Precipitation Behavior of Copper, Tin and Manganese Sulfide at High Temperature in Fe–10%Cu–0.5%Sn Alloys

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Tramp elements such as Cu or Sn cause a severe hot shortness. Any tramp elements have been rejected and diluted below a certain limit by the use of virgin iron source. On the other hand, the steel properties are improved if Cu precipitates are very fine and uniformly dispersed in steels. Cu is the useful alloying element for increasing hardness and improving r -value. Recently, it has been found that MnS precipitates have a good positive effect on the heterogeneous precipitation of Cu in grains. In this study a confocal scanning laser microscope with an infrared image furnace was used to carry out the *in-situ* observation of precipitation behavior at high temperature. To estimate the phase diagram, alloys were analyzed by a differential scanning calorimetry (DSC) method. It is clear that the domain of γ Fe phase becomes smaller and the domain of the liquid phase becomes larger with the addition of Sn. As a result of observation by the confocal laser microscope, the number of precipitates increased at higher temperatures with MnS than without MnS. The observed precipitates are classified into three types. Type "I" is the Cu (Sn) precipitate at the γ Fe grain boundary. Type "II" is the precipitate found in the γ Fe grains. One is the Cu (Sn) and another complex precipitate is composed of ϵ Cu, (Mn, Cu)S and $\text{Cu}_{7,2}\text{S}_4$. Type "III" is the smallest ϵ Cu precipitate in the α Fe grains. They nucleated after γ/α phase transformation and the size is less than 100 nm.

KEY WORDS: copper steel; tramp element; tin; interstitial-free (IF) steel; precipitation; MnS; confocal laser microscope; transmission electron microscopy; liquid Cu; ϵ -phase.

1. Introduction

Tramp elements such as copper (Cu) or tin (Sn) in steels are generally regarded as harmful because those elements cause the hot shortness.^{1–6)} The enrichment of Cu due to the preferential oxidation of iron on the surface takes place when the steels containing Cu are kept at high temperature under an oxidizing atmosphere. Once Cu content exceeds the solubility limit in γ Fe, Cu–Fe alloy precipitates on the surface. This Cu–Fe alloy will be melted if the temperature is above the melting point. Then the liquid Cu–Fe alloy easily wets steel and penetrates into γ Fe grain boundaries to tear. Sn will enhance the precipitation of Cu because Sn reduces the solubility of Cu in γ Fe.

In general, any tramp elements in steel have been rejected below a certain limit to avoid hot shortness. In steelmaking process the use of a large amount of virgin iron source is inevitable at any cost to dilute the steel contaminated by tramp elements. Recently, Hasegawa *et al.*⁷⁾ has found that MnS precipitates have a good positive effect on the heterogeneous precipitation of Cu in the grains. Therefore it will be expected that steels containing Cu are free from the hot shortness.

On the other hand, the steel properties are improved if Cu precipitates are very fine and uniformly dispersed in steels.^{8–13)} In extra-low-carbon titanium-added interstitial-

free (IF) steel sheets, Cu is the useful alloying element for increasing hardness and improving r -value. The mechanism of this improvement of hardness and deformability has been proposed due to the precipitation ϵ Cu of nano-meter size in IF steels.^{14,15)}

As for Sn in steel, some properties have been discussed.^{5,11,16,17)} However, the precipitation and transformation behaviors at high temperatures in steel containing Cu and/or Sn have not been sufficiently made clear yet. Therefore in view of precipitation behavior of the liquid Cu regarded as equivalent to that of hot shortness, Fe–10mass%Cu alloy system was chosen and Sn was added to this system. In this system the purpose of the present study is to make it clear where and how the Cu and Sn precipitate at high temperatures and what role MnS precipitates play in the successive precipitation behavior of Cu and Sn at lower temperatures.

2. Methods of Experiment and Analysis

A confocal scanning laser microscope with an infrared image furnace was used to carry out the experiment of *in-situ* observation of precipitation behavior at high temperatures. The principle and the method of operation of the laser microscope have been described in detail elsewhere.^{7,18–25)} Fe–10mass%Cu alloys^{7,18)} and Fe–

Table 1. Chemical composition of samples (mass%).

Sample	[C]	[Si]	[Mn]	[P]	[S]	[Cu]	[Sn]	T. [Al]	[O]	[N]
A	0.0011	0.003	<0.002	0.010	<0.0003	10.03	0.48	0.002	0.0192	0.0006
B	0.0010	0.003	0.62	0.010	0.041	10.06	0.42	0.002	0.0263	0.0006

0.05mass%C–Sn steels¹⁹⁾ have been already investigated. Based on the previous studies, Fe–10mass%Cu–0.5mass%Sn alloys were chosen in this study. The effect of Sn on the heterogeneous nucleation of Cu and MnS was considered to be so interesting that a large amount of Sn was intentionally added in this study.

Metallic iron, manganese, tin, copper and FeS agent were prepared and melted in the water-cooled copper mould by using an arc furnace with a tungsten electrode under argon atmosphere. Two mother alloys of the button shape of about 60 mm in diameter, 8 mm in height and about 120 g were made. Then the specimen of 4.2 mm in diameter, 2 mm in height and about 0.2 g for the observation experiment was machined from the mother alloy and mirror-polished.

The chemical composition of the samples is given in **Table 1**. The manganese (Mn) and sulfur (S) contents are very important and varied from zero to 0.6% and zero to 0.04% respectively, given approximately the same Mn/S ratio according to the previous works.^{7,18,19)} In the previous works Fe–10%Cu alloys were selected so as to investigate the precipitation of liquid Cu in γ Fe on the basis of the equilibrium phase diagrams of the Fe–Cu binary system.²⁶⁾ In this study the phase diagram of Fe–0.5mass%Sn–Cu quasi-binary system should be determined. Therefore Fe–0.5mass%Sn–0.5mass%Cu alloys and Fe–0.5mass%Sn–10mass%Cu alloys were also made to analyze temperatures of phase transformation and melting points by a differential scanning calorimetry (DSC) method.

In-situ observation of each specimen was carried out under the two cooling conditions as shown in **Fig. 1**.^{7,18)} The specimen was heated at the rate of 1.7 K/s to 1613 K and kept constant for 1.2 ks. Then it was cooled at the rate of 0.33 K/s to 1423 K. Two heat patterns were taken below 1423 K. One heat pattern is a continuous cooling pattern at the same rate of 0.33 K/s. The other is a pattern of holding treatment at 1423 K for 3.6 Ks followed by cooling at the rate of 0.33 K/s. This experiment of holding treatment was planned to clarify the precipitation of Cu(Sn) alloy of liquid phase in γ Fe. The images during *in-situ* observation were continuously recorded on the videotapes and later the images were analyzed in detail.

After the *in-situ* observation experiment all the specimens were analyzed by SEM and TEM to identify the precipitates. The extracted replica film or a thin film was made for TEM analysis. When the replica film was made to extract precipitates, a special care was taken to prevent the dissolution of Cu and sulfides into solvent by using the non-aqueous solvent. This non-aqueous electrolyte-potentiostatic etching method is called as SPEED method.²⁷⁾ For making thin films, an ion milling method was used. A field emission type (FE-) TEM operating at 200 kV and a high-resolution TEM operating at 300 kV were used. SEM and both TEM are equipped with an energy-dispersed spectroscopy (EDS). The morphology and the composition of the precipitates were investigated and analyzed in detail.

Fig. 1. Two heat patterns for *in-situ* observation experiment. The indications of a to f are the point where the images will be analyzed.

Fig. 2. Fe–0.5mass%Sn–Cu quasi-binary system phase diagram estimated by DSC analysis.

Furthermore the crystal structure of the typical precipitate such as Cu, Cu sulfides and Mn sulfides was determined by the EDS analysis and the electron diffraction technique. The obtained electron diffraction pattern was analyzed and assigned to the JCPDS data system for the d-spacing to identify the precipitates.

3. Results

3.1. Estimation of the Fe–0.5mass%Sn–Cu Quasi-binary System Phase Diagram

The phase diagram of Fe–Cu–Sn ternary system has not been well established yet especially below 1300 K in the previous works.^{1,2,5,28)} In order to estimate the phase diagram of Fe–0.5mass%Sn–Cu quasi-binary system DSC analysis was done. **Figure 2** shows the estimated Fe–0.5mass%Sn–Cu quasi-binary system phase diagram. The temperatures of the phase transformation and the melting points obtained by DSC were plotted in the figure. Calculated phase diagram was indicated in the same figure. The thermodynamic parameters of Imada *et al.*²⁹⁾ were used

Fig. 3. The sequential images of Cu(Sn) precipitation observed by the confocal laser microscope in sample A on the condition of continuous cooling.

Fig. 4. The sequential images of MnS and Cu(Sn) precipitation observed by the confocal laser microscope in sample B on the condition of continuous cooling.

in the calculation. Dotted lines obtained by calculation were most probably existed but the points were not confirmed in the DSC analysis.

Compared with the equilibrium phase diagram of Fe–Cu binary system,²⁶⁾ it is clear that the domain of γ Fe phase becomes smaller and the domain of the liquid phase becomes larger with the addition of Sn. On the basis of these results, it will be expected that hot shortness becomes worse when Sn coexists with Cu in steels.

3.2. In-situ Observation

The behavior of the precipitation and the phase transformation for the samples A and B on the same condition of continuous cooling were shown in Figs. 3 and 4, respectively. The identification of the precipitates has been separately done but it will be described in the later section.

Figure 3 shows the sequential images observed by a confocal laser microscope for sample A without MnS in the case of the continuous cooling. The alphabetical notation in each image in Fig. 3 corresponds to the point indicated in Fig. 1. As shown in Fig. 3(a), the matrix was γ Fe phase at 1613 K. The liquid phase should coexist at this temperature according to the estimated phase diagram. Actually the

grain boundaries looked slightly fluctuating during observation indicating the liquid phase at the grain boundary. No precipitates but hollows were observed. These hollows appeared during heating up to 1613 K and stayed during cooling. As shown in Fig. 3(b), the liquid phase at the grain boundary was more clearly visible and migrating at the grain boundaries. Between Figs. 3(b) and 3(c), the liquid phase spread out at 1420 K and wetted the surface. The emerged liquid phase gathered and became small particles during cooling as indicated in Figs. 3(c) and 3(d). Below 1060 K where the liquid phase became solid the precipitates appeared also at the grain boundary as shown in Fig. 3(e). At 974 K γ/α phase transformation occurred and the image at 919 K is shown in Fig. 3(f). After the phase transformation the numerous small precipitates appeared in the α Fe grains.

Similarly, Fig. 4 shows the sequential images in sample B with MnS in case of continuous cooling. The matrix is γ Fe phase and coexists with the liquid phase fluctuating at the grain boundaries at 1613 K as shown in Fig. 4(a). No precipitates but hollows were observed. In the case of sample B with MnS, the emergence of the liquid phase was not observed on the surface by contrast to sample A as shown

Fig. 5. Change in the number of precipitates with temperature counted on the images. The data from the previous works¹⁸⁾ were depicted and compared with the present work.

in Fig. 3(b). Only the liquid phase at the grain boundary was clearly visible as shown in Fig. 4(b). MnS precipitates possibly reduce the enrichment of Cu at the grain boundary in case of Fe–0.5mass%Sn–Cu–Mn–S alloy system.

As shown in Fig. 4(c) Cu–Sn precipitates with MnS were observed along the grain boundary. No other remarkable change was observed until the specimen was cooled below 1110 K as shown in Fig. 4(d). Then, many tiny precipitates appeared in the grains and grew during cooling down to about 1070 K as shown in Fig. 4(e). At 973 K γ/α phase transformation occurred and after the phase transformation many small precipitates appeared in the α Fe grains as shown in Fig. 4(f).

The comparison was made between two conditions of continuous cooling and holding treatment for sample A. The liquid phase was clearly and brightly observed until the specimen was cooled down below 1130 K. On the contrary much more precipitates appeared for sample B in case of holding at 1423 K. This temperature of precipitation was slightly higher than that in continuous cooling condition. Other behaviors were almost the same as mentioned above for both samples A and B.

Based on the above observation by a confocal laser microscope, the number of precipitates was counted. The liquid phase at the grain boundaries was taken into account and counted on the sequential images only after it solidified and the shape of precipitates was confirmed as separate particles. Figure 5 shows the change in the number of precipitates with temperature. The previous data¹⁸⁾ are also included in this figure.

There are a couple of characteristics seen in this figure. Firstly, in case of the Fe–Cu–Sn ternary system the difference of the change in number between samples A and B is very large. The number of precipitates in sample B increased at higher temperatures than that in sample A. This increase is due to the precipitation of MnS at high temperatures.

Secondly the difference for the same sample is very small between two heat patterns. However it should be noted that in case of sample B with MnS the precipitates appeared during the holding treatment at 1423 K which is higher than that for the continuous cooling pattern.

Finally comparing the present data with the previous ones for Fe–Cu binary system, the increase in the number of precipitates for both samples seems to be delayed at higher temperatures. Sn would certainly be responsible for the difference. In case of Fe–Cu–Sn ternary system the domain of the liquid phase was widened as already shown in Fig. 2 and the liquid precipitates at grain boundaries were often observed in the microscope at lower temperatures. It is neither accurate nor suitable to count the number of the liquid precipitates of a linear shape on the image analysis. This shape of liquid precipitates is responsible for the apparent difference between the binary and the ternary systems. Nevertheless once the liquid phase solidifies below 1060 K, the increase in the number of precipitates is meaningful. After γ/α phase transformation, many small precipitates were observed and the number increased sharply. This behavior is similar to that in Fe–0.05mass%C–Sn system.¹⁹⁾

4. Discussion

The morphology, the composition and the crystal structure of the precipitates are discussed in detail as compared with the precipitation behavior in this section. Figure 6 shows the typical precipitates by SEM analysis. The top half of figure is one for sample A and the bottom half for sample B. The left half of figure is one in the case of continuous cooling and the right half in the case of holding treatment. The morphology is classified into three types, “I”, “II” and “III” for any cases as shown in Fig. 6. Type “I” is the precipitate at the γ Fe grain boundary as shown in Figs. 6(a) and 6(b). The morphology is lens-like and each size is larger than about 1 μ m. The precipitates aligned at the grain boundaries indicate a liquid film at high temperatures. The precipitates are also equivalent to the liquid phase emerging in the γ Fe grains at high temperature as previously shown in Figs. 3(c) and 3(d). The composition is analyzed and later shown to make confirmation.

Type “II” is the precipitate of the irregular shape found in the γ Fe grains and the size is between 300 nm and 10 μ m. A big finger-like precipitate seen in Fig. 6(c) is very interesting because a kind of nucleus seems to exist at the junction of three fingers. Type “III” is the smallest precipitate in the α Fe grains. They nucleated after γ/α phase transformation and the size is less than 100 nm.

Figure 7 shows the detail of type “I” precipitate of about 1 μ m size in sample B analyzed by TEM. This figure corresponds to the precipitate in Fig. 6(d). The composition of the precipitate at the grain boundary indicated as 1 in Fig. 7(a) was analyzed by EDS as shown in Fig. 7(b). The crystal structure was identified by the electron diffraction pattern as shown in Fig. 7(c). As a result the composition of the precipitate is determined as Cu containing a small amount of Sn. The crystal structure is the same fcc structure as ϵ Cu. Apparently this Cu containing Sn is solid solution and defined as α Cu in the Cu–Sn phase diagram.³⁰⁾

The above confirmation by TEM has been repeated on some other precipitates. The type “I” precipitates in sample B is different from those in sample A. In the case of sample A without MnS, the type “I” precipitates are mainly Cu(Sn) solid solution and the size is between 0.5 and 10 μ m. Some precipitates in the γ Fe grains are found to con-

Fig. 6. SEM images of three types of the precipitates, I, II and III. (a): sample A, continuous cooling, (b) and (c): sample A, holding treatment, (d): sample B, continuous cooling, (e) and (f): sample B, holding treatment.

Fig. 7. The detail of Type I precipitates analyzed by TEM indicating Cu–Sn alloy in sample B. The figure corresponds to Fig. 6(d).

tain aluminum and silicon oxide inclusion.

On the contrary in the case of sample B with MnS, the precipitate of about $1\ \mu\text{m}$ size found at the grain boundary is identified as (Mn,Cu) sulfide precipitate by EDS analysis. It is interesting to suggest that this (Mn,Cu)S precipitate is the complex of MnS with Cu (Sn) precipitates. In the case of sample B containing both Mn and S, MnS precipitates firstly nucleate at higher temperatures and then Cu (Sn) precipitates nucleate at MnS precipitate by the heterogeneous nucleation principle. Thus the precipitate ends up with the complex precipitates of (Mn,Cu)S. It is clear that Cu precipitate is liquid at the grain boundaries at high temperatures and solidifies later at lower temperatures to form Cu (Sn) or (Mn,Cu)S precipitates as shown in Fig. 7(a).

Next, Figs. 8 and 9 show the detail of type “II” precipitate in sample B in the case of continuous cooling. The pre-

Fig. 8. TEM micrographs of Cu (Sn) classified into type “II” in sample B in the case of continuous cooling.

cipitate of 300 nm indicated as 2 in Fig. 8 was analyzed by TEM and it is identified as Cu (Sn) solid solution with fcc crystal structure. Another complex precipitate of about 300 nm as shown in Fig. 9 was also analyzed by TEM. The composition at the points indicated as 3, 4 and 5 is different, respectively. This complex precipitate is composed of ϵCu , (Mn,Cu)S and $\text{Cu}_{7.2}\text{S}_4$. The small particle of about 100 nm size indicated as 3 is identified as ϵCu . It is found that two larger precipitates indicated as 4 and 5 do not contain Sn, respectively. The part indicated as 4 is (Mn,Cu)S and the part indicated as 5 is Cu sulfide by EDS analysis. The latter part indicated as 5 was analyzed by the electron diffraction as shown in Fig. 9(e) and is identified as $\text{Cu}_{7.2}\text{S}_4$ with the fcc crystal structure of 5.57 angstrom lattice constant. Thus MnS precipitate nucleate at first and it is followed by Cu precipitate to form (Mn,Cu)S and $\text{Cu}_{7.2}\text{S}_4$. Finally ϵCu precipitate nucleates at the above complex precipitate to end up with type “II” precipitates.

Fig. 9. TEM micrographs of (Mn, Cu) S, Cu and $\text{Cu}_{7.2}\text{S}_4$ precipitates in sample B in the case of continuous cooling.

Fig. 10. TEM micrographs of Cu precipitate in sample B in the case of continuous cooling.

This finding is similar to the previous work¹⁸⁾ for Fe–10mass%Cu–Mn–S system without Sn where MnS precipitate of 200 nm size was surrounded by $\text{Cu}_{7.2}\text{S}_4$ precipitate in the case of continuous cooling. Again the heterogeneous nucleation mechanism is important. Because this heterogeneous nucleation with MnS occurs at high temperatures in sample B, the number of precipitates starts to increase at high temperature as shown in Figs. 4 and 5.

Figure 10 shows the detail of type “III” precipitate, extremely fine Cu particle of 15 nm sizes. The precipitate indicated as 6 is analyzed to be ϵCu particle with fcc crystal structure of 3.615 angstrom lattice constant. It is worth to mention that the precipitates smaller than about 50 nm classified as type “III” are ϵCu and do not contain Sn.

On the contrary, relatively larger particles than 100 nm classified as type “II” precipitates contain some Sn. Sn exists only in the liquid Cu film at the grain boundaries and also in the relatively larger Cu particles in the γFe grains. Sn is so easily dissolved into the liquid Cu phase that the domain of the liquid phase is widened. When MnS coexists

with Sn both at the grain boundaries and in the γFe grains, the heterogeneous nucleation of liquid Cu, Cu (Sn) and Cu sulfide will nucleate at MnS precipitates.

5. Conclusions

In order to evaluate the effect of Sn on the heterogeneous nucleation of MnS and Cu precipitates, the *in-situ* observation experiment was carried out for the Fe–10mass%Cu–0.5mass%Sn ternary alloys by using a confocal scanning laser microscope. The effect of the addition of Mn and S on the behavior of Cu precipitates was investigated in detail under the different heat pattern. The main results obtained are summarized as follows:

The precipitates are classified into three types. Type “I” is the liquid Cu (Sn) nucleating at the γFe grain boundaries with or without MnS. Type “II” is the complex of Cu (Sn), Cu and $\text{Cu}_{7.2}\text{S}_4$ precipitates. These are heterogeneously nucleated at MnS or oxide precipitates in the grains. The size of type “I” is larger than about 1 μm . The sizes of type “II” are 0.3–10 μm and type “III” is less than 100 nm. The many extremely fine ϵCu precipitates of 15 nm with fcc crystal structure were found in the αFe grains.

The domain of liquid phase is widened by the addition of Sn to the Fe–10mass%Cu alloys. This is the direct evidence why hot shortness gets worse with the coexistence of Sn with Cu in steels.

It is most interesting to find that the addition of Mn and S enhances the heterogeneous nucleation to form many small particles of Cu (Sn), complex precipitates combined with MnS of 100–500 nm size and many extra fine particles of Cu less than 50 nm in the αFe grains. The temperature of precipitation with MnS in the γFe grain is elevated by the addition of Mn and S. Compared with the behavior in Fe–10mass%Cu binary system, the effect of MnS is weakened by Sn addition. However the coexistence of Mn and S in Fe–Cu–Sn ternary system, the positive effect of MnS is still apparent. That is to say, it will be expected that Cu precipitation at the grain boundaries is reduced and hot shortness is avoided. Therefore Cu and Sn will be considered not as tramp elements but active alloying elements.

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