Copper Enrichment Behaviours of Copper-containing Steels In Simulated Thin-slab Casting Processes

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The copper enrichment behaviours of several copper-containing steels under conditions similar to those in the thin-slab casting processes are examined. Formation of a molten copper phase at the scale–steel interface can be avoided when the substrate phase is occluded in the scale during steel oxidation. Significant enrichment of nickel in the surface layer of the substrate is a necessary condition for the occlusion of the substrate phase into the scale before the precipitation of a molten copper phase. The critical nickel content above which the occlusion mechanism would be operative is between 0.02 % and 0.07 %. The critical temperature above which the occlusion mechanism becomes operative in the high nickel steels differs when the isothermal oxidation step, following continuous cooling in ambient air, is conducted in different atmospheres. When conducted in ambient air, this temperature is between 1 150°C and 1 230°C, whereas when conducted in moist air or in simulated furnace atmospheres, it is lowered to between 1 100°C and 1 150°C. Preferential oxide growth along the grain boundaries of the substrate is another important occlusion mechanism, however, the deep oxide penetrations in the substrate may lead to descaling difficulty.

KEY WORDS: surface hot shortness; occlusion; steel oxidation; copper; nickel; thin slab casting.

1. Introduction

World crude steel production has reached a new record in 2003 at 945 million metric tons (mmt), an increase of 6.7 % as compared to the annual production in 2002.1) World steel demand in the medium term is projected to increase continuously from 831 mmt in 2002 to 1 041 mmt in 2007. 2) This development is primarily driven by the continuing increase of steel demand in China, estimated from 211 mmt in 2002 to 290 mmt in 2004, and 355 mmt in 2007.2) With the continuing growth in steel demand, the steel industry world-wide is moving rapidly towards increased production through electric arc furnace (EAF) mini mill production.3) The mini mill sectors originally focused on long steel products, but due to the recent rapid development in the thin slab casting technology, its market share in flat product is also increasing.4) Currently, it is estimated that over 45% of the steel products are produced through the EAF mini mill route, and over 20% of the flat products are produced using the EAF–thin slab casting technology.5) An EAF mini mill uses returned steel, steel scraps, and direct reduced iron (DRI) to make steel. Because of the use of steel scraps, impurities are inevitably brought into the steel. The levels of impurities in the steel depend on the quantity and quality of the scraps used. The most harmful impurity brought in is copper, which is known to cause surface cracking during hot rolling, known as surface hot shortness,6–8) or in short, hot shortness.9) It is generally accepted that surface hot shortness of steel is caused by the formation of a molten copper-rich phase at the steel substrate surface as a result of steel oxidation at temperatures above the melting point of the copper-rich phase. Therefore, the oxidation history of the steel would affect the copper enrichment behaviour, and hence the susceptibility towards surface hot shortness. The presence of other impurities also affect the surface hot shortness behaviours. Tin usually coexists with copper, and exacerbates the severity of surface hot shortness. Nickel is another common impurity, however, the presence of nickel in steel alleviates the severity of surface hot shortness.

The thin slab casting process adopted by the EAF mini mills usually comprises three major steps. In the first step, molten steel is cast into slabs 40–90 mm thick.10) The slabs are then hot-charged into a long tunnel furnace to be heated and equalized to a temperature of 1 100–1 200°C. The final step is a finishing hot-rolling process with 4–8 stands to roll the thin slabs into the final hot rolled strips. During the slab casting process, the steel surface temperature is first decreased continuously from about 1 400°C to as low as 800°C, and then raised to the equalization temperature and maintained at that temperature for 20–30 min (depending on the casting speed and the tunnel furnace length), prior to descaling and finishing hot rolling.11) Because the surface temperature of the slab is high and the slab surface is usually exposed to ambient air, significant oxidation may occur during the initial continuous cooling process. In some thin
slab casting process, a descaling unit is also introduced at the entry of the tunnel furnace to remove scale and mould powder. Steel oxidation continues to take place in the tunnel furnace, which is usually fired with natural gas. Oxidation inside the tunnel furnace can be generally treated as an isothermal oxidation process. As a result of steel oxidation during continuous cooling after casting and isothermal holding inside the tunnel furnace, significant impurity enrichment may occur if the residual levels are high in the steel.

The current study was designed to simulate the steel oxidation and copper-enrichment behaviours during thin slab casting of high residual steels. A laboratory oxidation simulator was used for this study. The effects of isothermal holding temperature, holding time, and the composition of the gas phase inside the furnace were also examined.

2. Experimental

The experimental steels used in a previous study\(^\text{12}\) were used in the current study. The compositions of these steels are listed in Table 1. Steels 1, 2, and 3 were designed to evaluate the effect of different copper content in the steel while a relatively high level of nickel (\(\sim 0.07\%\)) was added, whereas Steels 3 and 4 were designed to evaluate the effect of different levels of nickel at a relatively high level of copper addition (\(\sim 0.3\%\)).

The laboratory simulator as illustrated in Fig. 1 was used to simulate the oxidation processes in the thin slab casting process. Two furnaces were required for the laboratory simulation, with an upper infrared furnace for simulating the oxide growth during the casting process, and a bottom resistant furnace to simulate further steel oxidation during isothermal holding in the tunnel furnace. Rectangular samples, with dimensions of \(30 \times 20 \times 4.5\) mm and surface ground to 600 grit finish, were used for the oxidation experiments. Before the start of each experiment, a thermocouple was spot-welded at the centre of the sample to monitor the sample temperature and control the upper furnace temperature. The temperature of the bottom furnace was monitored and controlled separately.

In a typical laboratory simulation, a steel sample was first heated to \(1375^\circ\)C and held at this temperature for two minutes in flowing high purity nitrogen. The sample was then rapidly retracted out of the furnace, allowing continuous cooling in ambient air. As soon as the surface temperature reached the desired isothermal holding temperature, the sample was plunged into the bottom furnace, which has been heated and maintained at the holding temperature, and then extracted to cool in air to room temperature. The isothermal holding temperatures evaluated were in the range of \(950–1230^\circ\)C. For comparison purposes, a group of samples were directly cooled in air from \(1375^\circ\)C to the room temperature.

Three different atmospheres were used for the isothermal holding simulation, which were ambient air, moist air and simulated reheat furnace atmospheres. When moist air was used, ambient air was bubbled through a water bath maintained at \(85^\circ\)C. Assuming that the air was saturated by vapour formed at this temperature, the gas composition contained about \(56\%\)H\(_2\)O–\(9\%\)O\(_2\)–N\(_2\).\(^\text{13}\) Two different simulated reheat furnace atmospheres were used for the experiments. These were \(18.7\%\)H\(_2\)O–\(9.5\%\)CO\(_2\)–\(1.6\%\)O\(_2\)–N\(_2\) and \(18.7\%\)H\(_2\)O–\(9.5\%\)CO\(_2\)–\(4.05\%\)O\(_2\)–N\(_2\), corresponding to \(8\%\) and \(20\%\) excessive air respectively, and were produced by bubbling two gas mixtures, containing \(11.2\%\)CO\(_2\)–\(1.94\%)\)O\(_2\)–N\(_2\) and \(11.3\%\)CO\(_3\)–\(4.81\%\)O\(_2\)–N\(_2\) respectively, through a water bath at \(56^\circ\)C. The isothermal holding temperature and time for each experiment are detailed in Table 2, and the actual thermal histories of these experiments were recorded and typically shown in Figs. 2 and 3.

The oxide scale structures and copper enrichment behaviours were examined primarily using the optical microscopy. Some of the samples were examined using scanning electron microscopy (SEM) for higher resolution observation, and energy-dispersive spectroscopy (EDS) for composition analyses.

### Table 1. Steel Compositions (wt%) Used in the Experiments.

| No. | C  | Mn | Si  | Al | Cu | Sn | Ni  | Cr  | P  | S  | N  |
|-----|----|----|-----|----|----|----|-----|-----|----|----|----|
| 1   | 0.049 | 0.24 | 0.020 | <0.01 | 0.16 | 0.010 | 0.084 | 0.0008 | 0.010 | 0.010 | 0.0102 |
| 2   | 0.045 | 0.14 | 0.016 | 0.0029 | 0.24 | 0.015 | 0.066 | 0.0024 | 0.013 | 0.010 | 0.0089 |
| 3   | 0.053 | 0.20 | 0.025 | 0.0340 | 0.34 | 0.023 | 0.072 | 0.0020 | 0.012 | 0.010 | <0.0006 |
| 4   | 0.050 | 0.17 | 0.025 | 0.0087 | 0.30 | 0.020 | 0.017 | 0.0007 | 0.010 | 0.010 | 0.0030 |

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3. Results

3.1. Continuous Cooling in Ambient Air to Room Temperature

Unlike those scales formed under isothermal holding conditions, blisters were not observed on all oxidized samples. Microscopic observation of the samples revealed a layer of compact scale at a thickness of around 50–100 μm formed on all the steels, as typified in Fig. 4. No copper-rich phase was observed on Steel 1, indicating that at a copper level of 0.16%, tin level of 0.01% and nickel level of...

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| Oxidation | Steel 1 | Steel 2 | Steel 3 | Steel 4 |
|-----------|--------|--------|--------|--------|
| 1375°C → 25°C | No copper found at interface | Fine copper particles at interface (Fig. 4) | Fine copper particles at interface | Copper spreading at interface |
| Continuous Cooling + Isothermal Holding at 950°C in Air | Small particles occluded in scale | n/a | Fine copper particles at interface | Copper spreading at interface |
| 1375°C → 950°C/5 min | None | n/a | Copper precipitates at interface | Copper precipitates at interface |
| 1375°C → 950°C/20 min | None | n/a | Copper precipitates at interface | Copper precipitates at interface |
| 1375°C → 950°C/60 min | None | n/a | Copper precipitates at interface | Copper precipitates at interface |
| Continuous Cooling + Isothermal Holding at 1150°C in Air | None | n/a | Copper spreading at interface | Copper spreading at interface |
| 1375°C → 1150°C/5 min | None | n/a | Copper spreading at interface | Continuous copper layer at interface |
| 1375°C → 1150°C/20 min | None | n/a | Copper spreading at interface | n/a |
| Continuous Cooling + Isothermal Holding at 1200°C in Air | None | n/a | Copper spreading at interface | Copper spreading at interface |
| 1375°C → 1200°C/5 min | None | n/a | Copper spreading at interface | Copper spreading at interface |
| 1375°C → 1200°C/20 min | None | n/a | Copper spreading at interface | Copper spreading at interface |
| Continuous Cooling in Ambient Air + Isothermal Holding in Moist Air | None | n/a | Copper spreading at interface | Copper spreading at interface |
| 1375°C → 1100°C × 30 min | None | n/a | Continuous copper layer at interface (Fig. 19) | n/a |
| 1375°C → 1100°C × 5 min | None | n/a | Fine copper particles at interface | n/a |
| 1375°C → 1150°C × 20 min | None | n/a | Oxide penetration in substrate (Fig. 26) | n/a |
| 1375°C → 1150°C × 30 min | None | n/a | Oxide penetration in substrate (Fig. 26) | n/a |
| 1375°C → 1100°C × 15 min | None | n/a | Oxide penetration in substrate (Fig. 26) | n/a |
| 1375°C → 1200°C × 10 min | None | n/a | Oxide penetration in substrate (Fig. 26) | n/a |
| Continuous Cooling in Ambient Air + Isothermal Holding in Simulated Furnace Gas I (2H2O+10.4CO+1.0N2) | None | n/a | Continuous copper layer at scale-steel interface | n/a |
| 1375°C → 1100°C × 30 min | None | n/a | Continuous copper layer at scale-steel interface | n/a |
| 1375°C → 1100°C × 5 min | None | n/a | Oxide enrichment at or around scale–steel interface | n/a |

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Fig. 2. Sample surface temperature changes during oxidation in ambient air under continuous cooling and isothermal holding conditions.

Fig. 3. Sample surface temperature changes during oxidation in moist air under continuous cooling and isothermal holding conditions.

Fig. 4. Oxide scale formed in Steel 2 during continuous cooling in ambient air from 1375°C to room temperature. Some fine copper particles are visible at the scale-steel interface (etched).
0.084%, the scaling rate during continuous cooling in air was not high enough to expel copper to the scale/substrate interface. When the copper level was increased to 0.24% (Steel 2) and 0.34% (Steel 3) with the nickel content maintained at similar levels as in Steel 1, some fine copper-rich particles became visible at the scale/substrate interface, but the amounts were very small, as shown in Fig. 4. In contrast, the scale–steel interface adhesion in the high copper, low nickel steel (Steel 4) was poor, and a relatively thick layer of copper phase was observed to spread along the scale/substrate interface (Figs. 5, 6).

3.2. Continuous Cooling/H11545 Isothermal Holding in Ambient Air

Oxide scales formed after continuous cooling from 1 375°C and then isothermally held at various temperatures were also blister-free. However, it was found that the adhesion between the scale and the substrate was poor for all steels, regardless of their copper and nickel levels. The scales were easy to spall off during sample preparation. Generally, a large gap was found between the oxide scale layer and the steel substrate in the samples prepared for microscopic observation.

As compared to steel oxidation under continuous cooling conditions from 1 375°C, additional isothermal holding at 950°C for 5 to 60 min did not change the copper distribution pattern very much. Some fine copper particles were observed in Steel 1, but only present inside the scale layer (Table 2). Some larger copper precipitates were observed at the scale/substrate interface of Steel 3, as shown in Fig. 7. Similar to that shown in Fig. 6, the amount of copper phase formed in Steel 4 was significantly more, spreading along the scale–steel interface.

After isothermal holding at 1 050°C for 5 to 60 min, following continuous cooling from 1 375°C in air, copper enrichment at the scale–steel interface was not observed in Steel 1 and very insignificant in Steel 2. But for Steel 3, greater copper-rich precipitates were observed in the sample with an isothermal holding duration of as short as 5 min (Table 2). Longer time exposure increased the copper amount formed at the scale–steel interface (Fig. 8(a)), and sometimes caused deep copper penetration along austenite grain boundaries, as seen in Fig. 8(b). The amount of the copper-rich phase formed at the scale–steel interface was even more in the low nickel steel (Steel 4) (Table 2 and Fig. 9).

Isothermal holding at 1 150°C after continuous cooling from 1 375°C in air, copper enrichment at the scale–steel interface was not observed in Steel 1. However, on Steel 2, a continuous layer of copper formed along the scale–steel interface (Fig. 10(a)), and some copper penetration into the steel substrate was also observed (Fig. 10(b)). A continuous layer of copper-rich phase was also observed to spread along the scale/substrate interface in both Steels 3 and 4. Deep copper penetration of up to 30 μm was also observed in Steel 3.

For all the high nickel steels, continuous cooling/H11001 isothermal holding in ambient air at 1 230°C for 3 or 20 min had occluded the surface substrate phase into the scale,
as typified in Fig. 11(a). The occluded phase was both rich in copper and nickel, detected by EDS. Associated with this, oxide growth along austenite grain boundaries was also observed (Fig. 11(b)). However, the occlusion mechanism was not operative for the low nickel steel, where the copper-rich phase was found to spread along the scale/substrate interface. The observations made here are consistent with those observed in the isothermal oxidation experiments at 1220°C for 30 min conducted previously.12)

3.3. Continuous Cooling in Ambient Air + Isothermal Holding in Moist Air

The isothermal holding experiments in moist air after continuous cooling from 1375°C were conducted only at 1050°C for 20 min, 1150°C for 30 min and 1230°C for 20 min.

As compared to those isothermally held in ambient air at the similar temperatures for the same durations, the steel oxidation behaviour and copper distributions in all steels oxidised under these conditions differed significantly.

In general, scales formed in moist air are blister-free and more adherent to the substrate. Very rare scale spallation was experienced during sample handling. Cross-sectional observation revealed a more uniform and compact scale structure, as typified in Fig. 12.
The scale–steel interface structure and copper enrichment were quite different for the high nickel steels after isothermal holding in moist air at 1150°C for 30 min and 1230°C for 20 min, following continuous cooling in ambient air from 1375°C. On all the high nickel steels (Steels 1, 2 and 3), copper-rich particles were occluded into the inner layer of the oxide scale, as seen in Figs. 14–16. In addition, deep oxide penetration along austenite grain boundaries was also observed (Figs. 14–16). Higher magnification observation and EDS analysis of the penetrating oxides revealed FeO and a compound containing oxygen, silicon, iron, phosphorus, and sometimes sulfur and copper. The phase structure of this compound is under further investigation, but it could comprise a fayalite phase (Fe₂SiO₄), which would be molten at the oxidation temperature and become the reservoir of other impurities left behind due to the consumption of iron. This compound also spread along the scale/substrate interface and penetrate the grain boundaries of the inner scale layer, as seen in Figs. 11, 14–16.

For the low nickel steel (Steel 4), the occlusion mechanism was not operative at either 1150°C or 1230°C, despite the formation of a wavy scale–steel interface, as seen in Fig. 17. A copper phase was observed to spread along the scale/substrate interface. Grain boundary oxide penetration into the substrate was not observed on this steel. The silicon-containing phase was also observed to spread at the scale–steel interface and along the grain boundaries of the oxide layer at the region near the scale–steel interface (Fig. 17).

### 3.4. Continuous Cooling in Ambient Air+Isothermal Holding in Laboratory Simulated Furnace Atmospheres

Isothermal holding experiments in the laboratory simulated atmospheres, following continuous cooling from 1375°C in air, were conducted for the high copper, high nickel steel (Steel 3) only, at 1100°C for 30 min in Gas I (defined in Table 2), 1150°C for 5–30 min in Gas I, 1150°C for 30 min in Gas II (defined in Table 2), 1180°C for 15 min, and 1220°C for 10 min in both gases.

After isothermal oxidation at 1110°C for 30 min in Gas I, following continuous cooling from 1375°C in air, a planar scale–steel interface developed in Steel 3, and a continuous layer of copper formed along this interface, as seen in Fig. 18.

After oxidation at 1150°C for 5 min in Gas I, following continuous cooling from 1375°C in air, a rugged scale–steel interface started to develop in Steel 3 and the amount
of copper-rich phase formed was much less, forming isolated precipitates as seen in Fig. 19. After longer time oxidation in Gas I following continuous cooling in air, many copper-rich precipitates were occluded into the scale, as seen in Figs. 20 and 21. However, some copper phase precipitates were still visible at the scale/substrate interface, as seen in Fig. 21. These precipitates were not spreading along the scale/substrate interface, suggesting that they were not molten when they formed. It is likely that the copper-rich precipitates were formed from the substrate phase during cooling, but at the time of oxidation, the copper component remained dissolved in solid solution in the substrate phase.

The scale structure and copper enrichment developed at 1180°C for 15 min and 1220°C for 10 min, following continuous cooling from 1375°C in air, in Gas I were similar to those developed at 1150°C for 20 to 30 min. These included a rugged scale–steel interface, occlusion of the copper-rich phase into the scale, and deep oxide penetration into the substrate, and some copper precipitates at the scale–substrate interface, as seen in Figs. 22 and 23.
The scale structure and copper enrichment behaviours developed at 1150°C for 20 min, 1180°C for 15 min, and 1220°C for 10 min, following continuous cooling in air from 1375°C in Gas II were very similar to those developed in Gas I, as seen in Figs. 24 and 25, despite the different levels of free oxygen in these two gases.

3.5. Internal Oxides

Two different internal oxides were observed in the high nickel steels at higher temperatures: larger FeO particles in the vicinity of the scale interface and a large population of fine silicon-containing particles distributing deeply into the substrate. Very often, the large internal iron oxide coexisted with the dark grey phase containing oxygen, silicon, iron, phosphorus, and sometimes sulfur and copper. The fine silicon-containing particles are believed to be either fayalite Fe₂SiO₄ or silicon oxide SiO₂, depending on the oxygen levels at the locations where these particles formed. When the oxygen level is relatively low, SiO₂ would normally form, whereas at the very shallow layer of the substrate, the oxygen level would be higher, and fayalite would become more stable than SiO₂ in these regions.

4. Discussion

Occlusion of the copper-rich phase into the scale layer has been proposed as an important mechanism to combat surface hot shortness. The observations made in the current study, and those made in a previous study, suggested that in order for the occlusion mechanism to operate, two conditions must simultaneously be met, which are (1) the steel must contain a relatively high level of nickel, and (2) the oxidation temperature must be sufficiently high.

The current study also reveals that for the high nickel steels (Steel 1–3, containing about 0.07–0.08% nickel), the composition of the oxidizing gas also affects the critical temperature above which the occlusion mechanism becomes operative. When the isothermal oxidation, following continuous cooling, was conducted in ambient air, the occlusion mechanism was operative at 1230°C but not at 1150°C, indicating that the critical temperature above which the occlusion mechanism became operative was between 1230°C and 1150°C. However, when the isothermal holding was conducted in moist air containing about 56% H₂O and 9% oxygen, or laboratory simulated atmospheres containing about 19% H₂O, 10% CO₂, and 2–4% O₂, this critical temperature was lowered to between 1150°C and 1100°C.

For the low nickel steel (Steel 4, containing 0.017%Ni), the occlusion mechanism was not operative under any of the oxidation conditions examined, even at temperatures above 1200°C, and the copper phase, if formed, always spread along the scale–steel interface. This indicates that the critical level of nickel contained in the steel above which the occlusion mechanism becomes operative would be between 0.02% and 0.07%.

Previous studies on the oxidation of Fe–Ni alloys also found that a nickel-rich phase would be occluded into the oxide scale. The mechanism dominating the occlusion process was thought to be the preferential oxidation of iron leading to the enrichment of nickel in the substrate and further entrapment of the nickel-rich areas in the advancing scale. Similar occlusion phenomenon was also observed in the oxidation of Fe–Cu steels at lower temperatures where the copper-rich phase was in its solid state. However, it was also found that, even though a rugged scale–steel interface developed in Fe–Cu steels at lower temperatures, the formation of a molten copper phase at the scale–steel interface at higher temperatures would result in the formation of a planar interface because of the high diffusivity of iron in the molten phase.

It was observed in the current study that when the occlusion mechanism was operating, a rugged scale–steel interface developed. Previous theoretical studies were carried out to determine whether a scale/substrate interface should take a planar shape or a rugged one during oxidation of a binary or ternary alloy involving one or two more novel metals and when all phases formed were in their solid state. The principles derived can be applied to the oxidation of Ni- and/or Cu-containing steels.

In the oxidation of Ni- and/or Cu-containing steels, the
Nickel and copper components in the steels are more novel than iron, and therefore, iron would be preferentially oxidized, whereas nickel and copper tend to be enriched at the surface layer of the steel substrate. Based on the results of the previous theoretical studies, a rugged scale/substrate interface would become stable when the interdiffusivity of iron in the Ni- and/or Cu-enriched surface layer of the steel substrate is much lower than the self-diffusivity of iron in wustite. In other words, if the oxidation rate of the iron component is so rapid that the surface layer is very much enriched with nickel and/or copper, a rugged scale–steel interface would become more stable than a planar one. Without the Ni- and/or Cu-enriched layer, a planar scale–steel interface would be more stable.

However, the development of a rugged scale–steel interface alone was not sufficient for the occlusion mechanism to operate, as seen in Fig. 17. In order to occlude the surface substrate phase into the scale, the protruding oxide fronts inside the steel substrate should also grow laterally. Very often, the formation and growth of internal oxides can assist in bridging the laterally-growing oxide fronts, as seen in Figs. 11(a), 14 and 15.

The possibility to form internal iron oxide depends on its thermodynamical stability inside the substrate. During steel oxidation, a local thermodynamical equilibrium would be established at the scale/substrate interface. Assuming that this equilibrium was held between wustite and the steel substrate, then the iron and oxygen activities at the scale/substrate interface were determined by the following reaction:

$$[\text{Fe}] + [\text{O}] = \text{FeO} \quad \text{(1)}$$

where [Fe] and [O] represent iron and oxygen components, respectively, on the substrate side. If the substrate contains iron only, the iron activity is approximately equal to unity and the oxygen activity is only determined by the dissociation pressure of FeO at the reaction temperature.

When the steel surface layer is enriched with copper and nickel, however, the iron activity in this layer would be significantly lowered. In order to maintain thermodynamical equilibrium at the scale/substrate interface, the oxygen activity in this layer is raised to a value that was much higher than that determined by the dissociation pressure of FeO only. As the steel oxidation proceeds, oxygen would diffuse into the substrate and iron would diffuse outwards to the substrate surface to sustain the reaction. Once the oxygen and iron in the substrate distribute in such a way that in some areas the solubility product exceeds the equilibrium constant of reaction (1), internal FeO would precipitate inside the substrate. This has been found to occur in the vicinity of the scale/substrate interface. Clearly, the depth of the internal FeO zone is a function of steel composition, steel oxidation rate, oxidation temperature and time.

Some dark grey phase(s) was very often observed at the scale/substrate interface and sometimes associated with the large internal iron oxides. This phase contains oxygen, iron, silicon, phosphorus, and sometimes sulfur and copper. Detailed analysis was not conducted in this study. As mentioned earlier, it could be the fayalite phase dissolved with other impurities, such as phosphorus and sulfur, accumulated at the scale–steel interface as the interface advanced into the steel. The presence of this structure seemed to promote the copper occlusion mechanism by accelerating the bridging process of the protruding oxide fronts.

The occlusion mechanism discussed above can be used to explain the observations made in the current study. When the isothermal holding was conducted in ambient air, a rugged scale–steel interface was developed at temperatures above the critical temperature (between 1 150°C and 1 230°C). At these temperatures, the copper-rich phase would be molten if it formed, however, because of the high oxidation temperature, diffusion of iron through the scale layer was relatively rapid, causing the more rapid depletion of iron at the surface layer of the substrate. The bulk diffusion of oxygen into the steel was also rapid, resulting in rapid lateral growth of the protruding oxide fronts, and the growth of internal iron oxide in the substrate to bridge them. In this way, the surface substrate phase would be occluded into the scale layer before a molten Cu-rich phase formed. However, at temperatures below the critical temperature, because of the relatively slower iron diffusion through the scale layer, and therefore, less significant enrichment of nickel and copper at the surface layer of the substrate, a rugged scale–steel interface failed to develop. In this case, the copper phase could not be occluded into the scale layer via the lateral oxide growth mechanism.

When the oxidation was conducted in moist air and in the laboratory-simulated gases, because of the improved scale–steel interface adhesion, iron diffusion through the scale layer was enhanced, and therefore the degree of copper and nickel enrichment at the surface layer of the substrate was increased. The enhanced copper and nickel enrichment in the surface layer of the substrate was found to be sufficient to maintain a stable rugged scale–steel interface and promote lateral growth of the protruding oxide fronts and/or growth of internal iron oxides at 1 150°C to occlude the substrate phase into the scale.

Due to the low level of nickel, Steel 4 behaved differently from the high nickel steels (Steels 1–3). It appeared that the presence of 0.017% nickel in this steel was not sufficient to generate sufficient surface enrichment of nickel in the substrate to promote the formation of a rugged interface, or promote the lateral growth of the protruding oxide fronts even when a rugged interface formed (Fig. 17).

The observations made in the current study for the high nickel steels (Steels 1–3) were consistent with those made by Fukagawa and Fujikawa, and by Imai et al. However, the observations made for the low nickel steel (Steel 4) were somewhat different from those made in the previous studies, where it was found that the occlusion mechanism was operative at 1 200°C and 1 300°C at a nickel level of as low as 0.02%. It is also noted that the oxidation durations in these previous studies were in the range of 2–3 h, which were much longer than the oxidation durations examined in the current study. It is likely that the critical nickel level required for the occlusion mechanism to operate would also be affected by the oxidation duration of the steels.

It was also observed that for the high nickel steels (Steels 1–3) within the oxidation conditions where the interface occlusion mechanism was operating, there was a significant growth of internal oxides along the substrate grain bound-
aries. These observations revealed another important mechanism for copper-phase occlusion. This mechanism was operating via the rapid preferential growth of grain boundary oxides to engulf the entire austenite grains into the scale. Clearly, the operation of this mechanism did not rely on the development of a rugged scale–steel interface, but rather it relied on the rapid diffusion of oxygen along the austenite grain boundaries. Although this mechanism would be more effective in occluding the copper-rich phase into the scale layer, it could also cause descaling difficulty.  

Unusual deep copper penetration was occasionally observed in all the steels. However, the most commonly observed morphology of the copper phase was a continuous or spreading layer over the substrate with slight protruding at the austenite grain boundary locations. These observations suggested that the copper penetration was unlikely caused by solid phase diffusion along austenite boundaries because if it were, the penetration would have uniformly taken place along all the austenite grain boundaries, which was not observed in the current study. The actual mechanism for the unusual deep copper penetration remained unknown.

5. Conclusions

The copper enrichment behaviours of several copper-containing steels under simulated slab casting processes are studied. The following conclusions can be drawn from the current study.

1. For the high nickel steels (Steels 1–3, containing 0.066–0.084% Ni), copper is occluded into the scale at temperatures above 1 230°C when the isothermal oxidation step is conducted in air, or at temperatures above 1 150°C when conducted in moist air or in laboratory-simulated reheat furnace atmospheres. When the occlusion mechanism is not operative, the copper-rich phase, if formed, spreads along the scale–steel interface. The amount of this copper-rich phase increases with the steel copper content.

2. For the low nickel steel (Steel 4, containing 0.017% Ni), a copper phase is always found at the scale–steel interface, regardless of the isothermal oxidation temperature, isothermal oxidation duration, and the oxidation atmosphere examined.

3. In order for the occlusion mechanism to operate, both the steel nickel content must be above a critical level and the isothermal holding temperature must be sufficiently high. The critical nickel level in the steel is between 0.02% and 0.07%, whereas the critical isothermal holding temperature above which the occlusion mechanism becomes operative in the high nickel steels is between 1 150 to 1 230°C in ambient air, or between 1 100°C and 1 150°C in moist air or in simulated reheat furnace atmospheres.

4. Development of a rugged scale–steel interface alone is not sufficient for the occlusion mechanism to operate. To successfully occlude copper into the scale, lateral growth of protruding oxide fronts into the substrate is essential. Formation and growth of large internal iron oxides also assist in bridging the laterally growing oxide fronts and therefore promote the occlusion mechanism.

5. High levels of nickel in the steel also result in preferential oxide growth along the austenite grain boundaries. If copper is occluded via this mechanism, descaling difficulty is expected.

6. Unusually deep copper penetration in the substrate was occasionally observed in all the steels. The actual mechanism of deep copper penetration remains unknown.

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