The elements of Cu and Sn are two of the main residual impurities in steel, especially in recycled scrap steel. Sulfur is one of the main impurities in steel, and it may result in a large emission of slag and CO₂ to remove sulfur from steel. Utilization of these elements has been an important and difficult matter for metallurgist. In the present paper, the as-cast steels containing different concentrations of Cu, S and Sn are prepared in laboratory. The effect of Sn addition on sulfide precipitation is investigated and discussed with respect to the morphology, size, and composition of sulfide. The experimental results show that the addition of Sn suppresses the sulfide precipitation at high temperature, promotes more copper bearing and smaller sulfides precipitation at low temperature. On the other hand, sulfide precipitates are shown to reduce the micro-segregation degree of Sn in steel, which may be because Sn dissolves in sulfide to some extent and sulfide particles provide more interfaces for Sn to distribute.

KEY WORDS: tin; as-cast microstructure; interface segregation; sulfide precipitation; ultra low carbon steel.
heating furnace. For series A–E, about 350 g of electrolytic iron is melted at 1 873 K under flowing argon gas in an alumina crucible. After the alloying elements (Cu, Sn, S, Mn) are added to the melted iron, the melt is cooled in the furnace to room temperature or quenched into water at some temperature together with crucible. An ingot with size of diameter 40 and height 40 mm then could be obtained. Series A and B are water-quenched at 1 623 K and 1 123 K, respectively. Series C–E are continuously furnace-cooled to room temperature from 1 873 K.

To compare with the above samples, samples G1 and G2 are prepared under vacuum atmosphere. After 3 kg of electrolytic iron is melted, the alloying elements (Mn, Si, Cu, S) are added to the melted iron. The melt is then cast into a water cooled copper mould and a specimen with size of \( S(\text{thickness}) \times 60(\text{width}) \times 200(\text{height}) \) mm can be prepared. More detail description of the preparation of samples G1 and G2 could be found in the previous papers.\(^8,9\)

A 5 mm thick slice, which is 15 mm away from the bottom, is cut out from the ingot. The part, at the half of the radius on the upside of the slice, is prepared for microstructure and precipitate observation conducted by optical microscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Specimens are etched by 3 vol% nitric acid (Nital) to reveal ferrite structure as well as prior austenite grain boundary. Specimens for SEM observation are also etched by Nital and the observation is performed on a LEO 1550 SEM with high-resolution. Carbon extraction replicas are prepared for TEM observation. The replicas are floated on Al, Ti, Mo or Nylon grids and a carbon specimen holder is used to avoid the possible detection of Cu from the grid and the specimen holder. The TEM observation is performed with a Hitachi 800 microscope operated at 200 kV and coupled to an Energy Dispersive X-Ray Spectroscopy (EDS).

The distribution of Sn in samples G1 and G2 on the 1/4 section of thickness are investigated with an Electron-Probe Micro-Analyzer (EPMA). The analysis is conducted on an area of \( 1.024 \times 1.024 \) cm\(^2\) by 512 \times 512 points with a beam size of 1.0 \( \mu \)m.

### 3. Experimental Results and Discussion

#### 3.1. Effect of Sn on Phase Transformation Temperature and Microstructure

Figure 1 shows the temperature curves of samples C1, C2 and C3 during continuous cooling. For high Sn sample C3, the liquid/solid transformation temperature is clearly lower than that of no Sn sample C1. The fol-
lowing $\delta/\gamma$ transformation temperature is not successfully detected. In addition, for high Sn sample C3, the $\gamma/\alpha$ transformation temperature is clearly higher than that of no Sn sample C1.

The microstructures of samples A1, A2 and A3 are shown in Fig. 2. Since these samples are quenched into water at 1 623 K when furnace-cooled from 1 873 K, these microstructures should be austenite just after $\delta/\gamma$ transformation according to Fig. 1. Although the grain is quite uneven, it is clearly shown that the grain in sample A3 is quite finer than that in sample A1.

The microstructures of samples B1, B2 and B3 are shown in Fig. 3. Since these samples are quenched into water at 1 123 K after furnace-cooling from 1 873 K, these microstructures should be ferrite just after $\gamma/\alpha$ transformation. Similarly, it is clearly shown that the grain in sample B3 is quite finer than that in sample B1.

The similar phenomenon that the microstructure becomes fine due to addition of Sn in sample is also observed in samples C1, C2 and C3 as shown in Fig. 4. The mean grain sizes of samples quenched at 1 123 K and samples furnace-cooled to room temperature are shown in Fig. 5. It shows the tendency that grain size of sample quenched at...
1123 K is finer than those of samples furnace-cooled to room temperature at the same concentration of Sn due to the grain growth below 1123 K during cooling. It is interesting that the difference of grain size between sample quenched at 1123 K and that furnace-cooled to room temperature at low Sn concentration is quite large than that at high Sn concentration. That means the grain growth tendency after γ/α transformation is suppressed to some extent in high Sn sample.

3.2. Effect of Sn on Sulfide Precipitation

Samples D1, D2 and D3 are prepared to investigate the effects of Sn on MnS precipitation in steel; while samples E1, E2 and E3 are for the effects of Sn on the competition precipitation of MnS and CuS in steel.

Two kinds of sulfide are observed in sample D1: coarse one and fine one. Most of the coarse sulfides in sample D1 are spherical and larger than 2 μm and they are mainly MnS. They usually show a net-like profile as shown in Fig. 6(a), which means these sulfides are formed along the last solidified zone on solidification. Some fine sulfides, usually less than 1 μm, are also observed in sample D1 (Fig. 6(c)). They are obviously precipitated from solid phase after solidification at lower temperature.

The coarse sulfides in samples D2 and D3 are less in amount than that in sample D1. These coarse sulfides are also formed at the last solidified zone but they usually could not patch up a continuous net-like profile as shown in Fig. 6(d). On the other hand, the fine sulfides in samples D2 and D3 increase in amount compared with in sample D1. That means Sn in steel could suppress sulfide precipitation at high temperature and promote it at low temperature.

In sample E3, the amount of coarse sulfide also decreases while fine sulfide increases compared with those in sample E1 as shown in Fig. 7. In addition, the EDS analysis based on extraction replica specimens shows that the main composition of fine sulfide in sample E1 is MnS including some CuS and FeS; while in sample E3 it is mainly CuS including some FeS and less MnS as shown in Fig. 8.

Tin is a well known ferrite stabilizing element and has a great effect on the phase transformation temperature. According to the Fe–Sn phase diagram, Sn decreases the liquidus and solidus of iron and also has a great effect on A4 and A3 temperature. Since Sn segregates very easily during solidification, it may have a greater effect on the local transformation temperature compared to that at the equilibrium state.

A lot of manganese sulfide particles with a large size are observed in low Sn sample while few are in high Sn sample. Tin may exert some influences on these sulfides formation due to its effect on the phase transformation temperature and the growth behavior of sulfide. The addition of Sn could decrease the liquid/solid transformation temperature, while enlarge the temperature range between liquidus and solidus. As we know, most of coarse MnS particles usually precipitate at the last stage of solidification due to redistribution of S and Mn between liquid and solid phases on solidification. The decrease of liquidus and solidus will also result in MnS particles precipitation at lower temperature. Lower precipitation temperature means lower growth speed after precipitation. In addition, the enlargement of the tem-
perature range on solidification will increase the total solidification time, which will provide more time for S and Mn to diffuse back into solid phase on solidification. More time for back diffusion gives less segregation of S and Mn at the last solidified zone, which will decrease the amount of MnS precipitated at the last solidified zone. That means the addition of Sn in steel decreases the precipitation temperature and the amount of coarse MnS precipitated on solidification.

The sulfides in E1 and E3 have quite different compositions besides the difference in size as shown in Figs. 7 and 8. As discussed in previous papers,8,9) MnS has advantages in precipitation at high temperature, while Cu$_2$S does at low temperature. Since Sn could suppress sulfide precipitation at high temperature, it seems reasonable that the main composition of sulfide in E1 sample is MnS while in E3 sample it is Cu$_2$S.

3.3. Interaction between Sn Micro-segregation and Sulfide Precipitation

The distribution of Sn in G1 and G2 samples, the latter of which contains sulfide forming elements and the former of which does not contain, are investigated by EPMA. Figure 9 shows the distribution of concentration of Mn, Cu, Sn and S elements. For both samples of G1 and G2, most of these elements are rich in the inter-dendrite region, and the dots with high concentration of elements portray the sketch of dendrite structure. That means the main micro-segregation of solute elements in the as-cast sample is caused during the liquid/solid transformation process, although there are several solid phase transformations after the solidification.

Parameters $K_1$ and $K_2$, which are defined as the following equation, are used to evaluate the micro-segregation degree of Sn in the present paper.

\[
K_1 = \frac{C_{\text{Sn,i}} - C_{\text{Sn,mean}}}{C_{\text{Sn,mean}}} \quad (1)
\]

\[
K_2 = \frac{C_{\text{Sn,max}} - C_{\text{Sn,min}}}{C_{\text{Sn,mean}}} \quad (2)
\]

where $C_{\text{Sn,i}}$ is the concentration of Sn for point $i$; $C_{\text{Sn,mean}}$ is the mean concentration of Sn for all the 512×512 points; $C_{\text{Sn,min}}$ and $C_{\text{Sn,max}}$ are the minimum and maximum concentration of Sn in the 512×512 points. The higher the value of $K_2$ and the absolute value of $K_1$ become, the more serious the micro-segregation of Sn in steel is.

Figure 10 shows the Relative Cumulative Frequency (RCF) vs. $K_1$ and $|K_1|$ in G1 and G2 samples. The concentrations of Sn for analyzed points in G2 sample are closer to the mean value than those in G1 sample, which shows that the segregation degree of Sn in G2 sample is lower than that in G1 sample.

This tendency is also supported by the data listed in Table 2, where it is shown that the micro-segregation degree evaluated by $K_2$ in G2 sample (5.01) is also lower than that in G1 sample (7.17). In addition, the concentration range, that is the difference between $C_{\text{Sn,max}}$ and $C_{\text{Sn,min}}$ in G2 sample is lower than that in G1 sample as listed in Table 2.

That means the micro-segregation degree of Sn decreases in sample (G2) containing sulfide particles. Although the
Recently, S. Suzuki has examined the interfaces between precipitate/matrix has scarcely been systematically investigated. Tin is well known as a grain boundary segregation element which may modify secondary recrystallization of Si steel. However, interface segregation of Sn between precipitate/matrix may also have great significance for oxide metallurgy technology. Several mechanisms have been proposed for the phenomena that inclusion could accelerate the nucleation of IGF, such as (a) Inclusion surface acts as an heterogeneous nucleus site; (b) A dislocation intersecting the precipitate/matrix interface of a large Cu precipitate and particularly in the region where a dislocation appears to intersect the precipitate.

It seems reasonable that the segregation degree of Sn in a sample containing sulfide particles is reduced if Sn has some solubility in sulfide particles and segregates to the interface provided by sulfide particles. The area of these interfaces will greatly increase especially when the sulfide particles are fine.

Once Sn could segregate to the interface between sulfide/iron, this will also cause some influence on the sulfide growth after precipitation. The sulfide growth behavior could be described by Ostwald ripening model as the following equation:

\[ r_r^3 - r_0^3 = \frac{8\pi D[M] V_m}{9RT} \cdot t \]

where, \( r_r \) is the particle radius at time \( t \), \( r_0 \) is the particle radius at initial time, \( \sigma \) is the surface energy of the particle-matrix interface, \( D \) is the diffusivity of the relevant atomic species, \([M]\) is the concentration of the relevant atomic species in the matrix, \( V_m \) is the particle molar volume, \( R \) is the gas constant, and \( T \) is the temperature. We can observe either a low \( \sigma \) or low diffusion coefficients results in a low growth rate. The grain boundary energy in δ-Fe is decreased from 0.795 J/m² in pure Fe to 0.575 J/m² in Fe containing 0.086% P at 1723 K, it is also anticipated that Sn will decrease the interface energy between sulfide/iron. Although there are few data about the effect of Sn on interface energy between sulfide/iron, it is reasonable that the segregation of Sn to the interface between sulfide/iron will restrict the growth of sulfide to some extent.

The segregation of Sn to the interface between precipitate/matrix may also have great significance for oxide metallurgy technology. Several mechanisms have been proposed for the phenomena that inclusion could accelerate the nucleation of IGF such as (a) Inclusion surface acts as an inert surface for nucleation and therefore large inclusions are potent sites; (b) Matching between ferrite and inclusion lattice will decrease the interfacial energy between inclusion and ferrite in comparison with inclusion–austenite interface; (c) Local depletion of austenite stabilizing elements such as carbon and/or manganese which might lead to an increase in driving force for nucleation of ferrite from austenite; (d) Strain energy near the inclusion may increase due to differences in thermal expansion between austenite and inclusion, which might reduce the activation energy for
nucleation. However, the above mechanisms could not satisfactorily explain all the phenomena that inclusion could accelerate the nucleation of IGF.

As discussed above, Mn-depleted zone around inclusion is thought to be one of the main reasons that the inclusion could accelerate the nucleation of IGF. Mn-depleted zone could play such role since Mn is an austenite stabilization element. In Mn-depleted zone, the austenite/ferrite transformation temperature is increased and then transformation could start at higher temperature. People have paid a lot of attention on element-depleted zone, such as Mn-depleted zone, B-depleted zone and C-depleted zone, but surprisingly little attention has been paid on the element-rich zone. For example, P and Sn, which are strong ferrite stabilization elements, are easily to segregate to interface such as grain boundary and the one between particle and matrix. Then a P-rich zone or Sn-rich zone may be formed in the grain boundary and the one between particle and matrix. The local austenite/ferrite transformation elements, are easily to segregate to interface such as precipitation are investigated. Tin is shown to suppress manganese sulfide precipitation at high temperature while promote copper sulfide precipitation with a finer size at low temperature. These effects may result from the effects of Sn on phase transformation temperature and the growth behavior of sulfide. The segregation degree of Sn in steel containing sulfide particles is reduced, which may be due to the fact that Sn has some solubility in sulfide particles and sulfide particles provide more interfaces for Sn to distribute.

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