

A Study of Network Defects of a Phosphated Si-containing Low Alloy Steel

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This study was to investigate the formation of network defects that appeared on a phosphated low alloy steel rod containing 1.1% Si. Laboratory oxidation, pickling, annealing, and phosphating were performed. A scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) was employed to analyze the surface morphology and the elemental distribution of the specimen from each stage. From the results, a mechanism of formation of network defects has been proposed. Fast finish rolling produced fragments of Si-containing iron oxides, which were not removed completely through primary pickling → annealing → secondary pickling. Then, small pits occurred on the substrate near the interface of the substrate and the residual scale. After phosphating, small pits grew to large pits and propagated along the grain boundaries. Some grains spalled off eventually and looked like a network by human naked eyes.

Keywords hot rolling, phosphating, pickling, pit, rod

1. Introduction

Phosphating is usually applied to tool steel rods for corrosion resistance during storage and, furthermore, for lubrication during drawing with significantly high reduction. The typical manufacturing process of phosphated steel rod is hot rolling → primary pickling → annealing → secondary pickling → phosphating. Defects shaped like network, which are defined as network defects, often appear on a low alloy steel rod containing 1.1% Si, after drawing. This kind of defect is detrimental to the surface properties of the final tool products. Figure 1 is a typical phosphated specimen with network defects. Subsequent processing, such as quench and temper treatment, after drawing is not included in this article.

According to the observation in the actual mill, as-rolled rods with marks on the pile-up surfaces possess smuts after the primary pickling. A typical as-rolled specimen with marks is shown in Fig. 2. After the secondary pickling, small pits occur on the surfaces of the corresponding rods. Furthermore, after phosphating, network defects appear on the surfaces of the corresponding rods if the phosphated layer is removed via mechanical polishing. It is, therefore, necessary to investigate the formation mechanism of the network defects.

2. Experimental Methods

The schematical diagram of experiments is shown in Fig. 3.

Test materials included phosphated rod and as-rolled rod. Both of them, with diameter 8 mm and chemical composition given in Table 1, were supplied from the mill of China Steel Corporation.

Mechanical polishing was done with a silicon carbide paper to remove the phosphated layer or the as-rolled oxide scale. This method to remove the phosphated layer was used to simulate the subsequent drawing of phosphated rods.

Pickling (primary and secondary) and phosphating were done by immersing the specimens, respectively, in pickling solution (HCl with pickling inhibitor) and phosphating solution. The temperature and time of immersion were 46 °C × 3 min for primary pickling, 55 °C × 3 min for secondary pickling, and 80 °C × (10 or 20 min) for phosphating.

Annealing was done in a furnace under with flowing nitrogen (flow rate 400 cc/min) at 765 °C for 5 h. Due to the slight impurity in nitrogen, oxidation may occur in this atmosphere.

Pile-up oxidation test was done in a tube furnace with static air. Specimens were cut into 15 mm length and mechanically polished to remove the scale on the as-rolled products. Each specimen was cut, according to the schematic diagram shown in Fig. 4, into two pieces, followed by tying up to the original orientation with a thin platinum wire for pile-up oxidation simulation. Thin platinum wire was used as the tying material because of its resistance to high temperature oxidation. For comparison, non-pile-up oxidation test was done on specimens without tying up after cutting. In contrast to the tied up specimen, the cross section of this kind of specimen was therefore completely exposed to air during high temperature oxidation. The oxidation temperature was 810–920 °C to simulate the various finish rolling temperatures, while the oxidation period was 5 min. After each test, the specimen was cooled down to room temperature via furnace cooling, air cooling, or fan cooling to simulate the various cooling rates after

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Fig. 1 A typical phosphated specimen with network defects (Phosphated layer was removed by mechanical polishing)

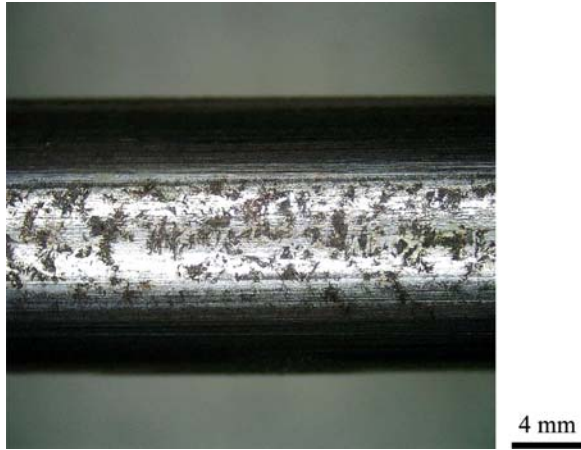


Fig. 2 A typical as-rolled specimen with marks

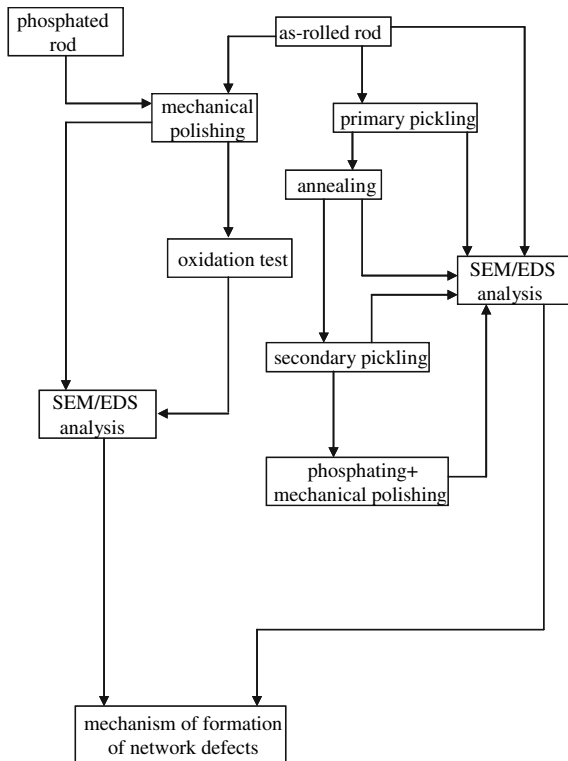


Fig. 3 Schematic diagram of experiments in this investigation

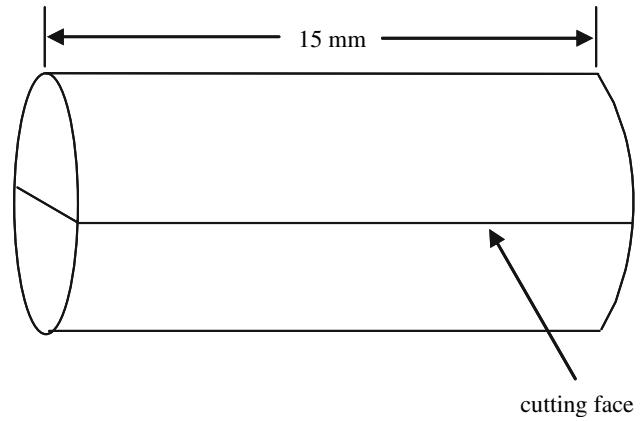


Fig. 4 Schematic diagram of the specimen in pile-up oxidation test

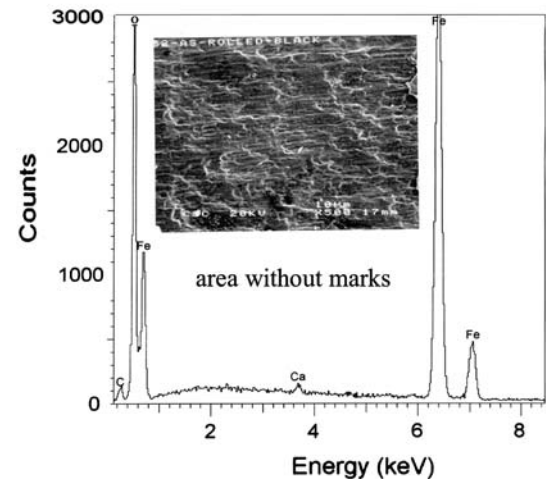
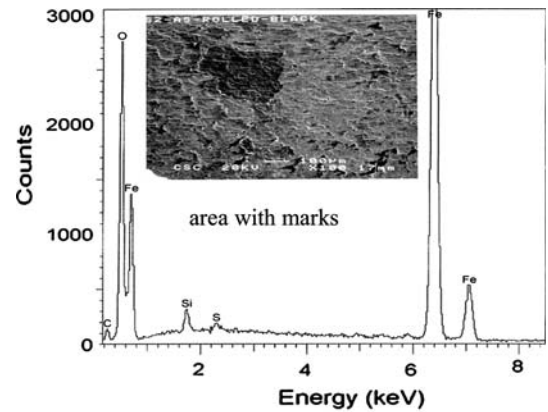


Fig. 5 Result of SEM/EDS analysis on the lateral surface of as-rolled specimen with marks

Table 1 Chemical composition of the steels investigated (wt.%)

C	Si	Mn	P	S	Mo	V	Cr	Al
0.67	1.10	0.56	0.024	0.004	0.42	0.165	0.14	0.042

Fe: balance

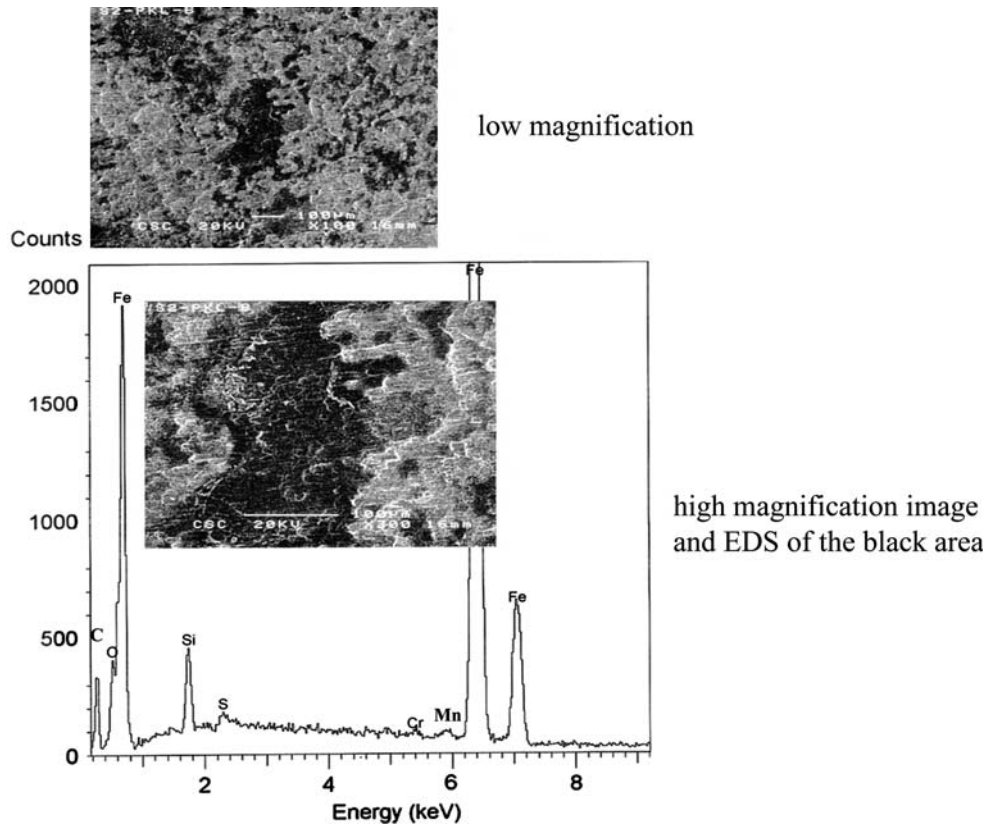


Fig. 6 Results of SEM/EDS analysis on the lateral surface of the specimen after primary pickling

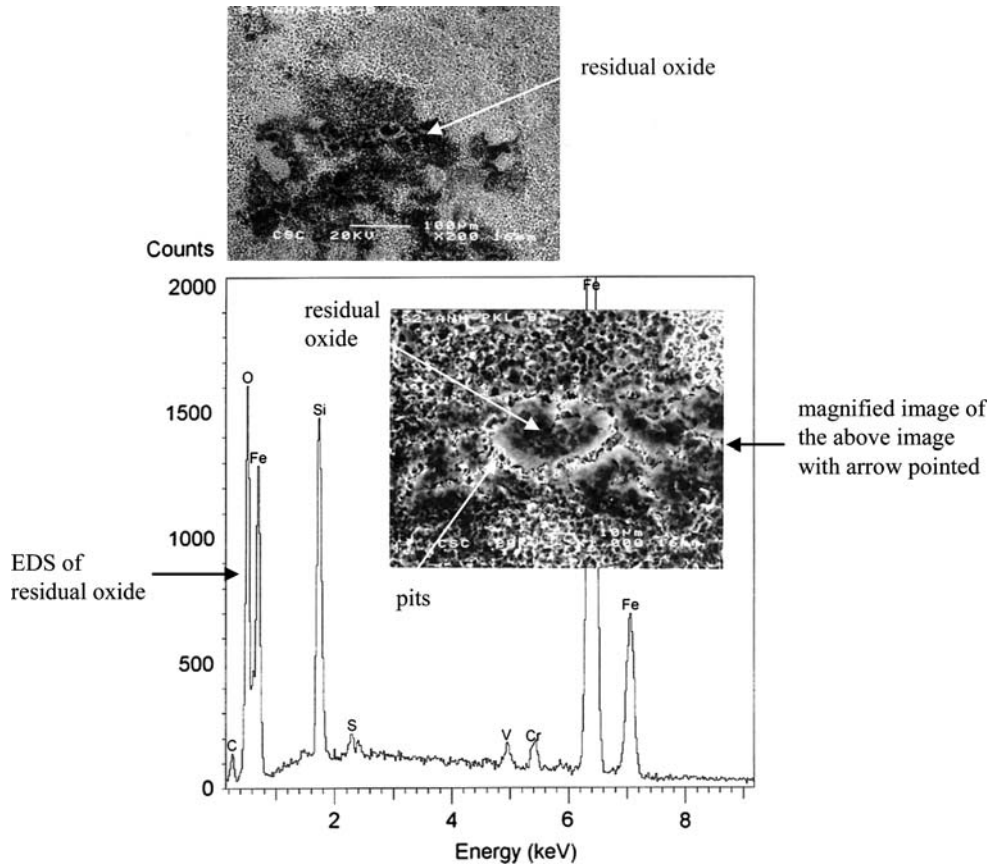


Fig. 7 Results of SEM/EDS analysis on the lateral surface of the specimen after primary pickling → annealing → and secondary pickling

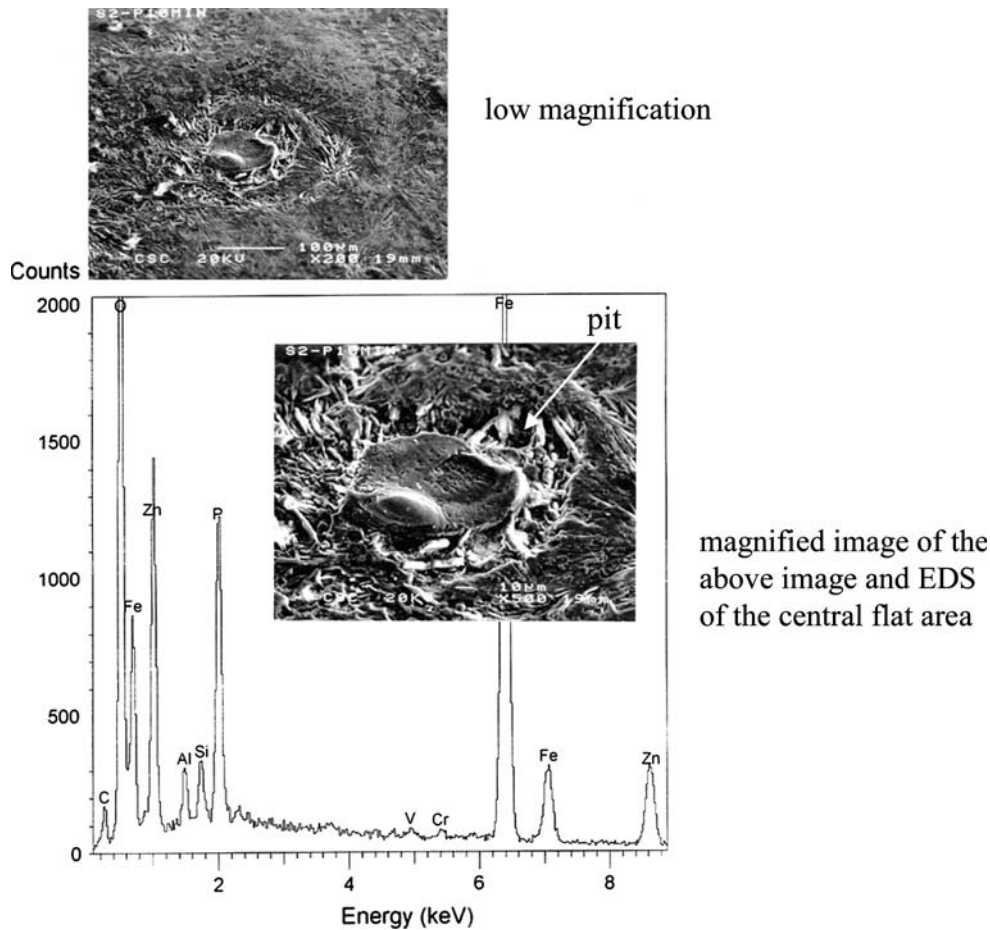


Fig. 8 Result of SEM/EDS analysis on the lateral surface of the specimen with marks after primary pickling → annealing → secondary pickling → phosphating for 10 min → slightly mechanical polishing

Table 2 Oxide scale on the steel surface after non-pile-up oxidation at various temperatures for 5 min followed by cooling with various rates

Temperature, °C	Furnace cooling		Air cooling		Fan cooling	
	Inner scale	Outer scale	Inner scale	Outer scale	Inner scale	Outer scale
810	Little F	W	W	W	Much F	W
860	W	W	W	W	Little F	W
920	W	W	Much F	W	Much F	W

W: iron oxide; F: Si-containing iron oxide

rolling. The latter two cooling methods can be done in actual mill, while furnace cooling can be done in laboratory study only.

A scanning electron microscope (SEM) together with energy dispersive spectrometer (EDS) was employed to investigate the surface morphology and the elemental distribution of the specimen from each stage.

3. Results and Discussion

3.1 Simulated Pickling and Phosphating

Figure 5 is the SEM/EDS analysis of the lateral surface of as-rolled rod with marks. It is evident that the surface of the

normal area was smooth and contained mainly iron oxide. In contrast, the area with marks was rough and contained fragmented protruded black islands which were composed of iron oxides with 0.8 to 1.5% silicon. Because of the difficulty of picking these tiny samples, we did not employ x-ray diffraction technique (XRD) to identify these compounds. However, based on most experiences (Ref 1-5), the Si-containing iron oxide was probably fayalite (Fe_2SiO_4). These island type Si-containing iron oxides looked like marks due to the different heights and colors from the normal area. After primary pickling, the marks became smuts that were visible to the naked eyes. Figure 6 shows that the smut was irregular black oxide composed of Si and other elements such as Cr. Cr was not observed in the marks before pickling because it

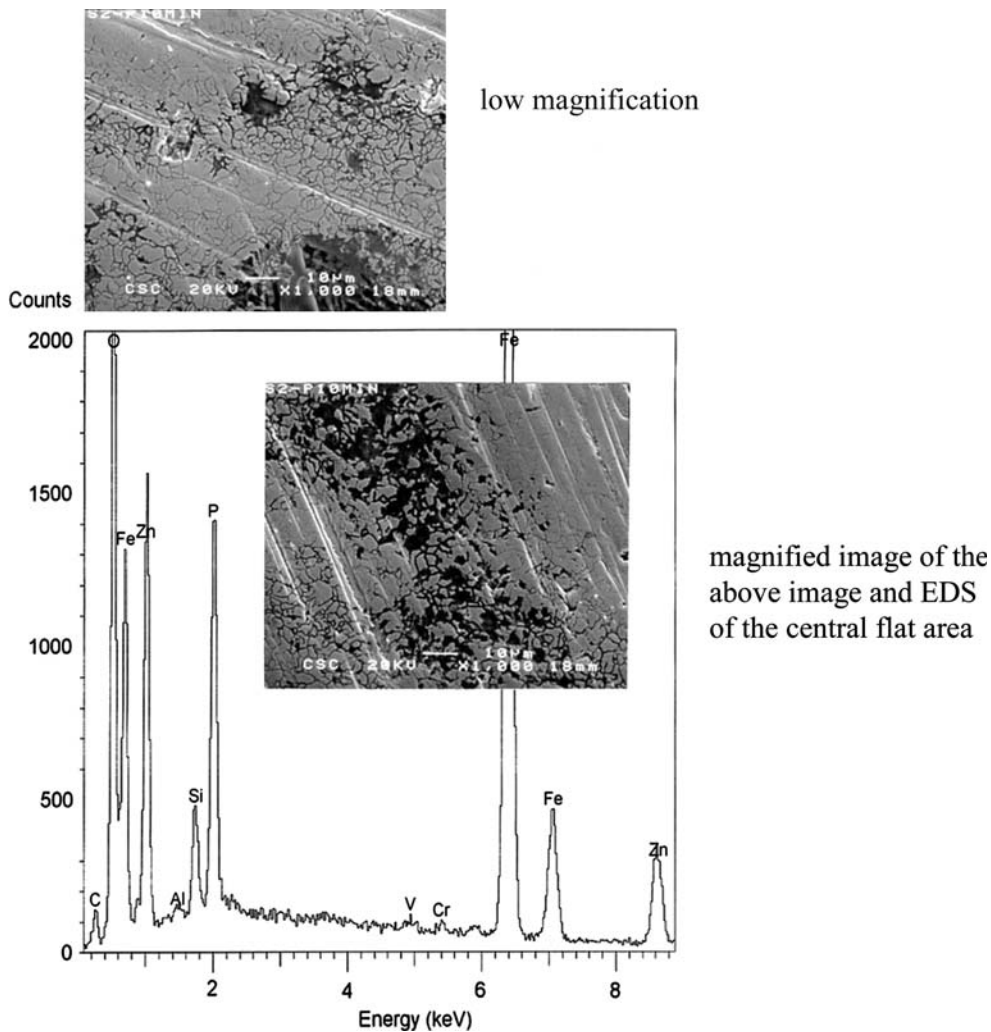


Fig. 9 Result of SEM/EDS analysis on the lateral surface of the specimen with marks after primary pickling → annealing → secondary pickling → phosphating for 10 min → prolonged mechanical polishing

Table 3 Oxide scale on the steel surface after pile-up oxidation test at various temperatures for 5 min followed by cooling at various rates

Temperature, °C	Furnace cooling		Air cooling		Fan cooling	
	Interface edge	Interface center	Interface edge	Interface center	Interface edge	Interface center
810	Inner Island-type F	F	Inner Island-type F	F	Inner Island-type F	F
860	W	F (much inside and little outside)	W	F	Inner Island-type F	F
920	W	Inner F and Outer W	Outer W and little Inner F	F	W	F

W: iron oxide; F: Si-containing iron oxide

existed in the internal layer. Similarly, we could not employ XRD to identify the Cr-containing iron oxide. Probably, it was FeCr_2O_4 from experience (Ref 6). According to literature (Ref 7), FeCr_2O_4 is difficult to dissolve in hydrochloric acid, while fayalite is easy to decompose to FeO and SiO_2 . In contrast to FeO , SiO_2 is difficult to dissolve in hydrochloric acid. Therefore, the Si-containing iron oxide might be the mixture

of $\text{FeO} + \text{SiO}_2$ decomposed from the Si-containing iron oxide or the mixture of $\text{SiO}_2 +$ retained Fe_2SiO_4 .

Figure 7 reveals the SEM/EDS analysis of the area with marks after primary pickling, annealing, and secondary pickling. The original scale had transformed to another type of scale. In addition to Si and Cr, this new type of scale also contained V which was not observed after the primary pickling

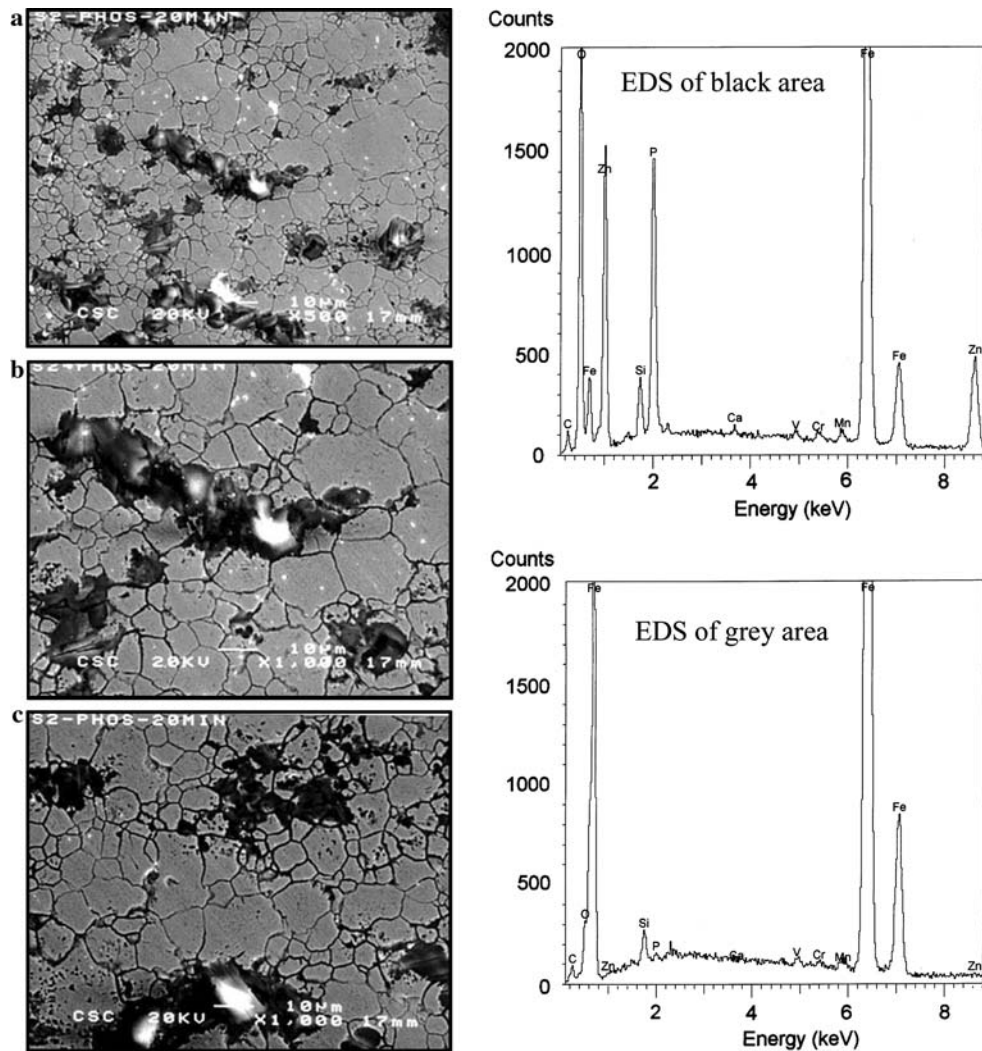


Fig. 10 Result of SEM/EDS analysis on the lateral surface of the specimen with marks after primary pickling → annealing → secondary pickling → phosphating for 20 min → prolonged mechanical polishing. b is magnified image of a, while c is another area with similar morphology. Both EDS's are analyses of b

because it existed in the internal layer due to its higher affinity for oxygen than iron. Furthermore, small pits occurred on the steel substrate near the scale/substrate interface. This is due to the different potential between the scale and the substrate. Small pits did not occur on the specimen in Fig. 6, because there existed a large amount of scale on the as-rolled rod and the temperature of the primary pickling was quite low. However, the amount of scale on the annealed rod was very small and the temperature of the secondary pickling was higher in Fig. 7, i.e., small pits were easy to induce during secondary pickling.

Figure 8 reveals the SEM/EDS analysis of the area with marks after primary pickling, annealing, secondary pickling, and phosphating for 10 min followed by mechanical polishing with #1200 SiC paper for a few minutes. Pits occurred on the steel substrate near the iron oxide containing Si and small amount of V and Cr.

After prolonged mechanical polishing (Fig. 9), more pits became visible. Furthermore, network defects became more severe in case the time of phosphating was even prolonged (Fig. 10) because small pits grew to large pits. These larger pits

were distributed along the grain boundaries and made some grains spall off.

3.2 Oxidation Test

Table 2 lists the oxide scale on the steel surface after oxidation at various temperatures for 5 min followed by cooling with various rates. In this test, the lamellar oxide easy to spall off was defined as outer scale, while that adhered to the substrate was inner scale. It is evident that after non-pile-up oxidation, the inner oxide scale gradually transformed from iron oxide to Si-containing iron oxide with increasing cooling rate (except at 810 °C followed by furnace cooling), while the outer oxide scale was iron oxide at all the oxidation temperatures and cooling rates. Due to the non-pile-up oxidation and the sufficient accessible oxygen, silicon was rich in the inner scale (Fig. 11). However, the temperature effect was not significant.

Table 3 shows that, after pile-up oxidation, except at 920 °C and furnace cooling, all the oxide scales at the interface center were Si-containing iron oxides at all temperatures and cooling

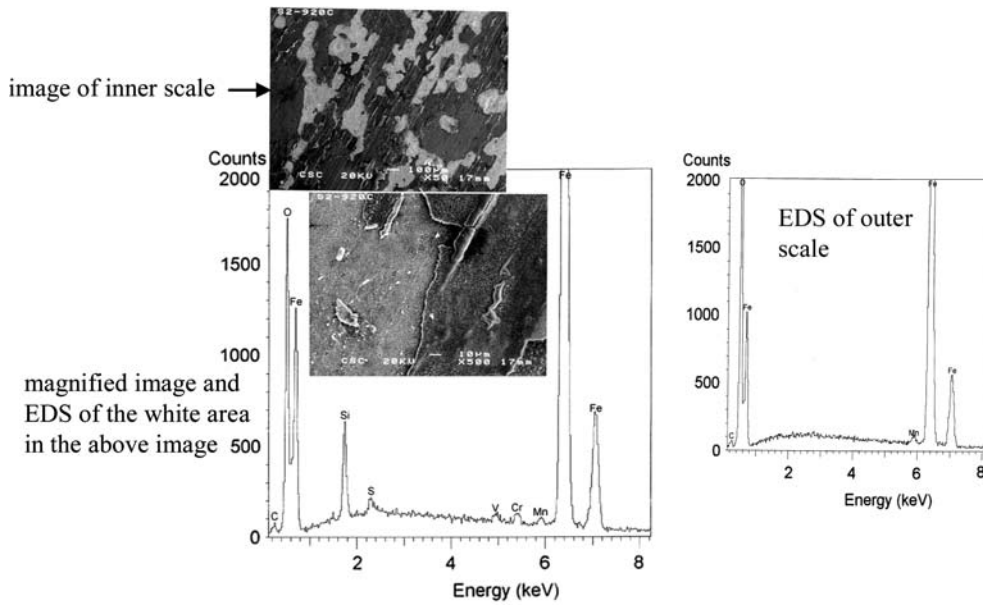


Fig. 11 Result of SEM/EDS analysis on the surface of the specimen after non-pile-up oxidation test at 920 °C for 5 min followed by air cooling

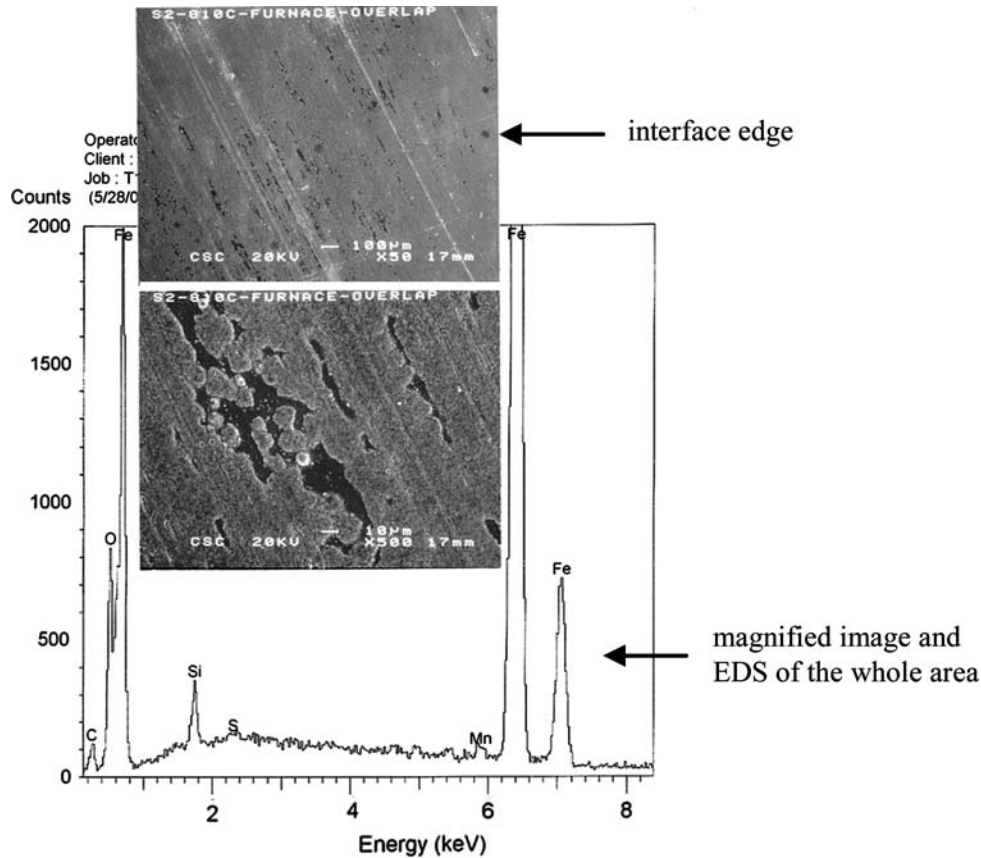


Fig. 12 Result of SEM/EDS analysis on the surface of the interface edge of specimen after pile-up oxidation at 810 °C for 5 min and furnace cooling

rates due to lack of accessible oxygen. On the other hand, the accessible oxygen at the interface edge was relatively high, but lower than that of the non-pile-up oxidation. Island-type Si-containing iron oxide was easy to form during pile-up

oxidation (Fig. 12). The amount of iron oxide decreased with increasing cooling rate, because of less residence time at high temperature and because silicon possessed greater tendency than iron to form oxide due to its higher affinity for oxygen

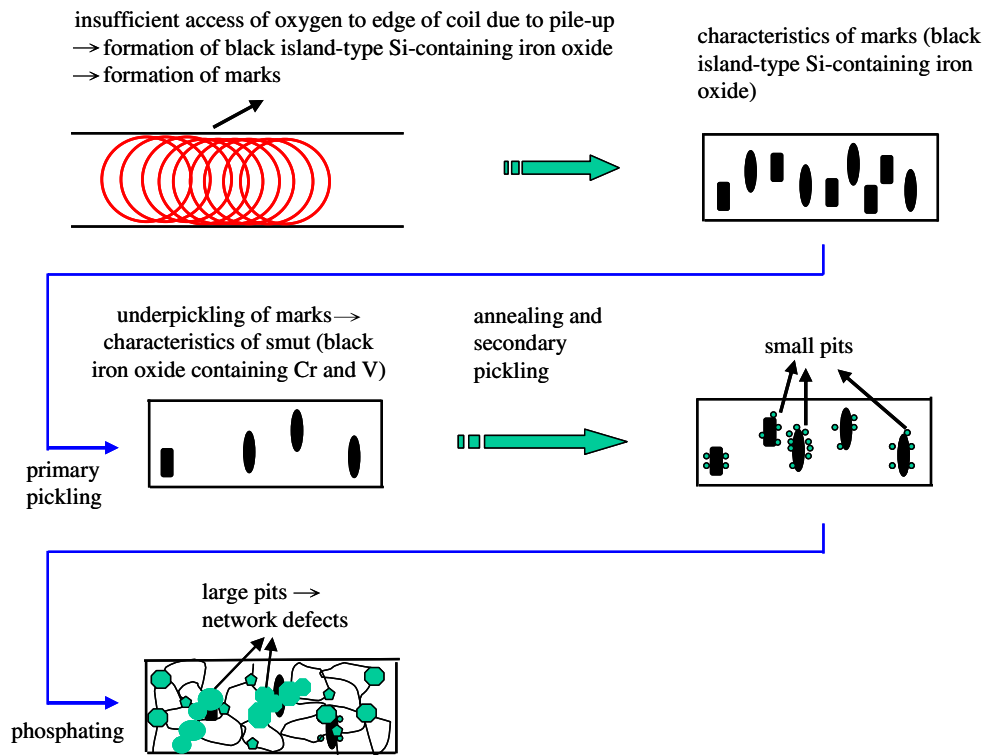


Fig. 13 Mechanism of formation of network defects from rods

than iron. The fact that formation of Si-containing iron oxide depends on the amount of accessible oxygen was also reported by Jepson and Lorimer (Ref 8). Basically Si-containing iron oxide was easy to form in atmosphere with insufficient oxygen, while iron oxide was easy to form in atmosphere with sufficient oxygen. In actual mill, marks were easy to form on rods with fast finish rolling, because when the coils were transported too quickly after rolling, the coils were stacked in such a way as to prevent significant contact with oxygen. This demonstrated that marks were composed of island-type Si-containing iron oxides, which were easy to form at the interface edge of the specimen from pile-up oxidation due to insufficient accessible oxygen.

Based on the above experimental results and the observations in the mill, the mechanism of formation of network defects from as-rolled rods with marks to phosphated rods is shown in Fig. 13. Marks were easy to form on rods with fast finish rolling, because when the coils were transported too quickly after rolling, the coils were stacked in such a way as to prevent significant contact with oxygen. These marks which were composed of island-type Si-containing iron oxides could not be pickled completely and smut was formed. After annealing and secondary pickling, small pits occurred on the substrate near the interface of the substrate and the residual scales. Furthermore, after phosphating, small pits grew to large pits and propagated along the grain boundaries. Some grains spalled off eventually and looked like a network to human eye.

4. Conclusions

From this study, the mechanism of formation of network defects has been proposed as follows.

The marks on the as-rolled rods contained fragments of Si-containing iron oxides. These oxides were not removed completely through primary pickling → annealing → secondary pickling. Then small pits occurred on the substrate near the interface of the substrate and the residual scale due to their different potential. After phosphating, small pits grew to large pits and propagated along the grain boundaries. Some grains spalled off eventually and looked like a network by human naked eyes.

The marks on the as-rolled rods might come from the fast finish rolling. This fact was demonstrated from the piling up oxidation tests which made the accessible oxygen insufficient leading to Si-containing iron oxide.

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