Effect of si-cr-mo on oxidation behavior of duplex steel and strip surface quality

C. Wang, Y. Yu, K. Liu, L. Wang, Z. Guo, T. Niu

The interactive effects of Si-Cr-Mo alloy elements on oxidation behavior at scale/metal interface in dual-phase steel are studied in present paper, through thermal simulation, scanning electron microscopy (SEM) and electron probe analysis. The influence of alloy elements on hot coil surface quality under industrial production conditions are also discussed. Results show that the oxidation resistance of Si-Cr steel is stronger than that of Si-Cr-Mo steel, because of Cr-rich protective oxide film at scale/metal interface under elevated temperature. Comparing with steel alloyed by Si, the primary scale of the Si-Cr and Si-Cr-Mo steel are easier to be removed, owing to the reduction of anchor structure at scale/metal interface. However, Si and Cr element will form dense oxide film under 1,100°C and above, which increases the difficulty of finishing descaling. Owing to the accumulation of Mo on the scale surface, the diffusion channel of Si and Cr elements is blocked, resulating in the increase of oxidation resistance and the decrease of Si-Cr oxide film at scale/metal interface. Therefore the surface quality of Si-Cr-Mo steel is significantly improved under industrial production. Suggestions conclued from present study can provide useful guidance for production of cold rolled dual-phase steel.

KEYWORDS: OXIDATION BEHAVIOR, ELEMENT ENRICHMENT, INTERACTIVE EFFECT, SCALE, DESCALING

INTRODUCTION

Basing on the phase transformation strengthening mechanism, the dual-phase steel composed of ferrite and martensite has been developed as advanced high-strength stamping steel for automobile. The cold rolled dual-phase steel are mainly classsfied by C-Si-Mn steel and C-Mn-Cr steel [1,2], which sometimes is micro-alloyed with Nb, Mo and B elements. In the widely used C-Si-Mn dual-phase steel, the mass percent of Si element is controlled between 0.2% and1.5%, which can improve the austenitic harden ability and improve the purity of the ferrite. However, when the mass percent of Si is more than 0.2% ,the red scale defect are easily generated during hot rolling process resultiing in surface color difference defect on the finished product[3,4]. According to the high surface quality standards, the Si is replaced by Cr or Cr-Mo as an option to produce C-Mn-Cr/C-Mn-Cr-Mo dual phase steel.

The effect of Si on oxidation resistance at high temperature has been adequately studied by predecessors.The Si element exists as hydrothermal Fe2SiO4 phase at scale/ metal interface at elevated temperatures above 1,173°C. When the temperature drops to 1173°C and below, the

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scale will tranformed to eutectoid structure in which FeO grains will be surrounded by Fe2SiO4. The FeO particles could be tightly sticked on the slab surface by the solidified eutectoid structure, which is difficult to be removed by descaling. The residual FeO will be squashed by following hot rolling process, leading to the increase of contact area with oxygen and giving rise to the red Fe2O3 phase[5, 6]. In the range of 700~1,000°C[7], with higher Si content, oxidation mass gain and scale thickness of the steel with high Si content are both reduced because of improved oxidation resistance. At present, some papers focusing on oxidation behavior of Cr-Mo in stainless steel and heat-resistant steel at elevated temperatures. Chen WY found that Cr2O3 protective oxide film accumulated at the strip surface of 3Cr13 stainless steel, in which the Cr content is about 13.46%, significantly improveing anti-oxidation properties[8]. Zhao Q H concluded that the SiO2 and MnCr2O4 oxide film was formed under 1100°C and SiO2 oxide film adjacent to metal matrix can obviously decrease the oxidation mass gain rate basing on one kind of ferritic heat resistant steel[9]. However, few reports have been publised focusing oxidation behavior of the cold-rolled dual-phase steel at elevated temperature, basing on C-Mn-Cr/C-Mn-Cr-Mo system. For the oxidation behavior of Mo element, it is reported that Mo element is easy to be oxidized in air when the temperature is heated up to 300°C. When the temperature increases up t0 600°C and above, Mo will be oxidized to volatile oxides with dark green color. Xie Hong-bo studied the influence of Mo on oxidation behvior of high-entropy alloy at elevated temperature and found that the oxidation resistance was seriously deteriorated because of volatile Mo oxide[10]. In the referenced papers listed above, the content of Cr/Mo in mass percent is around 10-20%, the scale of given steel grade mainly consists of compact single-layer oxidation film. However, the Si/Cr/Mo content in cold rolled dual-phase steel range from 0.2~1.15%, the interreaction of Si-Cr-Mo on oxidation behavior should be interesting and not be neglected.

In present work, the interreaction of Si-Cr-Mo elements on oxidation characteristics at scale/metal interfacei of dual-phase steel are studied. In addition, the effect of alloyed elements on coil surface quality under industrial production condition is also discussed, which can provide useful guidance for production of dual-phase steel.

EXPERIMENT METHOD

Three types of composition are designed for present study. The first sample contains1.15%Si without Cr-Mo; the second sample contains 0.55% Cr and 0.2% Si without Mo; and the third sample contains 0.2%Si in combination with 0.2% Cr and 0.25%Mo (as shown in Tab. 1).

Tab.1 - Designed omposition of high strength DP steel with different alloyed element (wt. %).

NO.	C	Si	Mn	P≤	S≤	Alt	[N]≤	Cr	Mo
Steel 1	0.76	1.15	1.7	0.015	0.005	0.035	0.0030	--	--
Steel 2	0.12	0.20	1.6	0.015	0.005	0.035	0.0030	0.55	--
Steel 3	0.10	0.20	1.5	0.015	0.005	0.035	0.003	0.20	0.25

The oxidation behavior of given three steels are studied under two different temperature ranges by STA449C type thermo gravimetric analyzer. To simulate the oxidation behavior in reheating furnace, the samples were heated up to 1250°C in the atmosphere contains 10% CO_2,5% O_2 and other argon gas. The samples were heated under given heating rate of 10°C/min and were kept for minutes under aimed temperature. Secondly, we simulated the oxidation during hot rolling process in the temperature range of 900-1150°C. In order to oxidation behavior during hot rolling process, the samples were heated up to 1150°C, 1100°C. 1050°C, 1000°C, 950°C and 900°C, respectively, in protective argon gas with the heating rate of 10°C / min. Then, the samples were kept in the air at the target temperature for 1 min. Finally, the samples will be put into the protective atmosphere again and be cooled to room temperature at the cooling rate of 10°C / min.
The surface topography, scale/metal interface topography

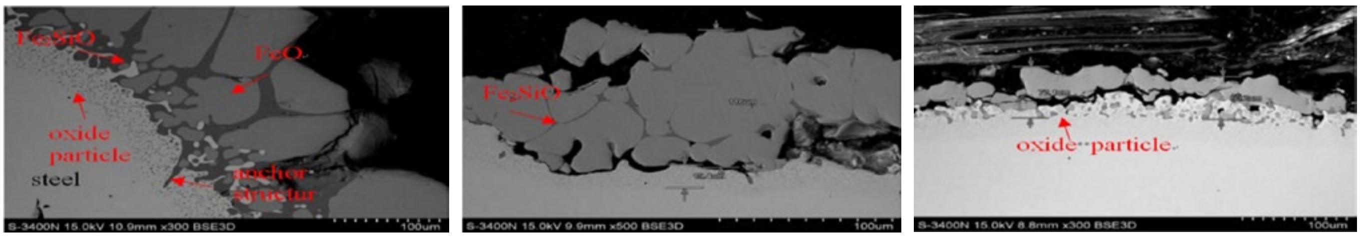
and energy spectrum, were investigated with the scanning electron microscopy (SEM). The elements distribution quantitative analysis at scale/metal interface was detected by EPMA-1720 electronic probe analysis .

The surface quality difference between differernt dual phase steels under industrial production condition was studied in a domestic hot rolling production line by Parsytec surface inspection equipment adopting CCD scanning digital camera with the resolution ratio of 500μm*1000μms. One of the key equipment for the surface quality control is high pressure descaling system, of which the pressure could achieve 20-22MPa. For the three designed steels, the rolling process parameters is the same in order to investigate the effects of alloyed elements on coil surface quality.

RESULTS

Oxide film morphology under heating furnace conditon

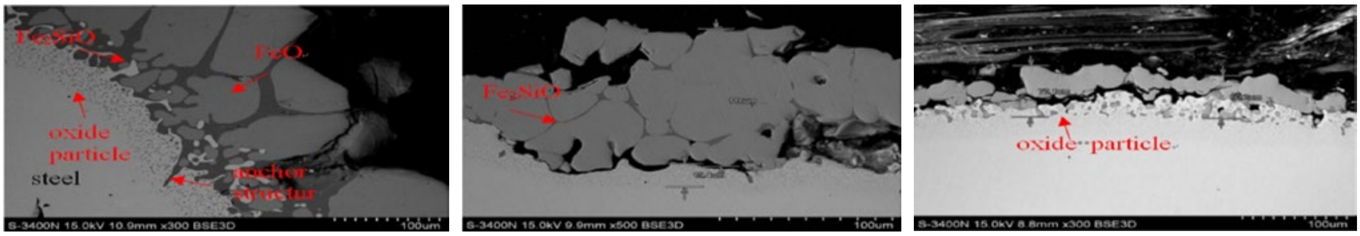
As shown in Fig. 1, the oxide film micromorphology of thres different steels under 1250°C are given. The oxidation film of steel No.1 at scale/metal interface shows typical anchor pinning morphology of Si alloyed steel, in which the ferrous oxide (FeO) is surrounded by Fe_2SiO_4. The anchor made by theFe_2SiO_4 is nailed into the metal matrix with a depth of 50 μm. Because of the anchor structure,the inner layer of scale has good adhesive force. In addition, the oxide particle layer under interface is about 50 μm. The anchor pinning morphology is originated from the melt behavior of Fe_2SiO_4 at the preset temperature and the molten Fe_2SiO_4 will infiltrate into the grain boundary of scale and the steel substrate. Steel No.2 contains 0.2%Si and 0.55% Cr element. The mesh scale morphology and anchor pinning morphology in oxide film are significantly reduced. Compared with steel 1, the depth of the liquid Fe_2SiO_4 infiltrated into the matrix decreased to about 20μm. During the samples' preparation process, due to the weakened anchor pinning structure, the scale is easy to crack and peel off. Cr content of steel No.3 is reduced to 0.2% on the basis of steel No.2 with an addition of 0.25% Mo. The mesh scale morphology and anchor pinning morphology is not obvious, but large oxide particle with a particle-layer thickness of 50μm present at sacle/metal interface. The outermost layer scale of steel No.3 was also easy to peel off during sample preparation process.



(a) Steel 1 (b) Steel 2 (c) Steel 3

Fig.1 - Scale/interface morphology of given three steels under heating furnace condition.

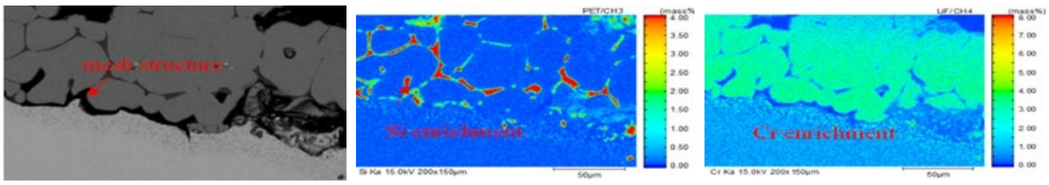
The distribution of Cr–Si element at scale/metal interface of steel No.2 is shown in Fig. 2 in detail. Si enrichment taking place in the mesh scale structure, anchor pinning structure and small oxide particles. The content of Si element in the mesh structure is highest illustrated as red color. Si-rich in the oxide particles originated from the internal oxidation of alloying element and the Si content in oxide particles is lower than that in the mesh scale. Cr element accumulates greater in the scale than that in metal matrix. In the oxide particles, Cr element enrichment could also be found. Complementary relationship between the distribution of Cr and Si is found in the scale. In the region of the mesh structure where the Si element is rich, the Cr element is poor. Because the content of Cr element in scale is higher than Si element, the anchor pinning morphology formed by Fe_2SiO_4 nearly disappeared.



(a) scale morphology (b) Si distribution (c) Cr distribution

Fig.2 - The element distribution of Cr – Si in oxidation film of steel 2.

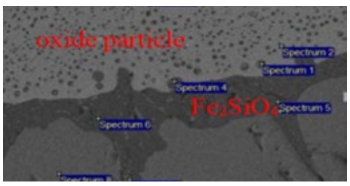
Oxidation scale morphology of steel 3 is given in Fig. 3. The mesh structure in the scale of steel No.3 is significantly weakened compared with steel 2, especially in the inner oxidation layer adjacement to matrix. The mesh scale almost disappeared. Complementary relationship between content of Cr and that of Si element in oxidation scale. In steel 3, the content of Cr and Si element are both about 0.2%. According to the free energy rule, Si is oxidized earlier than Cr, inducing Si-rich in oxide particles. Mo-rich layer distributed in the metal matrix around scale/metal interface, the depth of which is the same with internal oxidation zone. Mo is not involved in the formation of the internal oxide particles.



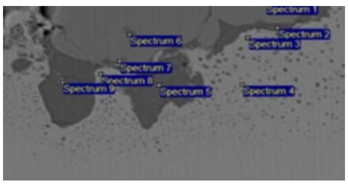
(a) scale (b) Si element distribution (c) Cr element distribution (d) Mo element distribution

Fig.3 - The Cr-Si-Mo element distribution at the interface in oxidation film of steel 3.

As shown in Fig. 4, energy spectrum analysis of the oxidation particles was applied at the interface of steel No.1 and steel No.2. The Si content in the band of molten Fe_2SiO_4 is as high as 10-13%. Meanwhile, with the internal oxidation of Mn, a series of oxides of low melting point are formed. With increase of Cr content and decrease of Si content, the width of the molten band decreases. It is inferred by the energy spectrum analysis that competition oxidation mechanism resuts in the complementary relationship between Si content and Cr content in scale.



1	1.64	6.71
2	11.66	15.63
3	1.34	3.63
4	9.34	2.98
5	12.03	3.74
6	10.29	3.20



1	0.35		2.30	0.92
2	10.71	0.67	0.55	2.71
3	1.60	0.32	3.17	7.74
4	1.12		7.17	12.60
5	11.00	0.74		2.45
6			22.06	1.30
7	8.83	0.66	1.73	3.02
8			1.67	6.38

(a) Steel No.1 (b) Steel No.2

Fig.4 - Energy spectrum analysis of scale/metal interface in steel 1 and steel 2.

Oxide morphology under hot rolling condition

The surface morphology of oxidation scale of given three types of dual phase steel under different temperature was simulated by thermo gravimetric analyzer. The scale morphology transformation patterns of the three given steels under different temperature is consistent. Fig. 5 illustrates the oxide film morphology of steel No.2 at different temperatures. Under tested condition, the scale is thin and smooth at 900°C and becomes rough and uneven when the temperature heated up to 950°C. The scale surface looks like tumor morphology at 1050°C. When the temperature rises to 1100°C, preferential growth of oxide particles is found on the surface and the scale mainly consists of coarse particles. Under the condition of 1150°C, oxide particles present obvious granular structure with a grain size of 50 μm.

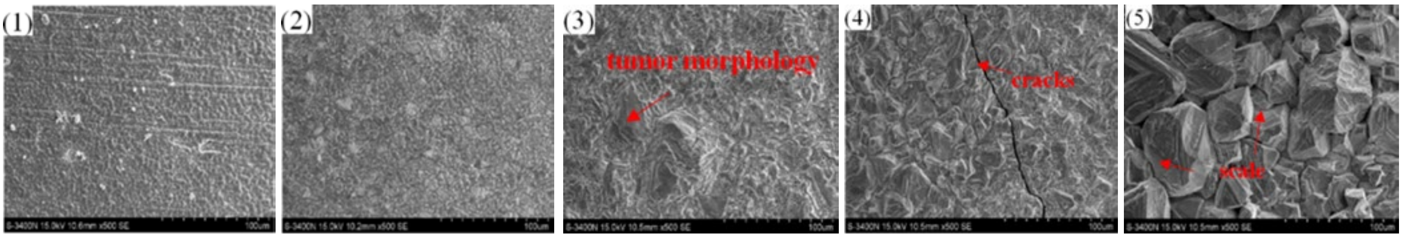


Fig.5 - Oxide film morphology under different temperature (1:900°C, 2:950°C, 3:1050°C, 4:1100°C, 5:1150°C).

More and more cracks can be observed on the scale surface as the test achieved higher and higher aimed temperature because thermal expansion coefficient difference between scale and matrix becomes larger and larger, inducing internal stress growth at scale/metal interface and surface scale spalling during sample preparation, as shown in Fig. 6[11].

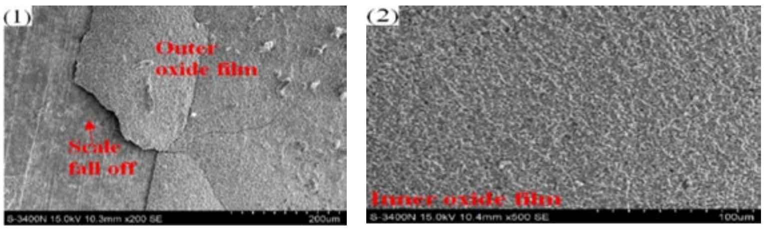


Fig.6 -Oxide film peeling morphology at 1050°C.

(1: broken and peeling of the outer oxide film, 2: internal compact oxide film)

Element enrichment in oxidation film under hot rolling condition

SEM was applied to determine scale thickness under different test temperature. Results is given in Fig. 7. steel No.1 alloyed with Si content of 1.15 mass% possesses the best oxidation resistance and thinnest scale thickness at 1150°C among the three predesigned steels. Benifit from the dense Si - Cr composite oxide film at scale/metal interface, steel No.2 alloyed with Si- Cr has better oxidation resistance than that of steel No.3 alloyed with Si-Cr-Mo. The scale thickness of steel No.3 is the thickest. The scale thickness of steel No.3 is about 20 μm thicker than that of steel No.1 at 1150°C.