

## Effect of Scale Formation on Copper Enrichment Behavior in Continuously Cast Slab

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**Abstract:** Copper enrichment behavior in continuously cast slab induced by scale formation during continuous cooling was experimentally investigated, and the effects of initial slab surface temperature and oxygen potential in atmosphere were discussed. The results showed that a loose scale adhered to the substrate was formed in  $H_2O-N_2$  atmosphere at higher slab surface temperature compared to a gap formed between the scale and the steel substrate after continuous cooling in  $H_2O-O_2-N_2$  atmosphere. Under the condition of continuous cooling in  $H_2O-N_2$  atmosphere, the copper enrichment occurred both within the loose scale and at the scale/steel interface with simultaneous Ni enrichment near the interface at higher slab surface temperature. The combined effects of the loose scale and nickel enrichment were thought to promote the back-migration of Cu-rich phase from the interface and occlusion within the scale layer. While in  $H_2O-O_2-N_2$  atmosphere, the Cu enrichment was found on the steel side and the formed gap prevented the migration of Cu to the scale.

**Key words:** copper enrichment behavior; slab surface temperature; oxygen potential; atmosphere; scale; nickel enrichment

The use of scrap in steelmaking, especially in electric arc steelmaking, induces inevitable residual elements problem. The residual elements such as copper, tin and arsenic which have oxidation potential less than iron, are retained in the steel because they are difficult to be removed in steelmaking process<sup>[1]</sup>. During subsequent processing operations such as continuous casting and hot rolling, residual elements tend to concentrate on the steel/scale interface as the surface of steel is oxidized and further penetrate along the grain boundary. This promotes cracking known as surface hot shortness caused by the penetration of the Cu-rich phases into the grain boundaries<sup>[2-4]</sup>. In the past, enrichment of residual elements during hot rolling and its influence on the surface quality of hot rolled plate have been extensively studied<sup>[5-8]</sup>.

On the other hand, significant residual build-up has also been detected at the scale/steel interface in continuously cast products during continuous casting.

The extent of residual build-up may depend on these factors such as the rate of scale formation, the occlusion extent of the residual elements into the scale and the diffusion rates of the elements from the surface to the steel matrix<sup>[9]</sup>. Additionally, different from the situation of the steel stock reheating, this residual element enrichment during continuous casting process has been related to the rapid oxidation of the slab surface with heat release in the secondary cooling zone. Thus, history of scale formation would have an effect on the copper enrichment behaviour<sup>[10-12]</sup>.

In the present work, a laboratory experiment was conducted involving the heated specimens of the commercial continuously cast slab which were continuously cooled in  $H_2O-O_2-N_2$  and  $H_2O-N_2$  atmosphere respectively to investigate the copper enrichment behavior induced by the scale formation, mainly the effects of initial slab surface temperature and oxygen potential in atmosphere during continu-

ous cooling process.

## 1 Experimental

A type of Cu-bearing continuously cast slab with the chemical composition listed in Table 1 was used. The contents of copper and nickel in the slab were 0.52 and 0.422 mass%, respectively. Sample preparation of continuously cast slab was similar to that in the previous work<sup>[13]</sup>. To ensure that the oxidizing surface of slab sample was the chilled layer composed of fine equiaxed grain, the upper layer of commercial continuously cast slab was firstly taken down and cut into rectangular samples with dimensions of 10 mm×10 mm×5 mm. Then, the original scale and mold flux adhered to the top surface of slab sample were removed by SiC abrasion paper and cleaned ultrasonically in ethanol.

In the laboratory experiment, the prepared slab samples were firstly heated to the desired temperature (1150 °C or 1250 °C) in a horizontal tube furnace and held at the temperature for 5 min in nitrogen gas flow. After the sample surface temperatures reac-

hing the desired ones, the slab samples were then rapidly taken out of the heating furnace and put into another horizontal atmosphere-controlled furnace, allowing continuous cooling to 800 °C in 63 vol. % H<sub>2</sub>O-N<sub>2</sub> or 63 vol. % H<sub>2</sub>O-8 vol. % O<sub>2</sub>-N<sub>2</sub> oxidizing atmosphere, respectively. Of the two continuous cooling cases from 1150 °C/1250 °C to 800 °C, the duration time was about 18–22 min. Finally, the sample was removed from the atmosphere-controlled furnace to cool consecutively to room temperature in air. The whole experimental process was designed to investigate the scale formation as well as the induced copper enrichment behaviour during the simulated continuous cooling process in the secondary and air cooling zones. The experimental conditions are shown in Table 2.

After oxidation experiment, the cross-section of the scale layer was observed to investigate the microstructure by scanning electron microscopy (SEM), and element distributions inside the scale layer and the steel substrate were respectively analyzed by energy dispersive X-ray spectrometry (EDS).

**Table 1 Chemical composition of Cu-bearing continuously cast slab** mass%

C	Si	Mn	P	S	Ni	Cr	Al	Cu
0.080	0.277	0.89	0.094	0.002	0.422	0.425	0.0635	0.52

**Table 2 Experimental condition of scale formation and Cu enrichment behaviour**

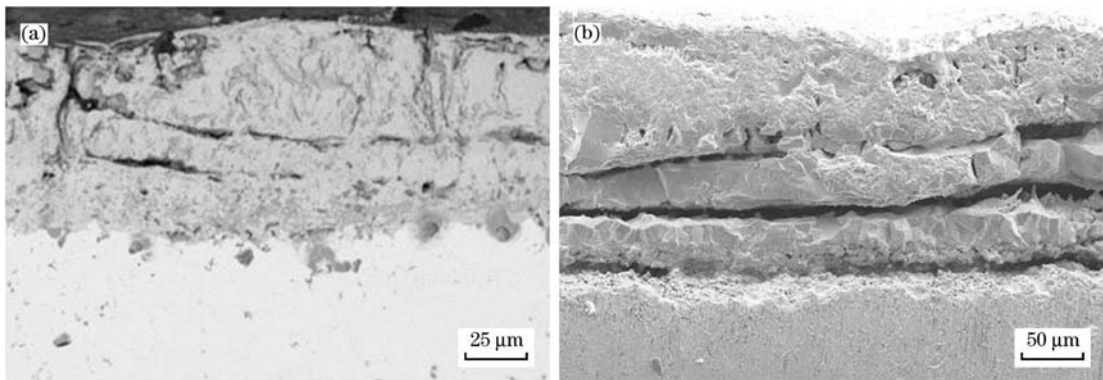
Initial slab surface temperature	Continuous cooling condition
1150 °C, 1250 °C	1150 °C or 1250 °C→800 °C in 63 vol. % H <sub>2</sub> O-N <sub>2</sub> or 63 vol. % H <sub>2</sub> O-8 vol. % O <sub>2</sub> -N <sub>2</sub> → Room temperature in air

## 2 Results and Discussion

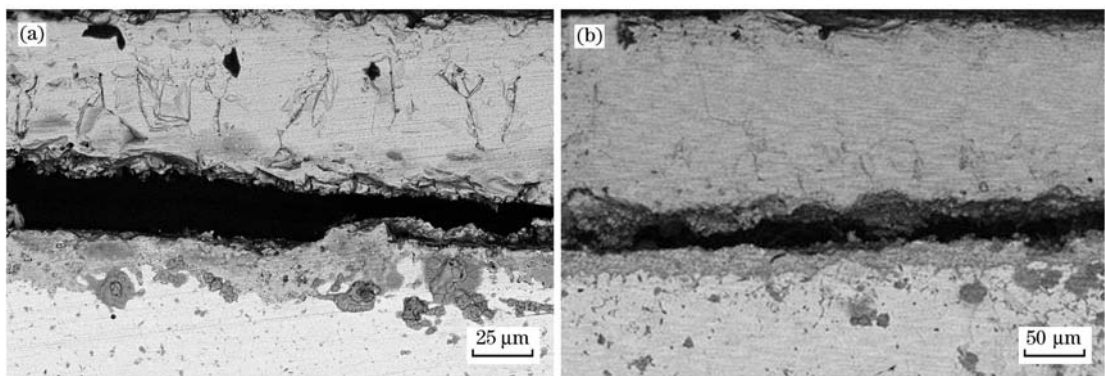
### 2.1 Microstructure and adhesion status

Figs. 1(a) and 1(b) show the scale microstructures and adhesion status to the steel substrate after continuous cooling from the different initial slab surface temperatures (1150 °C and 1250 °C) to 800 °C in 63 vol. % H<sub>2</sub>O-N<sub>2</sub> atmosphere, and then consecutively cooling to room temperature in air. It can be noted that the scales formed under the continuous cooling condition in 63 vol. % H<sub>2</sub>O-N<sub>2</sub> atmosphere show a relatively tight adhesion to the substrate irrespective of the different initial slab surface temperatures, while a loose microstructure with some microcracks inside the scale layer is observed at the higher slab surface temperature of 1250 °C. In contrast, for the case of continuous cooling in 63 vol. % H<sub>2</sub>O-8 vol. % O<sub>2</sub>-N<sub>2</sub> atmosphere, the adhesion between the scale

and substrate is poor for both the specimens with the different initial slab surface temperatures of 1150 °C and 1250 °C respectively, and a distinct gap is formed at the scale/steel interface, as shown in Figs. 2(a) and 2(b). This poor adhesion between steel matrix and scale can be explained as that for the continuous cooling case in 63 vol. % H<sub>2</sub>O-8 vol. % O<sub>2</sub>-N<sub>2</sub> atmosphere, the oxidation rate of the slab surface is higher than that in 63 vol. % H<sub>2</sub>O-N<sub>2</sub> atmosphere and the movement of iron ions from the steel matrix to the reaction site can cause loss of the scale adhesion and thus induce a gap at the interface, especially for the more rapid oxidation case in H<sub>2</sub>O-O<sub>2</sub>-N<sub>2</sub> atmosphere<sup>[14]</sup>. Additionally, the loose scale microstructure with some microcracks is thought to be caused by the volume expansion stress due to the phase transformation from wustite (face-centered cubic lattice crystalline with crystal axis of



**Fig. 1** Microstructure and adhesion status of the scales formed during continuous cooling in 63 vol. %  $\text{H}_2\text{O}-\text{N}_2$  + consecutively in air from different initial slab surface temperatures of 1150 °C (a) and 1250 °C (b)



**Fig. 2** Microstructures and adhesion status of the scales formed during continuous cooling in 63 vol. %  $\text{H}_2\text{O}-8$  vol. %  $\text{O}_2-\text{N}_2$  + consecutively in air from different initial slab temperatures of 1150 °C (a) and 1250 °C (b)

0.43070 nm) to magnetite (body-centered cubic lattice crystalline with crystal axis of 0.83967 nm) during cooling process, and the volume expansion stress increases remarkably at higher slab surface temperature because the wustite phase becomes more dominant in the scale layer<sup>[15]</sup>. The scale microstructure and its adhesion state are expected to have an important influence on the copper enrichment behaviour as the oxidation proceeds.

## 2.2 Copper enrichment induced by scale formation

The copper enrichment behaviour induced by scale formation in 63 vol. %  $\text{H}_2\text{O}-\text{N}_2$  atmosphere is shown in Figs. 3 and 4, respectively. For the slab with a lower slab surface temperature of 1150 °C (Fig. 3), neither obvious copper nor nickel enrichment is observed at the scale/steel interface or within the scale layer, and the distributions of copper as well as nickel are uniform along the cross section of the slab sample from scale to steel. The results can be explained from two aspects. First, although a relatively dense scale attached to the steel is formed

(Fig. 1 (a)) which offers a beneficial condition for copper accumulating and staying at the interface, the scaling rate on the slab surface during continuous cooling was too low to expel copper and nickel to the scale/substrate interface due to the lower slab surface temperature and oxygen potential in atmosphere. And secondly, addition of nickel can make an increase in the copper solubility in the  $\gamma$ -iron phase and a decrease in the oxidation rate<sup>[9,16]</sup>. On the other hand, for the slab sample with the higher slab surface temperature of 1250 °C, the Cu-enrichment is noted at the scale/steel interface and inside the scale layer, and simultaneously Ni-enrichment appears near the steel/scale interface, as illustrated in Fig. 4. This occlusion of Cu within the scale layer is considered to be the combined effects of loose scale and nickel enrichment at the interface. Fig. 5 shows the schematic expression of copper-rich phase occlusion into scale. At higher slab surface temperature, the scaling rate increases and thus the excluded copper and nickel tend to concentrate at the scale/steel interface as the scale formation proceeds. However,

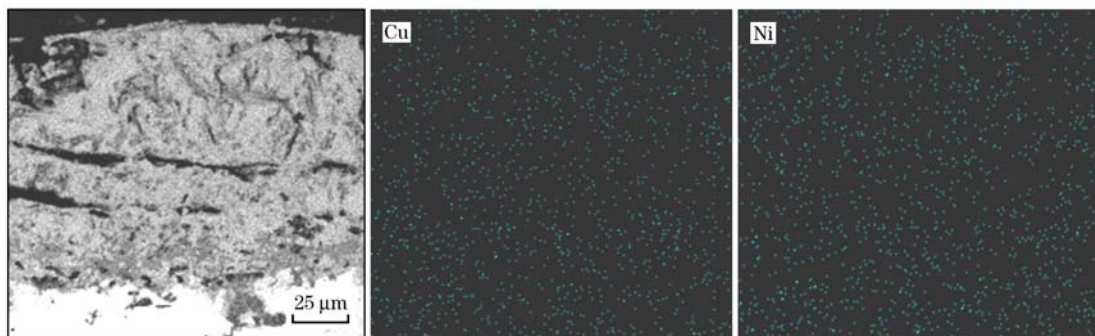


Fig. 3 EDS elements mapping of the slab sample after continuous cooling in 63 vol. %  $\text{H}_2\text{O-N}_2$  + consecutively in air from the initial slab surface temperature of 1150 °C

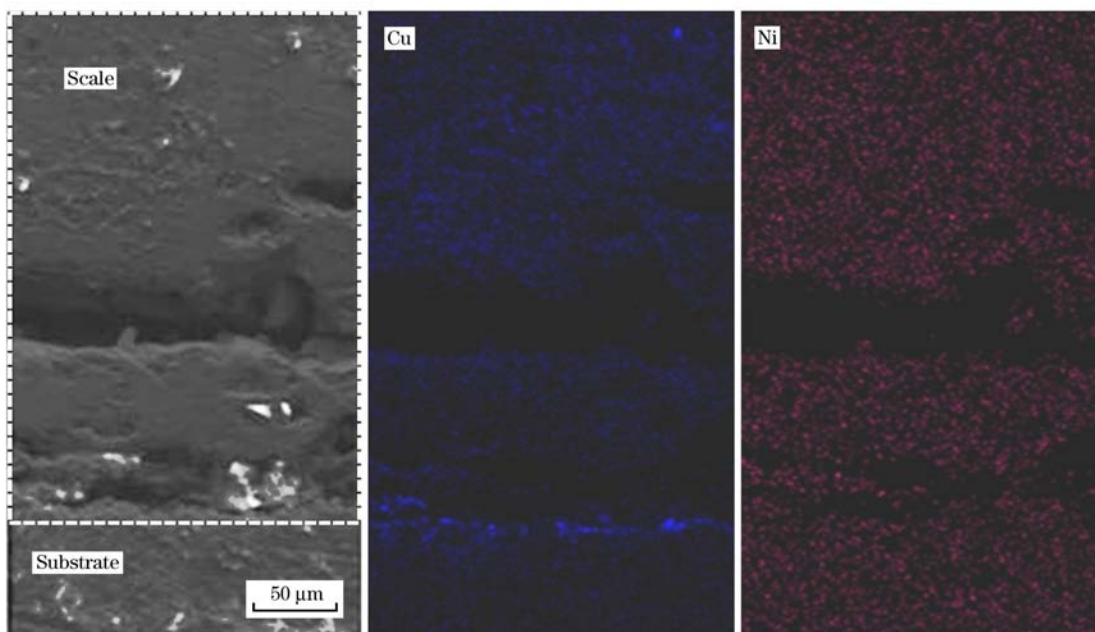
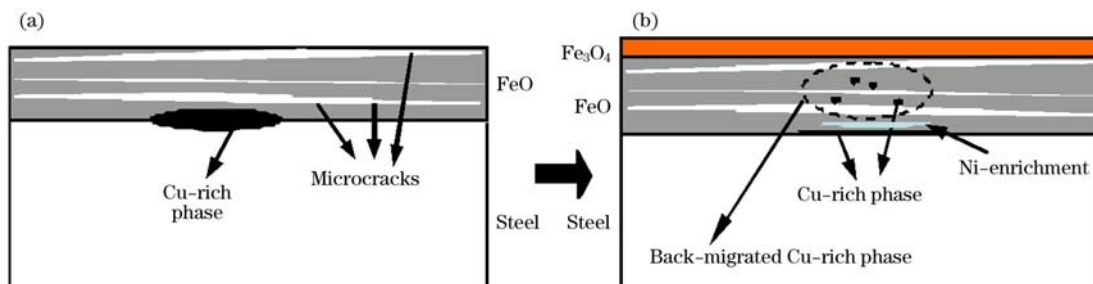


Fig. 4 EDS elements mapping of the slab sample after continuous cooling in 63 vol. %  $\text{H}_2\text{O-N}_2$  + consecutively in air from the initial slab surface temperature of 1250 °C



(a) Copper precipitation at interface; (b) Back-migration of copper from interface into scale.

Fig. 5 Schematic of Cu enrichment under the condition of loose scale and nickel enrichment near interface

as the scale becomes thicker, the enriched Cu phase at the scale/steel interface can migrate back to the upper part of scale layer through the loose microstructure which restrains the further penetration of copper-rich phase into the steel matrix. The signifi-

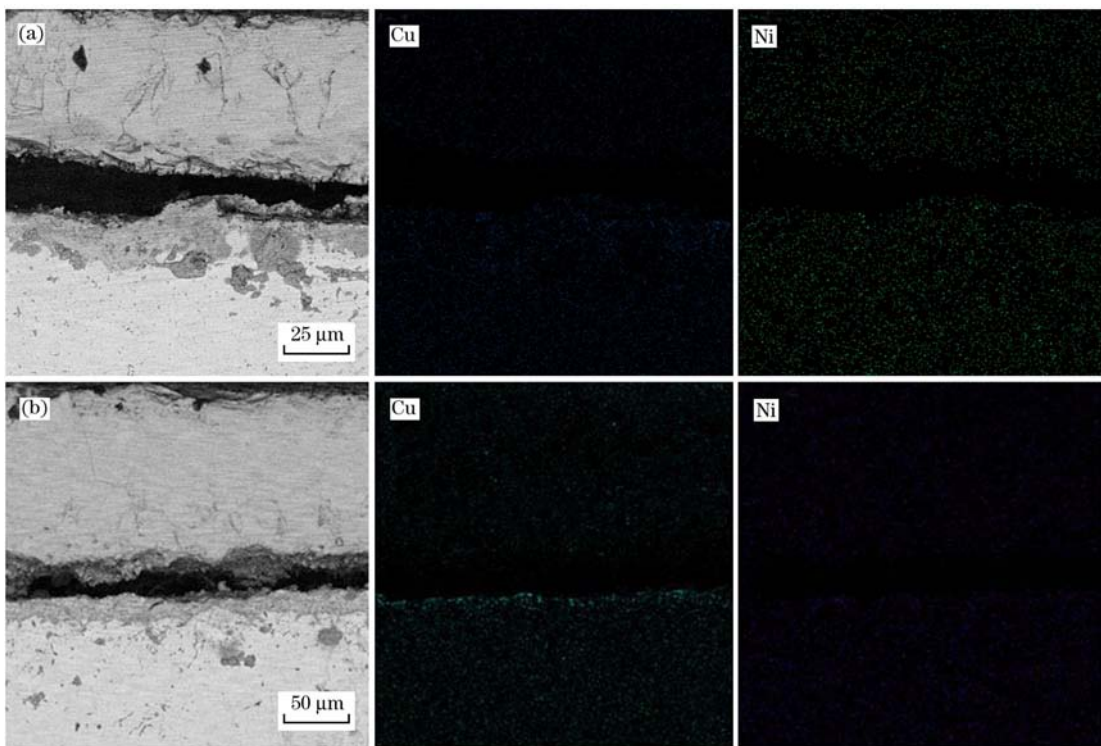
cant effects with the presence of Ni-enrichment can not only increase the melting point of Cu-rich phase but also reduce the oxidation rate<sup>[17,18]</sup>. In addition, Ni addition also plays the role in increasing the amount of occluded copper-rich phase into scale<sup>[19,20]</sup>. Positive

effects of the loose scale formed at higher surface temperature and nickel enrichment at interface work together to promote the back-migration of copper precipitate from the interface to the outer scale and occlusion within the scale.

Fig. 6 shows the EDS elements mapping of the slab specimens after continuous cooling in 63 vol. %  $\text{H}_2\text{O}$ -8 vol. %  $\text{O}_2$ - $\text{N}_2$  and consecutively in air from different initial slab surface temperatures. As shown in Figs. 6(a) and 6(b), with the increment of oxygen potential in atmosphere from 63 vol. %  $\text{H}_2\text{O}$  to 63 vol. %  $\text{H}_2\text{O}$ -8 vol. %  $\text{O}_2$ , a visible copper enrichment is observed on the steel side and meanwhile a gap is formed between the substrate and scale at both 1150 and 1250 °C. No nickel enrichment is found.

increases significantly at higher oxygen potential for  $\text{H}_2\text{O}$ - $\text{O}_2$ - $\text{N}_2$  atmosphere, copper would be more easily expelled than nickel because nickel and iron have complete soluble system but copper has a limited solubility<sup>[21]</sup>. Moreover, compared with the continuous cooling in  $\text{H}_2\text{O}$ - $\text{N}_2$  atmosphere, the gap formed between the steel and scale in  $\text{H}_2\text{O}$ - $\text{O}_2$ - $\text{N}_2$  atmosphere makes it hard for the back-migration of Cu from the interface to the scale layer as the scaling proceeds, and eventually the copper-rich phase accumulating at the interface of steel side possibly penetrates into the bulk steel. The above results also indicate that the occlusion effect is not operative without the proper effect of nickel enrichment near the interface.

Based on the different copper behaviors induced



**Fig. 6** EDS elements mapping of the slab sample after continuous cooling in 63 vol. %  $\text{H}_2\text{O}$ -8 vol. %  $\text{O}_2$ - $\text{N}_2$  atmosphere+ consecutively in air from the different initial slab surface temperatures of 1150 °C (a) and 1250 °C (b)

by the scale formation in  $\text{H}_2\text{O}$ - $\text{N}_2$  and  $\text{H}_2\text{O}$ - $\text{O}_2$ - $\text{N}_2$  atmospheres respectively, a lower level of oxygen potential in atmosphere during continuous cooling is favorable to reduce the scale formation, occurrence of copper enrichment and penetration of Cu-rich phase into steel even for a higher level copper in steel. Thus, during practical continuous casting process, inverting the environmental atmosphere around the slab surface, for example, applying nitrogen-mist cooling to replace air-mist cooling by using nitrogen gas

instead of air in secondary cooling zone, is proposed to reduce scale formation and hair crack caused by copper enrichment.

### 3 Conclusions

(1) Both the slab surface temperature and oxygen potential in atmosphere have effects on the scale microstructure and adhesion status to the steel. Compared to the distinct gap formed between the scale and substrate in  $\text{H}_2\text{O}$ - $\text{O}_2$ - $\text{N}_2$  atmosphere, a loose

scale adhered to the substrate is formed in  $H_2O-N_2$  atmosphere at higher slab surface temperature.

(2) In the case of continuous cooling in  $H_2O-N_2$  atmosphere, neither copper nor nickel enrichment is observed at the scale/steel interface at lower slab surface temperature. While at higher slab surface temperature, the Cu-enrichment at the scale/steel interface and inside the scale layer is visible with simultaneous Ni-enrichment near the interface. The combined effects of the loose scale and nickel enrichment near interface are thought to promote the back-migration of Cu-rich phase from the interface and occlusion within the scale layer.

(3) In the case of continuous cooling in  $H_2O-O_2-N_2$  atmosphere, a Cu-enrichment without Ni-enrichment is noted on the steel side at both 1150 °C and 1250 °C, and the gap formed between the scale and substrate is considered to prevent the Cu back-migration to the scale layer.

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