Copper in steels causes a hot shortness problem and it is important to know copper behaviours during high temperature oxidation in order to control the enriched copper amount. In this paper, the effects of atmospheric conditions on the copper behaviours during oxidation of a steel containing 0.1% copper are investigated. Oxidation in a dry atmosphere with oxygen has the effect of decreasing the enriched copper concentration at the scale/metal interface and broadening the copper concentration at the same point. Copper evaporates through the scale when a steel containing copper is oxidized in a low oxygen concentration atmosphere with water vapour. The oxidation in the low oxygen concentration atmosphere reduces the amounts of enriched copper at the scale/metal interface.

KEY WORDS: high temperature oxidation; copper; hot shortness; scale; magnetite; wustite; evaporation; diffusion; atmosphere; water vapour; oxygen.

1. Introduction

Scrap recycling is a useful process from an environmental perspective. However, the recycling of steel scraps accumulates copper in steel resources, which is subsequently difficult to remove during the steelmaking processes and can cause a hot shortness problem during hot rolling processes. When steel slabs are reheated in furnaces, copper is enriched at the scale/metal interface and precipitated as liquid metal. Following the hot-rolling process, liquid copper penetrates into the steel grain boundaries and causes cracks at the steel surface.

However, the addition of certain elements can help solve this problem. Here, nickel is useful, which is attributed to its ability to increase the solubility of copper in $\gamma$-Fe, which reduces the precipitation of liquid copper at the scale/metal interface.\(^1\)\(^-\)\(^4\) The addition of nickel above a critical level also has the effect of copper occlusion in the scale.\(^5\) Moreover, the addition of silicon has also been beneficial with this problem.\(^6\)\(^-\)\(^7\) This addition reduces the likelihood of hot shortness\(^8\) and decreases the amount of precipitated copper by the occlusion of copper in the oxide scale.\(^7\) Meanwhile, it is reported that the addition of phosphorus, carbon, and boron are favourable elements for hot shortness, since these elements are thought to change the distribution of liquid copper in the scale, steel grain size, and the toughness of the steel grain boundary for the crack propagation.\(^7\)\(^-\)\(^9\)

Controlling the reheating conditions such as temperature and atmosphere, also have beneficial effects in resolving this problem. The reheating temperature, namely 1373 K, is most severe for hot shortness. At conditions of higher or lower temperatures, the sensitivity of surface cracks is reduced.\(^5\)\(^-\)\(^8\) In addition, the oxidizing atmosphere also has an impact; atmospheric water vapour increases the number of crack on the steel surface.\(^10\) The copper occlusion in the scale is operative above the critical temperatures.\(^5\)

It is important that copper distribution behaviours are understood when steel is oxidized. This author reported that copper is distributed in the magnetite layer and precipitates along wustite grain boundaries during scale formation.\(^11\) Hot shortness is suppressed if more copper is distributed inside a scale, while a scale structure formed at high temperatures is influenced by atmospheric conditions. During this study, the effect of atmospheric conditions of water vapour and oxygen concentration on copper distribution behaviour is investigated when a steel specimen containing copper is oxidized at high temperature.

2. Experimental Process

A section of steel containing about 0.1 mass% copper was used for the experiments, with the analyzed compositions of the material shown in Table 1. Specimens were cut to rectangular shapes of 30 mm × 30 mm × 4 mm and oxidation was performed in an infrared heating furnace, during which time mass gains were measured.

Experimental conditions were listed in Table 2. Condition 1 (moist low oxygen concentration) is a condition whereby the atmosphere contains oxygen and water vapour. This represents a basic condition under the following conditions and the results of this condition have been reported already.\(^11\) Condition 2 (dry air) meanwhile is an oxidation condition of dry air atmosphere, with a dew point of −22°C, while the atmosphere contains 0.09% water.
vapour. The conditions of 3-1, 3-2, 3-3, and 3-4 (moist oxygen to dry oxygen) are conditions whereby the influence of the water vapour effect plays a role. Under these conditions, samples were initially oxidized in the moist oxygen atmospheres and the atmosphere was changed to dry oxygen at the oxidizing temperature. Condition 4 (water vapour) and condition 5 (moist high oxygen concentration) are conditions obtaining an effect of oxygen. In condition 4, a single layer of wustite scale is expected to be formed, while copper migrates through wustite grain boundaries and volatilizes.11) In order to check copper volatilization a bell shaped quartz cover was set over a sample, as shown in Fig. 1.

Examinations of the oxidized specimen were performed using optical microscopy, electron probe micro analysis (EPMA), and X-ray diffraction (XRD), while the amounts of enriched copper at the scale/metal interface were obtained based on quantitative EPMA analysis. Copper amounts in scales are measured using a chemical analysis.11) Material placed on the inside of the bell shaped quartz cover was dissolved in aqua regia, while elements and their concentration were measured by an inductively coupled plasma spectrometer (ICP).

3. Results

3.1. Effect of Water Vapour

EPMA line analysis results of moist low concentration oxygen condition and dry air condition are shown in Figs. 2 and 3 respectively, of which the former has been already reported.11) Copper is distributed in the upper magnetite layer and enriches at the scale/metal interface in Fig. 2. The concentration of enriched copper at the scale/metal interface in dry air condition (Fig. 3) meanwhile is lower than that in moist low oxygen concentration condition (Fig. 2). In addition, a thick hematite layer with about 200 μm thickness is formed at the surface of the scale in the dry air condition (Fig. 3). These results indicate that oxidation in a dry air atmosphere reduces the enriched copper concentration at the scale/metal interface. The mass gains during these two experiments are shown in Fig. 4. The condition in dry air initially shows a higher oxidation rate, and the oxidation rate is then nearly saturated after 2 000 s.

Figure 5 shows the mass gain during the experiments of condition 3–4 (moist oxygen to dry oxygen). Following the atmospheric change from moist oxygen to dry oxygen, there is a sudden drop in the oxidation rate, which indicates

Table 1. Chemical composition of the steel containing copper.

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>sol:Al</th>
<th>N</th>
<th>Ti</th>
<th>B</th>
<th>Cu</th>
<th>Sn</th>
<th>Ni</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0020</td>
<td>0.009</td>
<td>0.067</td>
<td>0.012</td>
<td>0.0065</td>
<td>0.039</td>
<td>0.0020</td>
<td>0.037</td>
<td>0.0003</td>
<td>0.096</td>
<td>0.012</td>
<td>0.038</td>
<td>0.056</td>
</tr>
</tbody>
</table>

Table 2. Experimental conditions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Moist low oxygen concentration (1473K, 2%O₂+12%H₂O+86%N₂)×7200 s</td>
</tr>
<tr>
<td>2</td>
<td>Dry air (1473K, dry air)×7200 s</td>
</tr>
<tr>
<td>3-1</td>
<td>Moist oxygen to dry oxygen (1473C, 5%O₂+12%H₂O+83%N₂)×7200 s</td>
</tr>
<tr>
<td>3-2</td>
<td>Moist oxygen to dry oxygen (1473C, 5%O₂+12%H₂O+83%N₂)×7200 s</td>
</tr>
<tr>
<td></td>
<td>+(1473C, 5%O₂+95%N₂)×600 s</td>
</tr>
<tr>
<td>3-3</td>
<td>Moist oxygen to dry oxygen (1473C, 5%O₂+12%H₂O+83%N₂)×7200 s</td>
</tr>
<tr>
<td></td>
<td>+(1473C, 5%O₂+95%N₂)×1200 s</td>
</tr>
<tr>
<td>3-4</td>
<td>Moist oxygen to dry oxygen (1473C, 5%O₂+12%H₂O+83%N₂)×7200 s</td>
</tr>
<tr>
<td></td>
<td>+(1473C, 5%O₂+95%N₂)×1800 s</td>
</tr>
<tr>
<td>4</td>
<td>Water vapour (1473K, 12%H₂O+88%N₂)×7200 s</td>
</tr>
<tr>
<td>5</td>
<td>Moist high oxygen concentration (1473K, 80%O₂+12%H₂O+8%N₂)×7200 s</td>
</tr>
</tbody>
</table>
that a dry oxygen atmosphere reduces the oxygen rate. The copper profiles at the scale/metal interfaces in experiments 3-1 to 3-4 are shown in Fig. 6. The peaks of copper concentration are sharp after the moist oxygen oxidation and after 600 s of dry oxygen oxidation after moist oxygen oxidation, while broadening after 1200 s of dry oxygen oxidation. However, the copper amounts at the scale/metal interfaces, obtained by integration of these peaks, are almost the same values. These results indicate that oxidation in a dry oxygen atmosphere causes enriched copper at the scale/metal interface to diffuse into the metal inside.

3.2. Effect of Oxygen

The pictures of the bell shaped quartz covers set over the sample oxidized under water vapour conditions are shown in Fig. 7. One is the picture before the experiment and the other is that afterwards. The quartz cover becomes red colour after the oxidation in water vapour condition. The analyzed results of the red stuff inside the cover are shown in Table 3. It contains copper and iron. The XRD on the surface of the oxidized sample detects only wustite, while the quartz cover set over the sample, under conditions of moist high concentration oxygen, remains transparent and a small amount of copper is detected inside the quartz cover (Table 3). Under this high concentration oxygen condition, a three layer scale with hematite, magnetite, and wustite is formed, which indicates that copper easily evaporates through the wustite scale formed in a water vapour atmosphere and that the hematite layer reduces the copper evaporation.
4. Discussion

4.1. Effect of Water Vapour

Following the change to dry oxygen, the enriched copper amount remained constant but the concentration profile becomes low and broad (Fig. 6), while the oxidation rate decreases after the atmosphere change (Fig. 5). These results are derived based on the assumption that a slowdown in the oxidation rate stops the scale/metal interface movement and the copper starts to diffuse inward into the metal. This decrease in the oxidation rate within a dry oxygen atmosphere was reported.\(^\text{12,13}\) In these cases, the wustite layer disappears and thick hematite and magnetite scale are formed,\(^\text{12,13}\) which is explained by the scale losing contact with the metal.\(^\text{13}\) Meanwhile, the mass gain after the change to dry oxygen in condition 3–4 (Fig. 4) is thought to be caused by the oxidation of wustite to magnetite.

In order to verify the assumption, copper diffusion behaviour is numerically simulated. This calculation simulates oxidation and copper diffusion and two kinetics regions are considered in oxidation. In a moist oxygen atmosphere, the oxidation rate follows the parabolic rate law, whereas in a dry oxygen atmosphere, oxidation is stopped.\(^\text{12,13}\) We give the condition of 7 200 s oxidation in a wet atmosphere, followed by 1 800 s of dry atmosphere oxidation. Iron is oxidized and the alloying element of copper remains as metal copper at the scale/metal interface during the oxidation. The copper concentration at the scale/metal interface is retained at the value of the upper limit of copper solution in γ-Fe, which is about 10\% at 1 473 K. Copper tends to diffuse into the metal but the interface also moves inward as oxidation takes place. Less copper diffuses inward at a higher oxidation rate and vice versa. The basic equation of copper diffusion, iron oxidation rate, and the initial and boundary conditions are shown below.

**Oxidation**

\[
\text{Oxidation rate } w = \sqrt{k_p t} \quad (0 \leq t \leq 7 200 \text{ s})
\]

\[
k_p = 6.5 \times 10^{-6} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1} \quad \text{(at 1 473 K)}
\]

**Copper diffusion**

\[
\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2}, \quad C \leq C_{\text{max}} \\
(x > X, t > 0)
\]

**Initial condition**

\[
C = C_i \quad \text{and} \quad X = 0 \quad (t = 0)
\]

**Boundary condition**

\[
\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2} + \frac{M_{\text{Fe}}}{M_{\text{O}}} \frac{dw}{dt} C \\
(x = X)
\]

**Interface movement**

\[
X = \frac{M_{\text{Fe}}}{\rho_{\text{Fe}} M_{\text{O}}} w \quad (t > 0)
\]

Here,

- \(w\): mass gain
- \(k_p\): parabolic constant
- \(x\): distance
- \(X\): distance of scale/metal interface from the original surface
- \(t\): time
- \(C\): copper concentration
- \(C_{\text{max}}\): maximum copper concentration in γ-Fe
- \(C_i\): initial copper concentration in steel
- \(D\): diffusion coefficient of copper
- \(M_{\text{Fe}}\): atomic weight of iron
- \(M_{\text{O}}\): atomic weight of oxygen

---

Table 3. Measured elements and their amounts on the quartz cover used in the experiment of condition 4 (water vapour atmosphere) and condition 5 (moist high oxygen concentration atmosphere). The amounts are divided by the sample surface areas.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condition 4</td>
<td>31 mg</td>
<td>13 mg</td>
</tr>
<tr>
<td>Condition 5</td>
<td>2 mg</td>
<td>4 mg</td>
</tr>
</tbody>
</table>

Fig. 7. The pictures of the bell shaped quartz cover, which is set over the sample in water vapour atmosphere condition. (a) Before the experiment. (b) After the experiment.
\( \rho \): density of iron

The calculation results are shown in Fig. 8. Copper is distributed near the scale/metal interface with a sharp peak because the scale/metal interface movement is faster than the diffusion rate of the copper inward metal during oxidation in the wet atmosphere. The concentration at the scale/metal interface reaches 10% of the maximum copper concentration in \( \gamma \)-Fe, even at 10 min oxidation. Once the oxidation stops, which simulates dry atmosphere oxidation, the interface movement does the same and copper diffuses inward the metal, whereupon the copper peak becomes low and broad. This result serves to positively explain the copper concentration profile (Fig. 6).

This suggests that holding oxidized steel in a dry oxygen atmosphere after scale formation is beneficial for the problem of hot shortness. The holding makes enriched copper at the scale/metal interface diffuse into metal. Hatano et al.\(^\text{10}\) reported that oxidation in air atmosphere suppresses hot shortness compared to oxidation in a moist oxygen atmosphere via high temperature tensile tests, while the result shown in Fig. 6 is similar to their result. They explained that air atmosphere oxidation makes an uneven interface, which differs from the explanation here.

4.2. Effect of Oxygen

The experiment shown in Fig. 7 and Table 3 indicates that copper evaporates through the wustite scale. Liquid copper is considered to migrate through the grain boundaries of wustite scale, due to the effective wettability between liquid copper and wustite (Fig. 9(a)). The liquid copper reaches the scale surface and evaporates as copper gas, as previously estimated.\(^\text{11}\) On the other hand, the hematite grain does not contain copper\(^\text{11}\) and reduces copper evaporation (Fig. 9(b)).

The mass balance of copper is also considered. Figure 10 shows the excluded coppers by oxidation, enriched coppers at the scale/metal interfaces, and coppers in scales. Excluded copper amounts by oxidations were obtained by mass gain during the experiments, while evaporated copper amounts are not shown on the graph because the quartz cover method does not catch all evaporated copper. The enriched copper amount at the scale/metal interface is less than 20% of excluded copper by oxidation. A lower oxygen concentration in the atmosphere, means less copper is enriched at scale/metal interfaces, and one reason is because the low oxygen atmosphere forms a thin oxide scale. The other is that a greater amount of copper evaporates under conditions of a lower oxygen atmosphere.

This study suggests two possible methods for hot shortness suppression. One is that steel is reheated in a lower oxygen concentration atmosphere, where the excess air ratio is closer to one, which decreases the enriched copper amount at the scale/metal interface. The other is that reheated steel is hold in dry air before rolling, which causes enriched copper at the scale/metal interface to diffuse into the metal inside.

5. Conclusion

This study examines the effects of atmospheric conditions on enriched copper at the scale/metal interface during high temperature oxidation of a steel containing copper. The following conclusions are drawn:

(1) Long time oxidation in a dry atmosphere with oxygen makes oxidation rate slow. It has the effect of reducing the enriched copper concentration at the scale/metal interface and broadens the copper concentration profile at the scale/metal interface.

(2) One layer of wustite scale is formed and copper evaporates through the scale when a steel containing copper is oxidized in low oxygen concentration atmosphere with
water vapour. It reduces the amount of enriched copper at
the scale/metal interface.

REFERENCES
9) Nagasaki, H. Uchino, K. Shibata, K. Asakura and M. Hatano: Tetsu-
to-Hagané, 89 (2003), 332.