Journal of University of Science and Technology Beijing
Volume 11, Number 1, February 2004, Page 57

Materials

Influence of copper on quality of hot strips by EAF-CSP process

Yuanli Wang[1), *Delu Liu*[1), *Weiran Shao*[1), *Jie Fu*[2), *Yonglin Kang*[1), *Deguang Zhou*[2), *and Zhongbing Wang*[3)

1) Materials Science and Engineering School, University of Science and Technology Beijing, Beijing 100083, China
2) Metallurgical Engineering School, University of Science and Technology Beijing, Beijing 100083, China
3) Guanzhou Zhujiang Iron and Steel Co. Ltd., Guangzhou 510620, China
(Received 2003-04-22)

Abstract: Electron microscopy and X-ray Energy Dispersive Spectroscopy (XEDS) study on influence of Cu on low carbon hot strips produced by CSP (Compact Strip Production) process has been carried out. The results indicated that copper segregation and enrichment at interfacial layer between oxidized surface and steel matrix is the key factor, which results in microcracks and edge flaws on the strips. The primary considerations to prevent detrimental effects from Cu include controlling copper content in proper level, higher soaking temperature and non-oxidizable atmosphere during soaking. Copper sulfide precipitates with nanometers in size were observed, they may be beneficial to the properties of CSP products, and influence of Cu on quality of CSP hot strips is discussed.

Key words: Cu segregation; surface flaws; CSP hot strips; copper sulfide; nano-scaled precipitates

1 Introduction

Waste steel scraps are the main raw materials for steelmaking by the electron arc furnaces (EAF). Residual elements, especially low melting point metals such as Cu, Zn *etc.* have always been the major concerned for the steels produced by EAF process [1-3]. These low melting point elements usually tend to segregate to the grain boundaries and interface at high temperature during soaking and subsequent rolling process. It may cause surface cracking of the steel products because the segregation weakens grain boundaries [4-6] (*i.e.* hot shortness). In copper containing steels Cu is rejected from the oxidized surface layer and builds up a Cu enriched layer between the scales and steel matrix. This is resulted from the fact that oxidation potential of copper is lower than iron. Iron will be oxidized in advance of copper in oxidizable atmosphere during soaking [7].

On the other hand, Cu-bearing steels have been studied and developed for years. It was reported that copper plays an important role for improving overall properties of microalloyed steels by precipitation during rolling and ageing process [8]. At the same time, nano-scaled precipitates have been observed in low carbon steels produced by CSP process, which also attracted great attention recently [9-12]. In the present work, both of the phenomena associated with Cu, surface cracking and copper sulfide precipitation, in the low carbon steels produced by an EAF-CSP process have been studied. Influence of copper on the quality of hot strips produced by EAF-CSP process was discussed.

2 Experimental

Specimens studied in the present work were taken from hot strips produced by EAF-CSP process at Zhujiang Steel Co. Ltd. They include container steel strips with thickness of 6 and 4 mm respectively (marked as JZX-6) as well as low carbon steel strips with thickness of 4 mm (marked as ZJ400). Compositions of the experimental steels are listed in **table 1**. Container strip samples were subjected 90 and/or 180 degree bending along rolling and transverse direction at room temperature. Surface flaws resulted from the bending were observed by SEM equipped with XEDS system. Specimens of the low carbon steels were cut from the hot strips along transverse section then polished for edge cracks observation by using SEM and XEDS. Extract replica were also prepared to study copper precipitation behavior in the low carbon steel strips by TEM (Transmission electron microscopy).

Table 1 Chemical composition (mass fraction) of the experimental steels %

No.	C	Si	Mn	P	S	Cu	Ni	Cr	Al(s)
JZX-6	0.051	0.39	0.42	0.012	0.007	0.29	0.298	0.413	0.034
ZJ400	0.19	0.10	0.30	≤0.018	≤0.006	≤0.25	—	—	≤0.032
ZJ330	0.06	0.10	≤0.50	≤0.025	≤0.035	≤0.20	—	—	0.025-0.040

Corresponding author: Delu Liu, **E-mail:** dlliu@mater.ustb.edu.cn

3 Experimental results

3.1 Surface cracking

When samples of the container steel JZX-6 were bended 90 and/or 180 degrees along rolling direction at room temperature, surface cracks appeared on a part of the samples. But the cracking does not happen when the samples were bended along the transverse direction. From the SEM image (**figure 1** (a)), it can be seen clearly that cracks along the rolling direction are about 1 to 8 mm long with width less than 300 μm. Figure 1(b) shows one of the cracks with a larger magnification. Many particles with various size and shape exist at the bottom of the crack. XEDS analysis showed that these particles mainly consist of iron oxide and Zn-enriched particles. Some of the particles possess similar compositions as the shielding slag for continuous casting. It is likely that some shielding slag was brought into the liquid steel during continuous casting owing to vibration of the liquid surface in the mould.

Figure 1(c) gives a secondary electron image from the transverse section of a crack. XEDS analysis showed that there is a thin layer of iron oxide on the inner-surface of the crack. This oxide layer can be very clearly seen on a backscattering electrons image as shown in figure 1(d). Between the iron oxide layer and steel matrix there exists a very thin layer, where copper is enriched obviously. XEDS results obtained at different sites along the interfacial zone between the iron oxide layer and steel matrix are given in **table 2.** It can be seen that at certain sites copper content can be more than 5 times higher than the average content of the steel matrix. Because the spatial resolution of XEDS analysis in the present study is about 1 μm^3 in volume, but the segregation usually concentrates at only several atomic layers between iron oxide and the matrix or at grain boundaries. The concentration of copper at interfacial zone between the iron oxide layer and steel matrix in fact is greatly higher than the experimental value determined by the XEDS on SEM as shown in table 2. Thus the actual content of Cu at these interfaces would be much higher than the XEDS analysis results.

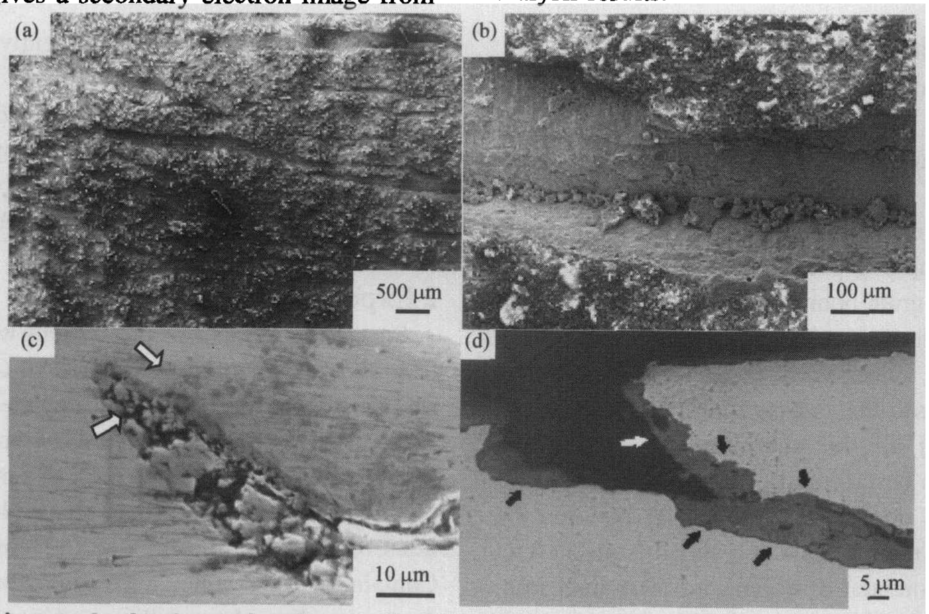

Figure 1 SEM micrographs showing surface flaws on the hot strip, (a) secondary electron image of microcracks on the strip surface; (b) one crack with larger magnification; (c) a crack feature along the transverse section; (d) backscattering electron image showing the oxide layer within the crack.

Table 2 XEDS results obtained at the interfacial zone between iron oxide layer and matrix (mass fraction) %

Samples	O	Al	Si	P	Cr	Fe	Ni	Cu	Zn
1	16.5	Trace	0.5	0.2	0.7	79.6	0.7	1.4	Trace
2	21.7	Trace	1.0	0.2	1.0	74.9	0.6	0.5	Trace
3	31.3	0.6	1.2	Trace	0.8	65.3	Trace	0.4	Trace
4	—	0.8	1.3	—	0.8	96.5	—	0.7	—
5	—	0.8	2.3	0.5	1.7	92.6	—	0.6	1.5

It is worth to notice that large numbers of pure zinc spherical particles exist on the strip surface of JZX-6 as shown in **figure 2**. Since the melting point of pure zinc is about 600°C, it is considered that these particles formed during approximately isothermal period at about 600°C after coiling. These residual Zn is from coating plates in scraps. Traditionally it is considered that Zn will be removed with melting slag or be vaporized during steel making because its low melting point. But in the present study pure zinc or Zn-Fe spherical particles on surface of the specimen JZX-6 were observed. The mechanism of its formation is not clear so far. Further study is needed to clarify the reason of Zn existence on the product strip surface.

A SEM image in **figure 3** (a) shows cracks on the edge of a transverse section from the low carbon strip. Cracks extend from the edge towards to inner area of the strip, depth of these cracks is less than 1 mm. In the cracks, there exists many spherical particles of zinc or zinc-iron alloy as shown in figure 3(b). It was confirmed by XEDS analysis that copper also segregates at the interfacial layer between iron oxide and steel matrix in the edge cracks. This phenomenon is similar as that in surface cracks on the container steel.

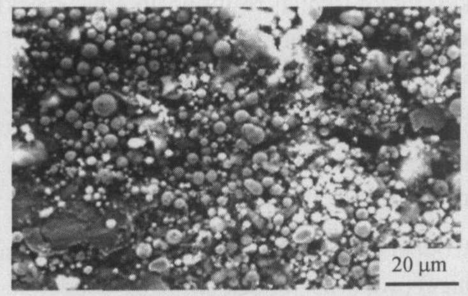

Figure 2 A large amount of pure Zn particles on the hot strip surface of JZX-6.

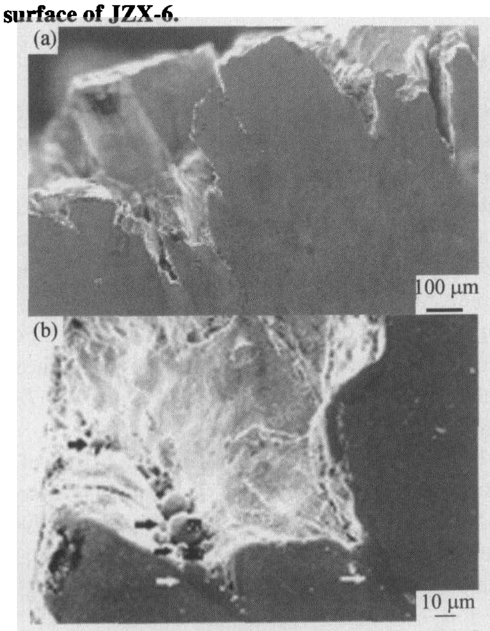

Figure 3 SEM photographs showing edge cracks on a transverse section of the low carbon strip, (a) transverse section features of edge cracks; (b) spherical particles of zinc and zinc-iron alloy in the edge cracks.

3.2 Copper sulfide precipitation

Carbon extract replica specimens of the strip ZJ330 were prepared and studied by TEM equipped with XEDS. Large number of copper sulfide precipitates with 50-100 nm in size have been observed. They were confirmed by XEDS analysis. One of the TEM micrograph is shown in **figure 4** (a). The copper sulfide particles are pointed out by arrows in the picture. One of the particles in larger magnification with its electron diffraction pattern is given in figure 4(b). Further study is needed for better understanding of this precipitation.

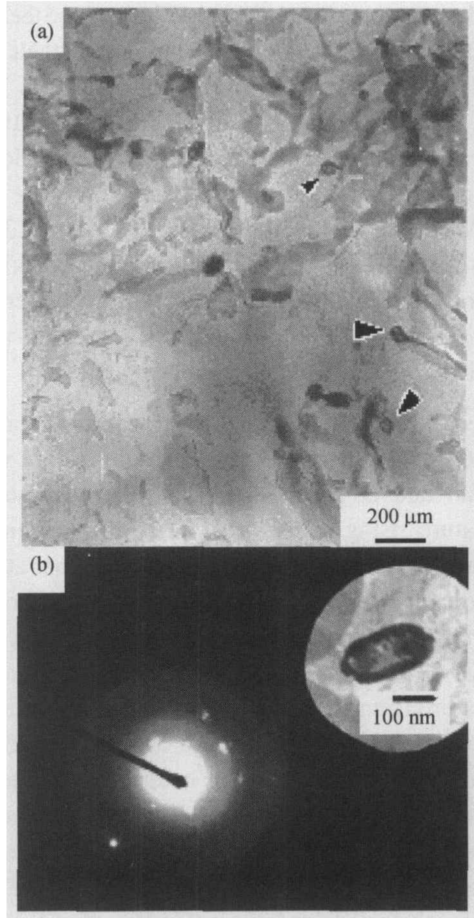

Figure 4 Copper sulfide precipitates in the steel, (a) TEM micrographs taken from an extract replica specimen showing small copper sulfides precipitated in the low carbon steel ZJ330; (b) electron diffraction pattern taken from a particle.

4 Discussions

4.1 Effect of copper on surface quality of the hot strips

Residual copper and other impurity elements are frequently introduced in steels by using scrap as raw material for EAF-CSP process. These residual elements with low melting point especially Cu, Zn *etc.* usually tend to segregate at grain boundaries during soaking period of the slabs and rolling. It is possible that a very thin layer of copper or copper enriched alloy would form along the grain boundaries when copper content reaches certain level in the steel.

This will result in extremely weakening of the grain boundaries at high temperature. In addition, oxidation takes place on the surface of the thin slabs during soaking and rolling. Since iron will be oxidized prior to copper in the steel as oxidation potential of copper is lower. The consequence of this prior oxidization is that copper enrichment at interface between the oxide scale of the surface and steel matrix further develops. This will further weakens the grain boundaries. Industrial statistic results from Zhujiang Steel Co. showed that copper concentration in liquid steels is the key factor for preventing from edge cracking. When copper content (mass fraction) is less than 0.1%, no edge cracking takes place for the CSP steels as long as there no other low melting point elements exist in the steel. When copper content ranges from 0.13% to 0.19%, the steels are susceptible to edge cracking or hot shortness. When copper content is larger than 0.19% possibility of hot shortness increases apparently [13].

In terms of grain boundary segregation theory, the free energy difference G between solute atom within the grain and at grain boundary will decrease with temperature rising. This will reduce the tendency of segregation. The local concentration of copper at grain boundaries caused by segregation will also decrease. Industrial experimental results for strips produced by the EAF-CSP process showed that elevating soaking temperature is an effective approach that could reduce the hot shortness problems such as edge cracking in strips apparently. Reductive or neutral furnace atmosphere for soaking is also very useful. At the same time Cu content and total amount of the residual elements with low melting point have to be limited below a proper level, for example keep Cu less than 0.13% in the steels.

4.2 Influence of copper on mechanical properties of the hot strips

It is already known that effects of Cu on mechanical properties of the steels are various. Cu additive increases corrosion resistance, hardness and strength of the steels. The basic mechanism for improvement of mechanical properties by Cu may be considered as the two major factors, i.e. precipitation and segregation. When copper content is properly controlled strength of the steels can be improved obviously by Cu dispersive precipitation as reported.

On the other hand, copper segregation at grain boundaries during soaking and hot working may retard austenite grain growth. Copper sulfide precipitates observed in the present work may inhibit original and recrystallized austenite grain growth. These sulfide particles are also effective nucleation sites for ferrite formation during $\gamma \rightarrow \alpha$ transformation as the misfit between this sulfide and ferrite is very small. These factors will benefit the refinement of final ferrite grains. Therefore, when copper content and process can be controlled properly this element could play an effective role to improve strength of the hot strips by segregation at grain boundaries and precipitation. Further study is needed for better understanding the behavior of copper in the steels by CSP process.

5 Conclusions

Investigation on role of the residual elements with low melting point such as copper in steels produced by EAF-CSP process has been carried out. The results are summarized as following:

(1) Copper enrichment along grain boundaries and at the interface between surface scale and steel matrix is the key factor, which resulting in edge cracking or hot shortness of the steels.

(2) The primary considerations to prevent detrimental effects from Cu include controlling copper content in proper level, elevating soaking temperature and non-oxidizable atmosphere during soaking.

(3) Copper could play a positive role to improve mechanical properties of hot strips by copper segregation and precipitation.

References

[1] Zhongbin Wang, Jing Li, and Jie Fu, *et al.*, A study on model of charging for an 150t EAF at Zhujing steel [J], *Special Steel* (in Chinese), 22(2001), No.4, p.55.

[2] Dabeng Zhang, Xiaohai Qin, and Zhibao Chu, Analyzing of star crack at CC slab and application of measures, [in] *Proc. Of CSM 2001 Annual Meeting* [C] (in Chinese), Beijing, Metallurgy Press, 2001, p.739.

[3] Deguang Zhou, Jie Fu, and Delu Liu, *et al.*, Forming mechanism and preventive measures of the surface crack in thin strip produced by CSP [J], *J. Univ. Sci. Technol. Beijing* (in Chinese), 24(2002), No.4, p.403.

[4] O. Hideyuki, G. Gautam, and N. Kotobu, Effects of Cu on diffusional transformation behaviour and microstructure in Fe-Mn-Si-C steel [J], *ISIJ Int.*, 37(1997), No.3, p.296.

[5] Zaoli Zhang, Qingying Lin, and Zongsen Yu, Grain boundary segregation in Ultra-low Carbon Steel [J], *Mater. Sci. Eng.* (in Chinese), A291(2000), p.22.

[6] M. Guttmann and D. McLean, *Interfacial Segregation* [M], the American Society for Metals, 1977, p.267.

[7] E.T. Stephenson, Effect of recycling on residuals, processing, and properties of carbon and low-alloy steels [J], *Metall. Trans. A Phys. Metall. Mater. Sci.*, 14A(1983), No.3, p.343.

[8] M.R. Krishnadev, G.J. Sojka, and S.K. Banerji, Strong tough HSLA steels via processing and heat treating of Cu-Ni-Cb and Cu-Ti-B compositions [J], *J. Eng. Mater. Technol.*, 103(1981), No.3, p.207.

[9] Delu Liu, Xiangdong Huo, and Yuanli Wang, *et al.*, Oxide and sulfide dispersive precipitation in ultra-low carbon

steels [J], *J. Univ. Sci. Tech. Beijing*, 8(2001), No.4, p.314.

[10] Delu Liu, Jie Fu, and Yonglin Kang, *et al.*, Oxide and sulfide dispersive precipitation and effects on microstructure and properties of low carbon steels [J], *J. Mater. Sci. Technol.*, 18(2002), No.1, p.7.

[11] Delu Liu, Yuanli Wang, and Xiangdong Huo, *et al.*, Grain refinement and strengthening of low carbon steel by the CSP process [J], *Acta Metall. Sin.* (in Chinese), 38(2002), No.6, p.647.

[12] Delu Liu, Xiangdong Huo, and Yuanli Wang, *et al.*, Aspects of microstructure in low carbon steels produced by the CSP process [J], *J. Univ. Sci. Technol. Beijing*, 10(2003), No.4, p.1.

[13] Zhongbin Wang, Liqun Xie, and Yizhong Chai, *et al.*, Effect and control on edge cracks of hot-rolled light gauge strips in CSP line, [in] *Proc. of CSM 2001 Annual Meeting* (in Chinese) [C], Metallurgy Press, Beijing, 2001, p.766.