference in dislocation density. This will be described in following discussion.

One more thing to be indicated from the DSC result of deformed ferrite is that the role of excess vacancy on copper precipitation. The fact that the peak position, especially peak A, of the DSC curve of ferrite and deformed ferrite are almost the same, strongly indicates that the excess vacancies introduced by deformation at room temperature do not affect the clustering and coarsening stage of copper particles. In a case of quench-and-temper experiment, the vacancies very quickly disappear during the specimen heating, and do not seem to enhance the clustering and precipitation of copper particles.

Fig. 7 HRTEM image of Cu precipitate in ferrite aged at 923 K for 1.8 ks. The incident beam was aligned to $\langle 111 \rangle$ direction of ferrite matrix.

Fig. 8 TEM micrographs of copper-containing (a) martensite and (b) deformed ferrite before aging.

IV. Discussion

1. Heat effect accompanied with transformation of copper precipitates

Othen *et al.* has concluded that the bcc particles are martensitically transformed to 9R particles from the analysis of crystallographic features of 9R structured

copper precipitate, such as if so, the habit plane and orientation relationship⁽¹⁰⁾. Thus, some heat effect associated with martensitic transformation (phase transformation, more generally) of copper particles should be observed. **Figure 10(a)** shows a DSC curve obtained from the peak hardness specimen of ferritic steel (steel FCU) aged at 823 K for 1.8 ks that mainly contains bcc-Cu precipitates. In this curve, a sharp exothermic peak with peak temperature 875 K is clearly identified, which is a

Fig. 9 DSC curves of solutionized and quenched (a) ferrite and (b) martensite, and (c) deformed ferrite. (Heat up rate: 10 K/min.)

Fig. 10 DSC curves of Cu-added ferrite aged at 823 K for (a) 1.8 ks and (b) 64.0 ks. (Heat up rate: 10 K/min.)

corresponding peak of exothermic C in Fig. 9. The heat of the exothermic reaction was 3.0 J/g. However, in the DSC curve of the over aged specimen aged at 823 K for 64.0 ks (Fig. 10(b)) in which the precipitates have already transformed from bcc to 9R or fcc, no peak at 875 K appears. From the results, it is quite reasonable to consider the exothermic peak C at 875 K is associated with bcc-9R transformation.

Here, we present a simple free energy calculation in order to confirm the validity of the experimentally obtained heat of the transformation. The model used in the calculation is experimentally possible model, which is similar one used by Othen *et al.*⁽¹⁰⁾, that 5.0×10^7 spherical particles with 4 nm in diameter transform from bcc to 9R, in which we assumed that all copper in 1 g of 1.5 mass%-Cu steel precipitate and transform at 873 K. Since the heat of bcc-9R transformation in the precipitate-matrix system ($\Delta H^{\text{bcc-9R}}$) is related to the total free energy difference in the transformation ($\Delta G^{\text{bcc-9R}}$), that is,

$$\Delta H^{\text{bcc-9R}} = \Delta G^{\text{bcc-9R}} - T(\partial \Delta G^{\text{bcc-9R}} / \partial T) \quad (1)$$

if $\Delta G^{\text{bcc-9R}}$ is known, $\Delta H^{\text{bcc-9R}}$ is obtained. $\Delta G^{\text{bcc-9R}}$ is taken as the sum of the volume free energy difference

($\Delta G_v^{\text{bcc-9R}}$), elastic strain free energy difference ($\Delta G_s^{\text{bcc-9R}}$), and interfacial free energy difference ($\Delta \gamma^{\text{mat./bcc-mat./9R}}$)⁽¹⁰⁾ during bcc-9R transformation. For $\Delta G_v^{\text{bcc-9R}}$, we used the value of volume free energy difference between bcc-Cu and fcc-Cu, $\Delta G_v^{\text{bcc-fcc}}$, because there is no thermodynamic data for copper with 9R structure. Energy contribution of an additional regular stacking fault on every third close packed plane in 9R and also twins should be considered but was neglected here because its energy contribution is small enough compared to $\Delta G_v^{\text{bcc-fcc(10)(25)(26)}}$. That is:

$$\Delta G_v^{\text{bcc-9R}} \cong \Delta G_v^{\text{bcc-fcc}} = 4017 - 1.255T \text{ J/mol}$$

where $\Delta G_v^{\text{bcc-fcc}}$ was taken from Thermo-Calc database⁽²⁷⁾. For $\Delta G_s^{\text{bcc-9R}}$, we used the value of hydrostatical strain free energy around coherent bcc-Cu precipitates reported by Goodman *et al.*⁽⁶⁾, and neglected the strain in and around 9R particles because most of the strain energy is expected to be released by introducing the internal twins and stacking faults. That is:

$$\Delta G_s^{\text{bcc-9R}} = G_s^{\text{bcc}} = 42 \text{ J/mol}^{(6)}$$

For $\Delta \gamma^{\text{mat./bcc-mat./9R}}$, there is also no data, although Goodman *et al.*⁽⁶⁾ has reported that interface energy of coherent bcc-Cu/iron matrix ($\gamma^{\text{mat./9R}} = 0.2 \text{ J/m}^2$), and of incoherent fcc-Cu/iron matrix ($\gamma^{\text{mat./fcc-Cu}} = 0.6 \text{ J/m}^2$). But here in this estimation, we used 0.4 J/m^2 as the tentative value of $\Delta \gamma^{\text{mat./bcc-mat./9R}}$, because the interface between 9R and iron matrix seems to show good coherency as is evident from HR-TEM image⁽⁹⁾. By incorporating these values to equation (1), the calculated transformation heat $\Delta H^{\text{bcc-9R}}$ per 1 g of 1.5 mass% copper bearing steel was evaluated to 3.5 J/g. Since an order of the calculated and experimentally obtained value (3.0 J/g) agrees well, it seems quite reasonable to conclude that the exothermic peak C at 875 K is associated with bcc-9R transformation.

Spherical fcc-iron particles precipitated in a copper matrix is martensitically transformed into an internally twinned bcc structure with the Kurdjumov-Sachs orientation relationship to the copper matrix⁽¹⁶⁾⁽¹⁷⁾. It has been found that the transformation occurs by plastic deformation or during cooling after thermal aging, but it does not occur during particle coarsening⁽¹⁸⁾⁽¹⁹⁾. The iron precipitates with a few hundred nm in size are not transformed only by the cooling to room temperature⁽²⁰⁾. In the case of the copper precipitates in iron matrix, however, the transformation from bcc to 9R occurred during particle coarsening at a very small size, because the exothermic peak in association with the transformation was clearly observed as exothermic peak at 875 K in the DSC heating curve. Since the copper atoms and vacancies can diffuse well during the transformation, it can be said from the result that the bcc-9R phase transformation may not be purely martensitic⁽¹⁰⁾ but may have somewhat diffusional contribution⁽²⁸⁾.

The difference in the transformation behavior between Fe-Cu and Cu-Fe alloy system may be mainly caused by the magnitude of volume free energy difference

(ΔG_v) in the transformation. Here we estimate the ΔG_v in each system. Since the free energy contribution of the regular stacking faults and twins to the volume free energy difference between bcc and fcc is small⁽¹⁰⁾, the volume free energy difference in the transformation was estimated by only taking the bulk volume free energy difference between bcc and fcc phase in each precipitate. From the calculation using Thermo-Calc database⁽²⁷⁾, the bulk free energy differences between bcc- and fcc-Cu, and that between fcc- and bcc-Fe at 873 K were 2920 and 920 J/mol, respectively. For a spherical particle with 10 nm in diameter, for example, the differences were 2.2×10^{-16} and 0.7×10^{-16} J per particle, respectively. This should be compared with the interfacial free energy. If the $\Delta\gamma$ is supposed to be the same in each system, the interfacial free energy difference per particle with 10 nm is estimated to be about 1.3×10^{-16} J, by using 0.4 J/m^2 as the tentative value of $\Delta\gamma^{\text{mat.}/\text{bcc-mat.}/\text{fcc}}$. This simple free energy estimation indicates that the iron particle embedded in copper matrix do not favor the transformation compared to the copper particles in iron matrix, because the bulk free energy differences between fcc- and bcc-Fe is rather smaller than the interfacial free energy difference $\Delta\gamma^{\text{mat.}/\text{bcc-mat.}/\text{fcc}}$. The above energy balance estimation is qualitatively in agreement with experimental results, although other factors such as difference in strain around the each precipitate and the difference in transformation mechanism are not considered here.

2. The different hardening behavior in martensite and deformed ferrite

(1) Effect of dislocation on precipitation and transformation

The TEM and DSC observations have revealed that the hardening and precipitation behavior in martensite are considerably different from those in deformed ferrite although both microstructures are similarly dislocated. As was described in Section III.2, one possible reason for the difference would be a difference in the main precipitation site resulting from a difference in dislocation density before aging. In martensite, as the results of most of the copper particles precipitate on laths and on dislocations where rapid growth of precipitates take place, the amount of coherent bcc copper particles, which is the most effective morphology of precipitates to increase hardness or strength of steels, is small compared in deformed ferrite. Alternatively, the dislocation density of approximately $10^9 - 10^{10} \text{ cm}^{-2}$ before aging may be the critical condition that the main precipitation site of copper particles is either in matrix or on dislocations/lath boundaries.

One more thing which should be noted as the role of dislocation is the amount of mobile and immobile dislocations in steels. During aging, a local rearrangement of the tangled dislocation and the formation of low angle boundary occur. Both processes called recovery involve climb of dislocation⁽²⁹⁾. Thus, if there are a lot of dislocations hard to climb in the material such as pure screw dislocation or dislocation with kinks and jogs, a lot of

particles will tend to precipitate on the dislocations. Then, it may be possible to say that the dislocations in TEM image of over-aged at 923 K (Figs. 4(e) and 4(f)) is the immobile-type dislocation because not all the dislocations before aging (Fig. 8) seem to act as the precipitation site as seen in the TEM image of over-aging. The difference between the amount of immobile dislocation may be thus the one reason for the different copper precipitation behavior in those steels.

Here, it is worth while to point out the acceleration of the bcc-9R transformation due to the stress field around the dislocation. If bcc-9R transformation is martensitic, the transformation from bcc to 9R may be triggered by the stress field around dislocation⁽³⁰⁾ which must be migrating during thermal aging. However, no evidence of stress induced transformation was observed through our TEM and DSC experiments. Since DSC measurements have revealed that the peak positions associated with particle coarsening (peak B'') and the bcc-9R transformation (peak C'') in deformed ferrite were the same as that in ferrite, in spite of containing a large number of dislocation moving around in the deformed matrix during isothermal aging, it is indicative that the phase transformation is not affected by dislocation. Therefore, it is concluded that the main reason for the decrease of hardness increment in martensite is the decrease of the amount of bcc-Cu resulted from the higher dislocation density, and at least in our experiment, the effect of the acceleration of the transformation would be a minor effect.

(2) Effect of alloying elements

Precipitation hardening of Fe-Cu alloy system is often accounted for Russel-Brown model⁽³¹⁾ in which the hardening is related to the difference in shear modulus between a copper precipitate and an iron matrix. Phythian *et al.*⁽³²⁾ has reported that the calculated shear modulus of bcc-Cu was smaller than that of fcc-Cu, and indicated that this is a main effect of a large increase of the hardness of Fe-Cu alloy in which bcc-Cu precipitates. If the shear modulus of copper particles has been changed by the addition of microalloying elements, the hardening behavior would be changed on the basis for Russel-Brown model. Since the martensite steel used in this study contains manganese and silicon as shown in Table 1, it is therefore valuable to examine the microalloying effect on the copper precipitation, and especially hardening behavior to make clear the reason for the considerable decrease of maximum hardness in martensitic steels (MBA, MCU).

Figure 11 shows the result of an atom probe analysis for a copper precipitate with a diameter of 8 to 10 nm observed in a copper containing martensite specimen aged at 823 K for 1.8 ks. Structure of the precipitate can not be determined directly from the FIM image, but may be 9R or fcc copper judging from the size of precipitate. It is apparent from the Fig. 11 that manganese atoms are segregated around a copper precipitate in martensite matrix. The average manganese content at the interface

Fig. 11 Atom probe cumulative profile of Cu across Cu-precipitate/Fe-matrix in martensite aged at 823 K for 1.8 ks.

was estimated to be 8.1 at% from examining 10 copper particles. Similar segregation has been found for nickel in Fe-Cu-Ni⁽⁷⁾ and for manganese in Fe-Cu-Ni-Mn⁽³³⁾. Segregation of silicon around the copper particles is not detected in our observation.

Figure 12 shows the effect of manganese addition on the hardness after isothermal aging for 1.8 ks in an ultra-low carbon (10 ppm-C) ferritic steel. In the region of aging temperature below 775 K, manganese addition makes the hardness increase 30–40 higher compared with a manganese free specimen, which is probably caused by solid solution hardening of manganese atoms. In the over-aged region, on the other hand, a rapid decrease of the hardness increment compared to the manganese free steel is observed. Since the decrease of the hardness increment in aged ferrite (Fig. 12) is observed at all aging temperatures, the effect of manganese on the decrease of hardness increment in martensite (Fig. 3) would be a minor one. Therefore, it is concluded that the main reason for the decrease of hardness increment in martensite is responsible for the larger dislocation density than ferrite or deformed ferrite.

Worrall *et al.* has reported that the addition of nickel does not substantially change the age-hardening behavior of copper containing steel, although nickel is segregated by 2.7 at% at the interface of fcc-Cu/bcc-Fe⁽⁷⁾ as well as manganese. If the hardening of Fe-Cu system is described by modulus hardening models (R-B model), one possible explanation of the rapid decrease of hardness increment in over-aged region in ferrite is that manganese around copper particle increases the shear modulus around the copper particles, and resulted in lowering the hardness in overaged region of Fe-Cu alloy system. Unfortunately, the shear modulus of manganese is unknown, while that of nickel (78.7 GPa at 298 K), iron (80.0 GPa), and copper (48.9 GPa) are known⁽³⁴⁾⁽³⁵⁾. To clarify the effect of alloying elements to hardness or strength, it is hoped to assess the effect of alloying elements on the shear modulus of precipitate. The investigation for the effect of segregation on the growth kinetics of copper particles would also be a subject of further investigation.

Fig. 12 Hardness variations with aging temperature in ultra low carbon (10 ppm-C) ferritic steels containing 1.5 mass%Cu, and 1.5 mass%Cu-2.0 mass%Mn.

V. Conclusion

Isothermal age-hardening behavior of copper containing steels with ferrite, martensite and deformed ferrite matrices was studied with emphasis on the precipitation and phase transformation of copper particles in steels. The conclusions are as follows.

(1) The TEM and DSC observations have revealed that the precipitation of copper particles and the corresponding hardening behavior in martensite are considerably different from those in deformed ferrite although both microstructures contain lots of lattice defects. The main reason for the different behavior in martensite is considered to be responsible for the larger dislocation density than ferrite and deformed ferrite before aging.

(2) In DSC curve of copper-supersaturated ferrite, three exothermic peaks at the temperature around 600, 850 and 875 K were observed. The activation energy of reactions associated with exothermic peaks at 600 and 850 K was estimated to be 60 and 230 kJ/mol, respectively, and the three exothermic peaks are suggested to be the clustering, coarsening of copper precipitation and bcc-9R transformation, respectively.

(3) A qualitative analysis of DSC curves and the free energy calculation in Fe-matrix/Cu-precipitate system showed that the bcc-9R transformation occurs during the coarsening of copper particle.

(4) The main structure of the copper particles in maximum hardness specimen in ferrite was bcc structure.

(5) The segregation of manganese around a copper particles was found in the martensite. Manganese addition in ultra-low carbon steel caused the decrease of the hardening increment of the over-aged region.

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