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Superfine Ce Oxide-Induced Precipitation Behavior of Copper in Steel

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Abstract. Residual copper is gradually enriched in short steelmaking and produces copper crunch. To solve this problem, this study explores the influence of rare earth element Ce on copper precipitation behavior in steel. Chemical composition analysis, scanning electron microscopy, and EDS are used to characterize the phases. Results show that the inclusions MnS, Al2O3, Ce2O3, and Ce2O2S in steel play a role in inducing the heterogeneous nucleation and precipitation of copper elements. The amount of segregation at the grain boundaries is significantly reduced, and the inclusions remain in the matrix and are uniformly dispersed to reduce the copper crunch problem.

Scrap is the main metal raw material for short-process steelmaking. The recycling of scrap steel introduces harmful elements such as copper, tin, arsenic, and antimony. These residual elements constantly accumulate in steel and lead to scrap “garbage” [1-4]. The increase in copper in scrap is mostly pronounced, and residual copper is gradually enriched in steel, leading to hot brittleness during hot process [5-7] and easy segregation at the austenite grain boundary. Liquid copper-rich phase infiltrates along the grain boundary and forms copper oxide (cuprous oxide) with oxide, which is reduced to copper by the iron matrix, permeating oxidation grain boundaries to destroy the matrix [8-10]. Copper severely deteriorates the hot working properties of steel [11] and reduces the yield of materials. Hence, studies on the effect of typical inclusions MnS and Al2O3 and rare earth inclusions on heterogeneous nucleation of copper in steel for controlling the precipitation of copper and reducing thermal embrittlement are crucial.

1. Theoretical Analysis

Bramfitt [12] and Turnbull proposed a 2D mismatch based on a 1D mismatch, which can reflect the lattice matching of the substrate and the crystal nucleus better when the lattice structure is different.

\[ \delta_{(hkl)}^{(uvw)} = \sum_{i=1}^{3} \left[ d_{[uvw]} \cos \theta - \left( \frac{d_{[uvw]}}{d_{[uvw]}} \right) \right] / 3 \times 100\% \]

In the following form, (hkl) is a low surface index of the base, (hkl) is a low exponential surface for the crystalline phase, [uvw] is a low-index direction on the (hkl), class of crystal faces, [uvw] is a low exponential direction on the crystal surface (hkl) , d[uvw] is the atomic spacing along the [uvw] direction, d[uvw] is the atomic spacing along the [uvw] direction, and \( \theta \) is the angle between [uvw] and [uvw]. According to Bramfitt [12], in homogeneous nucleation, the core at \( \delta<6\% \) is the most effective, that at \( \delta=6\%–12\% \) is slightly effective, and that at \( \delta>12\% \) is invalid.
Given the strong affinity of rare earth elements with oxygen and sulfur, the existing forms of rare earth elements in steel are rare earth oxides, oxygen sulfides, and sulfides, whereas the form of copper in steel is mainly ε-Cu[13-15]. On the basis of MnS, Al2O3, Ce2O3, CeS, and Ce2O2S as nucleation basements and ε-Cu and Cu2S as nucleation phases, the validity of the method is calculated. The use of the abovementioned inclusions as particles for the heterogeneous nucleation of copper in steel is determined, and the calculation results are shown in Table 1.

|       | MnS | Al2O3 | Ce2O3 | Ce2O2S | CeS |
|-------|-----|-------|-------|--------|-----|
| ε-Cu  | 2.4 | 7.5   | 6.7   | 8.8    | 27.2|
| Cu2S  | 6.7 | 19.2  | 31.3  | 29.9   | 20.8|

Table 1 shows that MnS, Al2O3, Ce2O3, and Ce2O2S can be used as effective nucleation particles for ε-Cu. However, MnS is only the effective nucleation particle of Cu2S. Moreover, the ability of the other inclusions to become Cu2S nucleation particles is weaker than that of MnS.

2. Experimental Process and Research Method

Experimental raw materials for industrial use include pure iron, electrolytic pure manganese powder, pure copper, pig iron (carbon content 2.94 wt.%), electrolytic aluminum tablets, rare earth cerium, and experimental steel melted in medium-frequency induction furnace. The main chemical constituents are shown in Table 2.

| Sample | C   | S   | Cu  | Mn  | Ce  | Fe  |
|--------|-----|-----|-----|-----|-----|-----|
| S1     | 0.053 | 0.034 | 0.820 | 0.360 | 0.000 | balanced |
| S2     | 0.230 | 0.024 | 0.620 | 0.560 | 0.010 | balanced |
| S3     | 0.310 | 0.015 | 0.720 | 0.550 | 0.023 | balanced |
| S4     | 0.320 | 0.005 | 0.720 | 0.580 | 0.069 | balanced |

After completing casting, demolding, and sampling under an initial forging temperature of 1050 °C and final forging temperature of 850 °C, the steel ingot is forged into a Ф30 mm × 300 mm steel bar. The metallographic sample is prepared by wire spark cutting, inlaying, sanding, polishing, and corroding with 4% nitric alcohol solution. The ZEISS-SUPRA55 scanning electron microscope and energy spectrometer are used for observation and analysis.

3. Result Analysis and Discussion

3.1. Effect of Rare Earth Ce Elements on the Inclusions in Steel

After the addition of rare earth Ce element, the inclusions in the steel are obviously refined, made spherical, and increased in quantity [16]. To study the effect of rare earth elements on the distribution of inclusions, 50 different fields of view are randomly selected from two samples to observe their main distribution state, quantity, and form. The statistical results are shown in Figure 1.
In Figure 1, the inclusions in S1 samples without adding Ce are generally large, and about 50% or more of them have a particle diameter of more than 4 μm. In the S2 sample with Ce, the inclusion size is smaller than that of the S1 sample and concentrated in the 2–4μm interval. After adding Ce, the inclusions in steel are obviously refined, spherical, and high in quantity. The particle size of nearly half of the inclusions is at 2–3 μm, providing a large number of nucleation particles for the heterogeneous nucleation of residual copper elements in steel.

3.2. Induction of Heterogeneous Nucleation of Copper in Steel by Ultrafine Ce Oxide

The validity of the method is calculated based on MnS, Al₂O₃, Ce₂O₃, CeS, and Ce₂O₃S as nucleation basement and ε-Cu and Cu₂S as nucleation phase. The results show that MnS, Al₂O₃, Ce₂O₃, and Ce₂O₃S can be used as nucleation sites for ε-Cu. However, only MnS can become the effective nucleation particle of Cu₂S.

The EDS analysis in Figure 2 shows that spectrum 10 is Al₂O₃ and the copper content is 5.8%, which is far larger than the average content of 0.72% in the steel matrix. The matrix continues to cool down after the solidification of molten steel. When the temperature drops to the melting point of copper, the copper element begins to grow in the Al₂O₃ inclusion, where there is no obvious stratification between the two. On spectrum 11, its composition is analyzed as Al₂O₃ and MnS, and the content of copper is 9.9%, which shows that Al₂O₃ and MnS are mixed and precipitated together during solidification. When the temperature continues to drop to the melting point, copper solidifies and nucleation precipitation occurs.

Figure 3 shows that the contents of Ce, O, and S in point 36 are the highest. However, the atomic percentage is not strictly in accordance with Ce₂O₃S (i.e., 2:2:1) probably because the phase
The composition of each point is a mixed inclusion of Ce$_2$O$_3$ and Ce$_2$O$_2$S. Its content is 7.10%, which is far higher than the average copper content in sample 3 (0.72%). Thus, Ce$_2$O$_3$ and Ce$_2$O$_2$S of rare earth inclusions in steel induce the precipitation of copper heterogeneous nucleation. During the solidification of molten steel, copper precipitates around the rare earth inclusions, and a common mixture of rare earth inclusions and copper is formed.

![Figure 3. Morphology and energy spectrum analysis of the heterogeneous nucleation of inclusions](image)

3.3. Effect of Superfine Ce Oxide on the Distribution of Copper in Steel
Copper is highly prone to segregation in steel and easily precipitates at the grain boundary [17]. Given the redox reaction, iron copper oxide occurs in the matrix redox reaction during the solidification of molten steel. Copper and oxygen react to form copper oxide, which is reduced by iron to form copper. As the reaction continues and the grain boundary erodes, the matrix is destroyed. With ten points randomly selected for detection and the average value obtained to analyze the copper content, the data are shown in Table 3.

| Sample | Average (wt%) | Intragranular (wt%) | Grain boundary (wt%) |
|--------|---------------|---------------------|----------------------|
| S1     | 0.82          | 1.11                | 6.72                 |
| S2     | 0.62          | 0.90                | 2.92                 |
| S3     | 0.72          | 0.87                | 1.39                 |
| S4     | 0.72          | 0.76                | 0.92                 |

Table 3 shows that the Ce content increases with decreasing copper content in the grain boundary. When the Ce content in sample S4 is 0.72%, the copper content at the grain boundary is 0.92%. Compared with the grain boundary of sample S1, the copper content is reduced by 86.3%.

![Figure 4. SEM morphology and EDS surface sweep distribution of copper in sample S4](image)
Figure 4 shows that the randomly selected area of S4 sample is employed to test the distribution of copper, which is basically homogenized. Increasing Ce content results in a state of dispersion homogenization.

3.4. Effect of Ultrafine Ce Oxide on the Distribution of Copper in Hot Working Process

The hot working temperature of steel is determined by its composition. It ranges from 1000 °C to 1200 °C during which copper-containing steel is prone to cracks during hot working process [18-20]. Cracks are formed when the temperature reaches the melting point of copper, which forms a copper-rich phase between the substrate and oxide layer. Moreover, the redox reaction of iron, copper, and oxygen makes the grain boundary embrittlement crack.

In this experiment design, four sets of samples are heat treated at 1050 °C, 1100 °C, and 1150 °C for 1 h to observe the distribution of copper at high temperature. Figure 5 shows the distribution of copper at 1150 °C for each sample. For all samples, as the rare earth content increases, the copper distribution is gradually reduced on the boundary of the matrix and decreases in content.

Figure 5. Distribution of copper for each sample at 1150 °C

Figure 6. Distribution of copper content for each sample at different temperatures
Figure 6 shows the distribution of copper content at different temperatures for each sample. As the temperature rises, copper is heavily enriched on the boundary. When the temperature reaches the melting point of copper, copper is diffused to the boundary to form a copper-rich phase. At the same temperature, as the content of rare earth elements increases, the copper content on the boundary is greatly reduced. The copper content on sample S4 at the boundary under hot working treatment is the lowest at 1.8%, and its hot brittle tendency is also the lowest among the four samples. As a result of grain refinement and increased amount of grains, the number of grain boundaries increases, and the copper content decreases in the unit grain boundary to increase the solubility of copper in steel. Simultaneously, after the addition of rare earth elements, numerous fine inclusions in steel form, which induce the precipitation of copper to decrease its diffusion to the boundary.

4. Conclusion
(1) Theory of 2D lattice mismatch calculation shows that MnS, Al2O3, Ce2O3, and Ce3O5S can all become nucleation particles of residual copper in steel. Experiments reveal that the inclusions MnS, Al2O3, Ce2O3, and Ce3O5S in steel induce the heterogeneous nucleation and precipitation of copper. Moreover, they limit its segregation to the grain boundary and cause dispersed homogenization in the matrix.

(2) Rare earth inclusions produced by rare earth elements in steel provide a large number of nucleation particles for the heterogeneous nucleation of residual copper in steel, thereby inducing the precipitation of copper.

(3) After the addition of rare earth elements, the precipitation of copper changes. The precipitation of copper at the grain boundary is greatly reduced, resulting in distributed dispersion. The copper brittleness of steel can be alleviated during hot working processes.

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