Growth Rate of Copper Sulfide Precipitates in Solid Low Carbon Steel

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(Received on May 13, 2014; accepted on September 11, 2014)

The kinetics of copper sulfide growth has been investigated using low carbon steel samples such as Fe-0.3mass%Cu-0.03mass%S-0.1mass%C and Fe-0.1mass%Cu-0.01 mass%S-0.1mass%C. The samples were heat-treated at 1 273, 1 423 and 1 573 K for 100 s – 14.4 ks for precipitation of copper sulfides and then subjected to observation by a scanning electron microscope (SEM) and a transmission electron microscope (TEM) to measure the size of copper sulfides precipitated in the samples. The growth kinetics of copper sulfides has been found to be well described by the Ostwald ripening model, as follows:

\[ R_t^3 - R_0^3 = (k_O / T) t \]

where \( R_t \) and \( R_0 \) are the radii of copper sulfide precipitates, respectively, at \( t = t \) and \( t = 0 \) where \( t \) is time, \( k_O \) is the rate constant in this model and \( T \) is thermodynamic temperature. The diffusion coefficients and activation energy derived from values of \( k_O \) are close to those of copper in austenitic iron. On the basis of the growth kinetics, it has been proposed that the heat-treatment for as-cast strip steel should be conducted at around 1273 K, at which the size of copper sulfide precipitates can be controlled to be as small as 20–30 nm in several tens of minutes.

KEY WORDS: copper sulfide; precipitation; impurity; strip casting; low carbon steel.

1. Introduction

Growing attention has been paid to the steel production from steel scrap in the respect that it yields less energy consumption and lower environmental impact compared with the ironmaking process by blast furnace. However, steel scrap usually contains a considerable amount of impurities such as copper; furthermore, repeated use of steel scrap gradually increases the concentrations of impurities. These impurities have harmful effects on recycled steel. First, copper in steel deteriorates steel toughness. Second, much worse, selective oxidation of iron forms iron oxide called “scale” on the surface; resultantly, a copper-condensed liquid phase appears around the interface between scale and steel, and finally penetrates into grain boundaries of the iron matrix. This penetration of liquid copper results in development of cracks around the steel surface during the rolling process. This phenomenon is termed ‘surface hot shortness’ by copper.1–3)

This problem due to copper is very difficult to be solved because it is in actuality impossible to remove copper during the steel refining process. The main reason is that copper is nobler than iron and cannot be eliminated by oxidation. Thus, another measure is required and, for instance, it has been proposed to add nickel, which can prevent surface hot shortness inasmuch as nickel helps copper to be occluded into the scale6) and also raises the melting point of the copper-condensed phase. However, this process costs more since nickel is expensive, moreover, nickel behaves as tramp element and is accumulated in steel as well as copper.5) Silicon and boron have also been found to be effective to suppress surface hot shortness probably due to their effects on morphology and/or physical property of the copper-condensed phase6,7) although the effects have not been well clarified up to now.

Apart from additions of elements, rapid solidification and cooling processes such as strip casting can be one of the approaches to solve the copper problem. Rapid solidification can suppress the formation of liquid copper and then prevent surface hot shortness.9) In addition, copper reacts with sulfur dissolved in scrap steel and precipitates in the form of copper sulfide in the casting process.9) This formation is favorable to conduct the strip casting without surface hot shortness by copper. There have been three findings reported regarding the precipitation of copper sulfides. First, this precipitation inevitably occurs even if the concentration of copper in steel is lower than 0.01 mass% which level is almost the same as that for impurity copper in common steel.10) Second, copper sulfides are classified mainly into three types11) as follows:
1. Plate-like copper sulfide (PS)
2. Shell-like copper sulfide (SS)
3. Nano-scale copper sulfide (NS)
Third, the morphology strongly affects the mechanical

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property of steel. In particular, NS copper sulfide is known to increase yield strength by precipitation hardening rather than grain refinement.\(^{12,13}\) As-cast strips have higher work hardening ability than heat-treated strips in case steel contains a little amount of copper and sulfur.\(^{13}\) The reason has been reported as follows: nano-size copper sulfide is precipitated in as-cast strip and, by heat-treatment, the precipitate grows to have the mean size ten times larger than that in as-cast strip. This difference in precipitate size would dominate work hardenability.

To improve the recycling capacity of steel scrap by strip casting, the stability and growth rate of copper sulfides should be better understood because the precipitates gradually grow by heat-treatment, which results in the decrease in the mechanical properties of steel after the casting process. On the basis of these backgrounds, the present work aims to investigate the growth rate of copper sulfide precipitates in steel to propose a suitable heat-treatment condition after strip casting.

2. Experimental

2.1. Sample Preparation

Table 1 shows the chemical compositions of two steel samples used in the present work: it is noted that sample 1 contains higher concentrations of copper and sulfur than sample 2 and that these concentrations of copper and sulfur do not exceed the respective solubilities\(^{14,15}\) in each sample. These samples were prepared from electrolytic iron plates (99.99 mass% purity), copper granules (99.5 mass% purity), FeS powders (99 mass% purity) and carbon-saturated iron lumps (Fe-3.36 mass% C), the last being prepared by pre-melting the iron plates and graphite powders (99.7 mass% purity) in an alumina crucible. Sample 1 was employed for easier identification of copper sulfide precipitates, while sample 2 was for simulating copper sulfide growth in the practical operation condition.

Figure 1 shows the thermal history of heat treatments. The horizontal and vertical axes represent holding time and temperature for heat-treatment, respectively. Mixtures of starting materials as above were placed in alumina crucibles and heated up to 1873 K for 1 h in a flow of argon. After melting, the samples were water-quenched and cut into small pieces. For precipitation of copper sulfides, sample 1 was heated up again to 1273 K for 100 s, 900 s, 3.6 ks and 14.4 ks in an alumina crucible; in the same manner, sample 2 was also heated up again to 1273, 1423 and 1573 K.

2.2. Microscope Observation

2.2.1. SEM Analysis

The size of copper sulfide precipitates was determined using a scanning electron microscope (SEM) for sample 2. Specimens for SEM observation were cut and embedded in polyester resin and then were polished with alumina abrasives having particle sizes from 0.1 to 3 μm. The SEM used was coupled to a back scattered-electron detector and operated at the accelerating voltage of 10–15 kV to obtain high resolution performance.

2.2.2. TEM Analysis

The chemical compositions of precipitates were determined by a transmission electron microscope (TEM) for sample 1. Specimens for TEM observation were cut into pieces about 3 mm thick. These specimens were abraded sequentially using 200, 400, 600, 900, 1200, 2400 and 4000 grit SiC papers with a motor driven disc polisher and were further polished sequentially using 9 and 1 μm grade diamond pastes. Subsequently, the specimens were etched by 10 vol% acetylacetone–1 vol% tetramethylammonium chloride–methyl alcohol (AA electrolyte solution). Carbon extraction replicas were also prepared through the standard procedure. Finally, specimens were etched again by AA electrolyte solution. The replicas were floated on nickel grids and a molybdenum double tilt specimen holder was used. The TEM was operated at 200 kV and was coupled to an energy dispersion spectrometer (EDS). EDS analysis was
performed with high-resolution and high-speed regarding the four elements, namely, Fe, Cu, S and O, and mapping images were obtained within 5 min.

3. Results

3.1. Morphology and Chemical Compositions of Copper Sulfide and Oxide Phase

Figure 2 shows SEM images of samples 1 heat-treated at 1273 K for 0 – 14.4 ks. SEM images of the matrix seem different because the surface condition of the sample was strongly influenced by treatment for SEM observation like polishing, washing and Au coating. There exist precipitates having different shapes and sizes. These precipitates can be classified into three types: iron oxide, shell-like copper sulfide covering inclusions (SS) and nano-scale copper sulfide (NS). Figures 3 and 4 show morphology and chemical compositions of SS and NS precipitates observed by TEM, respectively. Precipitate SS is copper sulfide covering iron oxide having about 1 μm diameter. The chemical composi-
tions of iron oxide is approximately Fe–30mol%O, which is probably a reflection of the presence of both iron and Fe$_{1-x}$O, while copper sulfide precipitate seems Cu$_{1.6}$S or Cu$_{1.8}$S according to the concentration ratio of copper to sulfur from EDS analysis. This composition of copper sulfide is similar to those previously reported by other researchers.$^{16-18}$ On the other hand, there are also NS precipitates observed in the sub-micron meter size. Precipitate NS seems different from SS in size and morphology but their chemical compositions are close to each other. According to the previous reports,$^{17,18}$ NS is considered to be Cu$_{1.8}$S.

3.2. Growth Rate of Copper Sulfide at 1 273–1 573 K

Figures 5 and 6 show SEM images of samples 2 heat-treated for 0 – 14.4 ks at 1 273 and 1 573 K, respectively. These samples contain almost the same types of precipitate: iron oxide, SS copper sulfide and NS copper sulfide as observed in Figs. 3 and 4. Figure 7 shows a relationship between holding time and weighed average radius of NS precipitates with the standard deviation as the error bars. These data have been obtained from 20 of the largest precipitates in the SEM image of some photographs having the area from 4.26 to 17.04 μm$^2$. The size of NS precipitates increases with holding time. In addition, as the heat-treatment temperature is higher, the size is larger and the number of precipitates is smaller compared with Figs. 5 and 6. In the present experimental conditions investigated, the number of precipitates is the largest in case of heat-treatment for 14.4 ks at 1 273 K, and the size of precipitates is the largest in case of heat-treatment for 14.4 ks at 1 573 K. Precipitate NS obtained by heat-treatment for 14.4 ks at 1 573 K is comparable to those produced by Liu et al.$^{12}$ In their report, the size of copper sulfide precipitates provided by heat-treatment for 10.8 ks at 1 473 K ranged from 100 to 800 nm and the mean size was about 200 nm. The mean size of NS precipitates in the present work is about 140 nm.

4. Discussion
4.1. Application of Ostwald Ripening Model to Copper Sulfide Precipitation

The Ostwald ripening model has widely been employed to describe the growth rate of precipitates in a solid matrix. Liu et al.$^{19}$ have also applied this model to the growth of NS precipitates in iron to predict their size distribution. According to the Ostwald ripening model, radius $R_t$ of precipitates can be expressed by the following equation:$^{20}$

\[
R_t = R_0 e^{kt}
\]

Where $R_0$ is the initial radius of the precipitate, $k$ is the growth rate constant, and $t$ is the holding time. Fig. 7 shows the relationship between holding time and radius of NS copper sulfide precipitates.

![Radius of NS copper sulfide precipitates vs holding time.](image)
where $k_0$ (m$^3$/s) = $8\sigma D[M]/V_m^9 R$, which represents the rate constant in this model, $\sigma$ is the interfacial energy between copper sulfide and iron, $[M]$ is the mole fraction of copper in iron and $V_m$ is the molar volume of copper sulfide. Figure 8 shows the relationship between holding time and values of the left-hand side of Eq. (1). The value of $(R^3_t - R^3_0)$ is also in linear proportion to holding time. Rate constants $k_0$ derived from the slope of the linearity are 2.8 x $10^4$ nm$^3$K/s at 1573 K, 9.6 x $10^3$ nm$^3$ K/s at 1423 K and 2.5 x $10^2$ nm$^3$K/s at 1273 K.

The Arrhenius relation is applied to the values of $k_0$, resulting in Fig. 9 showing the relationship between reciprocal of temperature and logarithm of $k_0$ in the temperature range from 1273 to 1573 K, in comparison with a value of $k_0$ derived from data reported by Liu et al.\textsuperscript{12)} These data are also in consistent with each other. The activation energy has been derived as 264 kJ/mol from the slope of the straight line, which value is in very good agreement with the activation energy reported for copper diffusion in austenitic iron, 272 kJ/mol.\textsuperscript{19)}

The diffusion coefficient is also calculated from the relationship $k_0 = 8\sigma D[M]V_m^9 R$ according to a previous work.\textsuperscript{19)} The interfacial tension between copper sulfide and \gamma-Fe is taken as 0.83 N/m. This value was basically measured for 1073 K; however it is now assumed to be constant because the temperature coefficient of interfacial tension between Fe and Cu$_2$S is small, ranging from $-0.61 \times 10^{-3}$ N/mK\textsuperscript{21)} to $-0.09 \times 10^{-3}$ N/mK.\textsuperscript{22)} The molar volume of copper sulfide is $2.75 \times 10^{-5}$ m$^3$/mol\textsuperscript{19)} at 1073 K and the mole fraction of copper in the matrix is $8.79 \times 10^{-4}$ from the chemical composition. Table 2 gives values of diffusion coefficient derived from values of $k_0$. The diffusion coefficients from the Ostwald ripening model are in very good agreement with those of copper in austenitic iron, indicating that the growth rate of copper sulfide precipitates is dominated by copper diffusion. These agreements in the activation energy and diffusion coefficient conclude that the Ostwald ripening model can well describe the growth of copper sulfide precipitates in iron. This would be because the Ostwald ripening requires driving force as small as interfacial energy.

4.2. Suggestion to Heat-treatment Conditions After Strip Casting

On the basis of the growth rate of copper sulfide, it is proposed that the heat-treatment should be conducted at around 1273 K to give the good mechanical property to as-cast strip steel because copper sulfide precipitates grow as small as 20–30 nm in several tens of minutes. Control of the size of copper sulfides leads to formation of many copper sulfide precipitates at around 1273 K, as can be seen from Fig. 5. Figure 10 shows the time-temperature-precipitate curves of copper sulfides and manganese sulfides\textsuperscript{18)} reported by Sakai et al., who have investigated these sulfides by analyzing their amounts in samples of Fe-0.06mass%Mn-0.17mass%Cu-0.027mass%S heat-treated after solution.

### Table 2. Diffusion coefficients of copper in austenitic iron (m$^2$/s$^{-1}$).

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>Ostwald ripening model</th>
<th>Reported data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1573 K</td>
<td>$1.27 \times 10^{-14}$</td>
<td>$1.72 \times 10^{-14}$</td>
</tr>
<tr>
<td>1423 K</td>
<td>$4.24 \times 10^{-15}$</td>
<td>$1.92 \times 10^{-15}$</td>
</tr>
<tr>
<td>1273 K</td>
<td>$1.16 \times 10^{-16}$</td>
<td>$1.27 \times 10^{-16}$</td>
</tr>
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Fig. 8. ($R^3_t - R^3_0$) of NS copper sulfide precipitates vs holding time.

Fig. 9. Arrhenius plot based on Ostwald ripening model.

Fig. 10. Time-temperature-precipitation curves of Cu$_2$S and MnS (a/b = [S in MnS (ppm)]/[S in Cu$_2$S (ppm)]).\textsuperscript{18)
treatment. This figure indicates that the nose of copper sulfide precipitation exists at around 1 273 K, where copper reacts with sulfur in iron to produce more nano-scale copper sulfides than at any other temperatures, and supports Fig. 5 in the present work. However, the trade-off between the size and number of copper sulfide precipitates needs to be optimized to keep the mechanical properties of heat-treated strip as good as that of as-cast strip. Further work will be required for this optimization.

5. Conclusions

The growth rate of copper sulfide precipitates in solid low carbon steel has been investigated at temperatures from 1 273 to 1 573 K. Findings are summarized as follows:

- The growth rate of the precipitates can well be described by the Ostwald ripening model and expressed by the mathematical form

\[ R_t^3 - R_0^3 = (k_0 / T)t \]

The rate constants \( k_0 \) are 2.8 \( \times \) 10^4 nm^3 K/s at 1 573 K, 9.6 \( \times \) 10^3 nm^3 K/s at 1 423 K and 2.5 \( \times \) 10^2 nm^3 K/s at 1 273 K.

- Applying the Arrhenius relation to the rate constants has given the activation energy of copper diffusion as 264 kJ/mol. The diffusion coefficients have also been calculated from the rate constants, as given in Table 2. Both the diffusion coefficients and the activation energy are in good agreement with those for copper diffusion in austenitic iron.

- On the basis of the growth rate of copper sulfide precipitates, it has been proposed that the heat-treatment for as-cast strip steel be conducted at around 1 273 K, at which copper sulfide precipitates grow as small as 20–30 nm in several tens of minutes, possibly leading to good balance between strength and ductility of steel.

Acknowledgments

The authors would like to express their gratitude to POSCO for providing TEM analysis and financial support. The authors also wish to thank National University Corporation Tokyo Institute of Technology, Center for Advanced Materials Analysis for their help to the analytical work.

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