INFLUENCE OF SCALE FORMATION ON COPPER ENRICHMENT BEHAVIOUR IN CONTINUOUSLY CAST SLAB

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Abstract

Copper enrichment behavior in continuously cast slab induced by scale formation after continuous cooling in H2O vapor atmosphere and consecutively in air has been experimentally investigated by combining with SEM-EDS analysis, for the purpose to examine the effects of initial slab surface temperature and contents of copper and nickel. For Slab 1 with copper content of 0.1 percent, no visible copper enrichment is found at scale-substrate interface irrespective of the various scale microstructures formed at different initial slab surface temperatures. For Slab 2 with higher contents of copper and nickel, copper-rich phase accumulates and stays at scalesubstrate interface under the condition of lower initial slab surface temperature; while Cu-rich phase in the porous scale formed at higher initial slab surface temperature is noted with simultaneous Ni-enrichment appearing in front of the steel-scale interface. Both a porous scale and high nickel content work together to provide pores for copper-rich phase migration away from interface and occlude within the scale layer.

Introduction

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 whose oxidation potential are less than iron, are retained in the steel because they are difficult to be removed during steelmaking process. During subsequent processing operations such as continuous casting and hot rolling, residual elements tend to solidification segregation, concentration at the steel-scale interface and penetration along grain boundary, which promote cracking known as hot shortness or hair cracks [1]. In the past, enrichment of residual elements during hot rolling and its influence on surface quality of hot rolled plate have been extensively studied [2-6].

On the other hand, significant residual enrichment has also been detected at the oxide scale/matrix interface in continuously cast slab. This has been related to the rapid oxidation of strand surface with heat release to environment in the secondary cooling zone. The past study results on continuously cast products showed that the hot shortness occurrence was mainly in connection with an oxide layer with clear Cu enrichment at the scale-steel interface. Thus, the residual enrichment may depend on the several factors including scale formation, occlusion of the residual elements into the scale and diffusion of these elements away from the interface into the steel [7-9]. In the current work, an experimental was conducted to investigate the copper

enrichment induced by scale formation in continuously cast slab, mainly the effects of initial slab surface temperature in secondary cooling zone and contents of copper and nickel in steel.

Experimental

Two types of Cu-bearing continuous cast slabs, namely Slab 1 and Slab 2, with the chemical compositions listed in Table 1 were used. The copper contents in Slab 1 and Slab 2 were 0.10 and 0.52 mass percent respectively. To evaluate the effect of Ni content on copper enrichment, a relatively higher content of nickel (0.422 mass percent) in Slab 2 compared with Slab 1 (0.040% Ni) was maintained. The slab sample preparation is similar to that in the previous work [10]. To ensure that the oxidizing surface of slab sample is the chilled layer composed of fine equiaxed grain, the upper layer of commercial continuously cast slab was first took down and cut into rectangular samples with dimensions of 10 mm \times 10 mm \times 5 mm. Then the original scale and mold flux adhered to the sample surface were removed using SiC abrasion paper and cleaned ultrasonically in ethanol.

In the laboratory experiment, the prepared slab sample was firstly heated to the desired temperature (1100 \degree C/1300 \degree C) in a horizontal tube furnace and held at the desired temperature for five minutes in argon gas flow. Once the sample surface temperature reached the desired initial temperature, the samples with different initial surface temperatures were then rapidly taken out of the heating furnace and put into another horizontal atmosphere-controlled furnace to cool in H₂O vapor atmosphere to about 800°C. Finally, the sample was removed from the atmospherecontrolled furnace to cool to room temperature in ambient air. The whole experiment process was designed to investigate scale formation and induced copper enrichment during the simulated secondary and air cooling zones. The experiment conditions were shown in Table 2.

Microstructure of the scale was observed by scanning electron microscope (SEM) and element distributions of copper and nickel in scale layer and steel substrate respectively were analyzed by energy dispersive X-ray spectra (EDS).

Table 2 Experimental conditions for scale formation and Cu enrichment		
	Type of slab Initial slab surface temperature, °C	Continuously cooling condition
Slab ₁	1100/1300	$(1100/1300)$ °C \rightarrow 800°C in H ₂ O vapor \rightarrow room temperature in ambient air
Slab ₂	1100/1300	$(1100/1300)$ °C \rightarrow 800°C in H ₂ O vapor
		\rightarrow room temperature in ambient air

Table 2 Experimental conditions for scale formation and Cu enrichment

Results and Discussion

Microstructure of the Formed Scale on Continuously Cast Slab

Figure 1 shows the scale microstructure of Slab 1 after continuous cooling from different initial

slab surface temperatures (1100 \degree or 1300 \degree) to 800 \degree in H₂O vapor atmosphere, and then consecutively cooling in air to room temperature. The scale microstructures of Slab 2 under the same cooling condition are shown in Fig. 2. It is noted that all the oxide scales show a relatively adherent to the steel substrate irrespective of the different initial surface temperatures and slab types, but a loosen and porous microstructure formed under the condition of higher initial slab surface temperature (1300 \degree C), as seen both in Figs 1(b) and 2(b). This type of loosen and porous scale is considered to be caused by the volume expansion stress due to the phase transformation with decomposition from wustite to magnetite during cooling process. The stress increases at higher initial slab surface temperature because the wustite phase becomes more dominant in the scale layer. The tight adhesion and microstructure (dense/loosen) of scale is expected to have a significant influence on copper enrichment behaviour [4, 8].

2000 2000

Fig. 1. Scale microstructure of Slab 1 after continuous cooling in H₂O vapor + consecutively in air for different initial surface temperatures. (a) 1100° C. (b) 1300° C.

2000

Fig. 2. Scale microstructure of Slab 2 after continuous cooling in H₂O vapor + consecutively in air for different initial surface temperatures. (a) 1100° C. (b) 1300° C.

Copper Enrichment Induced by Scale Formation

Figure 3 shows the line-scan profiles of copper element along scale layer and steel substrate of Slab 1 sample after continuous cooling in H2O vapor atmosphere and consecutively in ambient air. Fig. 3(a) is the sample of Slab 1 with initial surface temperature of 1100° C and Fig. 3(b) is with the initial surface temperature of 1300° C. No copper enrichment is observed either inside scale layer or at scale-substrate interface regardless of the surface temperature, indicating that for the Slab 1 samples with low copper content, as the scaling proceeds, the copper accumulation

rate is not high enough to form notable copper enrichment at the scale/steel interface. Accordingly, the dense and loosen scales in Fig. 1 have not any influence on the copper enrichment. Thus, the recommendation to maintain a copper content less than 0.1 percent is considered to be important to reduce copper enrichment and hot shortness occurrence [11].

On the other hand, line-scan profiles of copper and nickel elements in Slab 2 samples are shown in Fig. 4. For the sample of Slab 2 with lower initial surface temperature (1100 \degree C), the copper enrichment is found at scale-substrate interface, as shown in Fig. 4(a). Meanwhile, no notable nickel enrichment is observed in Slab 2 at 1100° C, as shown in Fig. 4(b). It suggests that for the slab with high contents of copper and nickel but low surface temperature, the oxidation rate is lowered because of the lower temperature and the presence of Ni, and the scaling rate is not rapid enough to expel copper and nickel simultaneously due to the higher oxidation potential of Ni. Thus, diffusion of Cu-rich phase away from the interface into the matrix is possible since the formed scale (Fig. 2(a)) is tightly attached to the substrate. While for the sample of Slab 2 with higher surface temperature (1300°C) , it is clearly noted that Cu-enrichment inside the scale layer but a little away from the steel-scale interface, and simultaneously Ni-enrichment appears in front of the steel-scale interface, as illustrated in both Figs. 4(c) and (d). A porous scale formed at high initial slab surface temperature (1300°C) and positive effect resulting from Ni enrichment in front of the scale/substrate interface are both regarded to promote Cu-rich-phase migration from interface to the porous scale through pores and occlude Cu within the scale layer [1, 8].

Fig. 3. Copper element line scan profiles along scale layer and steel substrate of Slab 1 with different slab surface temperatures. (a) initial surface temperature of 1100° C. (b) initial surface temperature of 1300° C.

Figure 5 shows the SEM image and EDS analysis result of Slab 2 sample with the initial surface temperature of 1300° C. It is clearly visible that copper-rich phase particles are occluded into the inner layer of oxide scale, which is consistent with the line-scan result of copper element in Fig. 4(a). Compared with that of Slab 2 sample at 1100° C, the different copper-enrichment behaviour in Slab 2 with initial surface temperature of 1300° reveals that with respect of the influence of scale microstructures (dense/porous scale formed at low/high initial slab surface temperature), the critical contents of copper and nickel in slab and initial surface temperature are also required simultaneously for the occlusion mechanism of copper into scale layer to operate. During continuously casting process, under the oxidizing atmosphere condition of water vapour in secondary cooling zone, scale formation promotes Cu accumulation at scale-substrate interface

as oxidation proceeds, whereas a porous scale at higher initial slab surface temperature and high nickel content work together to occlude the copper-rich phase within the scale layer.

Distance/µm
Fig. 4. Element line scan profiles along scale layer and steel substrate of Slab 2 with different surface temperatures. (a) Cu element at 1100° C, (b) Ni element at 1100° C, (c) Cu element at 1300 °C, (d) Ni element at 1300 °C.

Fig. 5. Copper-rich phase occluded in the scale layer. (a) SEM image. (b) EDS map.

Conclusions

(1) A scale layer tightly adherent to the steel substrate is formed on continuously cast slab surface after continuous cooling from different initial slab surface temperatures in H₂O vapor atmosphere and consecutively in air. Compared with the dense scale formed at lower initial slab surface temperature, the scale microstructure is loose and porous at higher temperature. The different scale microstructures have significant effects on copper enrichment behaviour.

(2) For Slab 1 with lower copper content, no visible copper enrichment is found at scalesubstrate interface regardless of the initial slab surface temperature. A copper content level less than 0.1 percent is recommended to be proper to reduce copper enrichment induced by scale formation.

(3) For Slab 2 with high contents of copper and nickel, under the condition of lower initial slab surface temperature, copper-rich phase accumulates and stays at scale-substrate interface with a formed dense scale tightly attached to the substrate. While at higher initial slab surface temperature, Cu-rich phase in the porous scale layer is noted with simultaneous Ni-enrichment appearing in front of the steel-scale interface. Both a porous scale formed at higher initial slab surface temperature and high nickel content act together to occlude the copper-rich phase within the scale layer.

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