

# Effect of Ni Content in a Low Alloy Steel on the High Temperature Oxide Scale Adherence

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This study is to investigate the effect of Ni content in a low alloy steel on the oxide scale adherence at 1085°C in an atmosphere containing 1.8% O<sub>2</sub>, 19.9% water vapor, 7.6% CO<sub>2</sub>, and N<sub>2</sub> for balance. The experimental methods included preparation of steels, oxidation tests, XRD analyses, and metallographic analyses. The results showed that each Ni-containing steel after high temperature oxidation contained inner scale and outer scale, and that the surface of the substrate before oxidation was exactly at the inner/outer scale interface. After water quenching, some portion of the outer scales spalled off and all inner scales remained on the substrate. The spalled oxides included iron oxides only, while the remained oxides included Fe<sub>16</sub>Ni<sub>9</sub> particles dispersed in iron oxides. As the Ni content in steel substrate increased from 3% to 5%, the adherence of the scale increased significantly due to the increased amount of Fe<sub>16</sub>Ni<sub>9</sub> in the inner scale. A further increase in Ni content to 7% did not initiate further significant change. Furthermore, an oxidation mechanism has been proposed in this investigation.

## 1. INTRODUCTION

Alloying nickel in a low alloy steel is sometimes necessary for special purposes, for example, to promote the hardening energy of armored steel plate. However, in the manufacturing process, the scale that forms on the nickel-bearing steel slabs during reheating is notoriously hard to remove before hot rolling. Scale pits and rolled-in-scale are surface defects that should always be prevented during rolling. Therefore, it is important to study the high temperature oxide scale adherence in a reheating furnace. In conventional high temperature oxidation studies, the effect of nickel in low alloy steels is that the iron matrix of the steel is selectively oxidized and the nickel is enriched at the oxide-metal interface.<sup>(1)</sup> The effect of the reheating furnace atmosphere on the adhesion of scale to Ni-bearing steels was investigated by Tuck and Barlow<sup>(2)</sup> and confirmed that nickel

increased the adhesion with low free oxygen, while the use of a high oxygen atmosphere reduced the amount of adherent scale. Therefore, this study is to investigate the effect of Ni content in a low alloy steel on the high temperature oxide scale adherence and to find an appropriate nickel content in this steel for favorable scale adherence.

## 2. EXPERIMENTAL METHODS

### 2.1 Preparation of Steels

Steels with thickness 12 mm and nickel contents 3%(A), 5%(B), and 7%(C) were prepared in the laboratory. The chemical compositions are listed in Table 1.

### 2.2 Oxidation Tests

Figure 1 is the schematic diagram of the oxidation tests. Nitrogen and air flowed through a constant bath

Table 1 The Chemical Compositions of the Steels in this Investigation (wt%)

Steel	C	Si	Mn	P	S	Cr	Ni	Mo	Al
A	0.35	0.22	0.84	0.009	0.0032	1.51	<b>2.95</b>	0.58	0.020
B	0.35	0.23	0.83	0.009	0.0030	1.50	<b>4.91</b>	0.58	0.024
C	0.35	0.22	0.82	0.009	0.0032	1.45	<b>6.70</b>	0.57	0.013

Fe : Balance

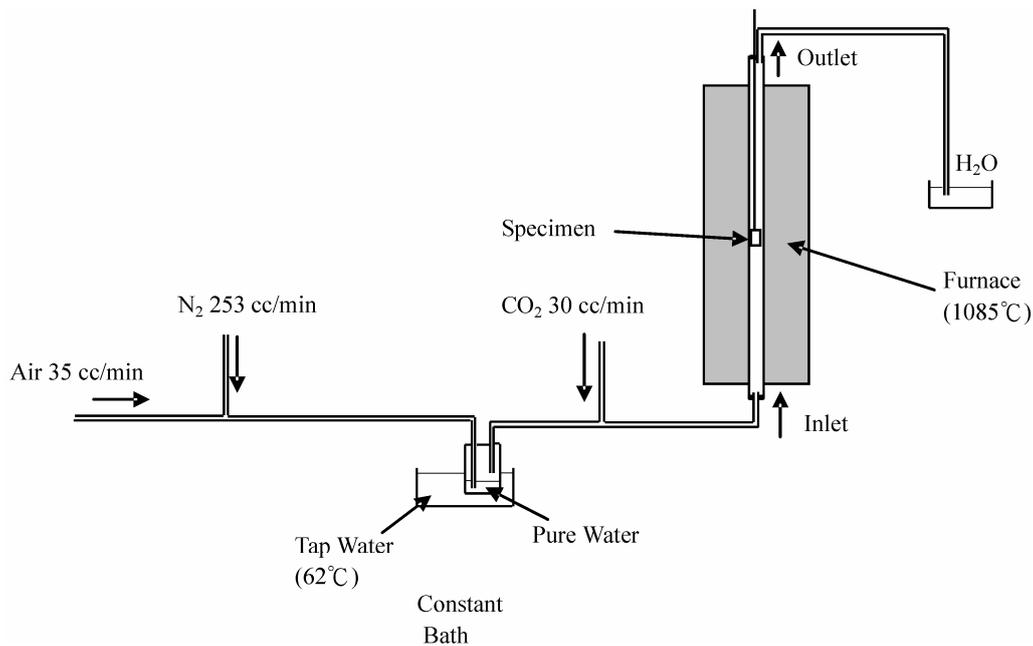


Fig. 1. Schematic diagram of the oxidation tests.

at 62°C to absorb water vapor after which the resultant mixture was combined with carbon dioxide to obtain 1.8% O<sub>2</sub>, 19.9% water vapor, 7.6% CO<sub>2</sub>, and N<sub>2</sub> for balance. This composition is a simulated atmosphere found in a typical reheating furnace of a hot rolled steel plate mill.

Steel plates were cut into sample pieces with a size of approximately 14 mm × 11 mm × 55 mm. Prior to oxidation, the surface was mechanically polished with #600 silicon carbide paper, followed by cleaning with acetone and measurements taken of weight and size. The oxidation temperature and duration were 1,085°C and 2 hours respectively, which are the heating parameters in most steel plate mills. After the test, the specimen was immediately water quenched. The specimen together with the remaining scale was dried and reweighed. Furthermore, the remaining scale on the specimen after water quenching was removed by pickling in a hydrochloride acid solution with a pickling inhibitor. After the pickling, the specimen was reweighed and the weight compared with that before the oxidation test. In addition, the spalled scale in water after quenching was also collected to be dried and weighed. Two characteristics were obtained, one was the weight loss due to oxidation, the other was the adherence parameter of water quenching. Assuming  $\Delta W'_{WQ}$  was the weight gain per unit surface area after water quenching from the collection of the spalled scale, and  $\Delta W_{WQ}$  was the weight gain per unit surface area after water quenching excluding the spalled scale (the value was negative in case the weight after quench-

ing was less than that before oxidation), then  $\Delta W'_{WQ} - \Delta W_{WQ}$  is defined as the adherence parameter in this investigation. The lower the value of this parameter, the greater the adherence of the oxide to the substrate was. A similar method of measuring high temperature oxide scale adherence was first proposed by Sherwood and Shatynski.<sup>(3)</sup> The difference is that they measured  $\Delta W_{AC} - \Delta W_{WQ}$  as the adherence parameter ( $\Delta W_{AC}$ : weight gain per unit surface area after oxidation and air cooling), and neglected the extra weight gain during air cooling. Therefore, in this study  $\Delta W_{AC}$  was replaced by  $\Delta W'_{WQ}$  to obtain more accurate measurements. In addition, the weight loss in this study was the difference in weight of the specimen before the oxidation and the weight after water quenching and pickling.

### 2.3 XRD Analyses

The oxide scales were analyzed using a Bruker D8-Advance X-Ray Diffractometer (XRD). The scan rate was 3°/min. Two kinds of oxide scales were analyzed. One was the spalled oxide. This kind of oxide was picked up from water after quenching and dried, followed by grinding to powder. The other was the oxide remaining on the specimen after quenching. This kind of oxide was dried and scraped with a blade, followed by grinding to powder.

### 2.4 Metallographic Analyses

Prior to each metallographic analysis, the oxidation condition was the same as that described above except that the specimen thickness was only 3.0~3.5

mm for observation of the specimen throughout the whole thickness in a microscope with low magnification. The analyzing instrument was a JEOL JSM-6300 Scanning Electron Microscope (SEM) with energy dispersive spectroscopy (EDS).

### 3. RESULTS

#### 3.1 Oxidation Tests

The results of the oxidation tests are shown in Fig. 2 in which each value is the average of two measurements with error  $\leq 6 \text{ mg/cm}^2$ . It is evident that, as the Ni content increased from 3% to 5%, both the substrate weight loss and the adherence parameter decreased significantly. Further increase in Ni content to 7% did

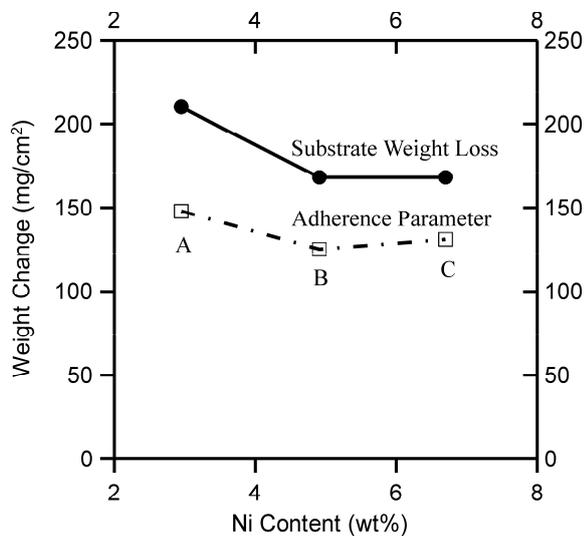


Fig. 2. Results of the oxidation tests.

not reveal further significant change. Therefore, the favorable Ni content in this investigation was 3%.

#### 3.2 XRD Analyses

The results of XRD analyses are shown in Fig. 3 and Fig. 4. Figure 3 shows that the major composition of the spalled oxide scale of Steel A (3% Ni) was FeO and the minor composition contained  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . Similar analyses were done on the spalled oxide scales of Steels B and C, and the identified species together with those of Steel A are listed in Table 2.

Figure 4 shows that the major composition of the remaining oxide scales due to water quenching of all steels was FeO too. However, the minor composition contained  $\text{Fe}_{16}\text{Ni}_9$  and  $\text{Fe}_3\text{O}_4$  (for Steels B and C). No other iron-nickel alloys were observed, because the primary peak of taenite with 32% Ni is at  $3.34 \text{ \AA}$ , while that of iron nickel with 30% Ni is at  $1.87 \text{ \AA}$  and that of  $\text{FeNi}_3$  is at  $2.04 \text{ \AA}$ . Table 2 also lists the major and minor species of the remained oxide scales on all steels. The d values (lattice constants) of the primary peaks of FeO,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_{16}\text{Ni}_9$  are approximately  $2.15 \text{ \AA}$ ,  $2.53 \text{ \AA}$ , and  $2.07 \text{ \AA}$  respectively. One can estimate the value  $I_{2.07\text{\AA}}/(I_{2.15\text{\AA}}+I_{2.53\text{\AA}}+I_{2.07\text{\AA}})$  (where I: Intensity of the peak) and predict the ratio of  $\text{Fe}_{16}\text{Ni}_9$  in the remaining oxide. The results are listed in Table 3. It is evident that, as the Ni content increased from 3% to 5%, the ratio increased significantly. A further increase in Ni content to 7% did not initiate further significant change. This is consistent with the oxidation tests (Fig. 2), and it can be explained by the fact that the effect of Ni content in the steel on the high temperature oxide scale adherence is due to the amount of  $\text{Fe}_{16}\text{Ni}_9$  in the inner scale.

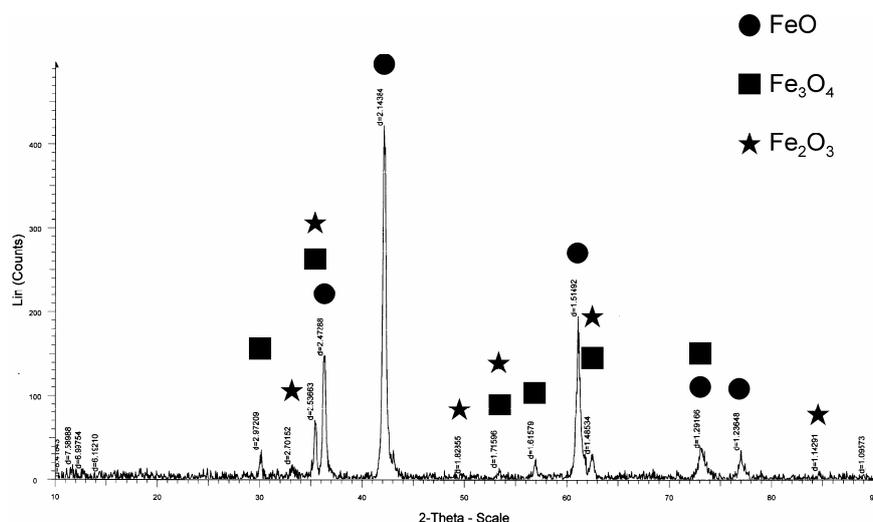


Fig. 3. Result of XRD analysis of the spalled oxide scale of Steel A.

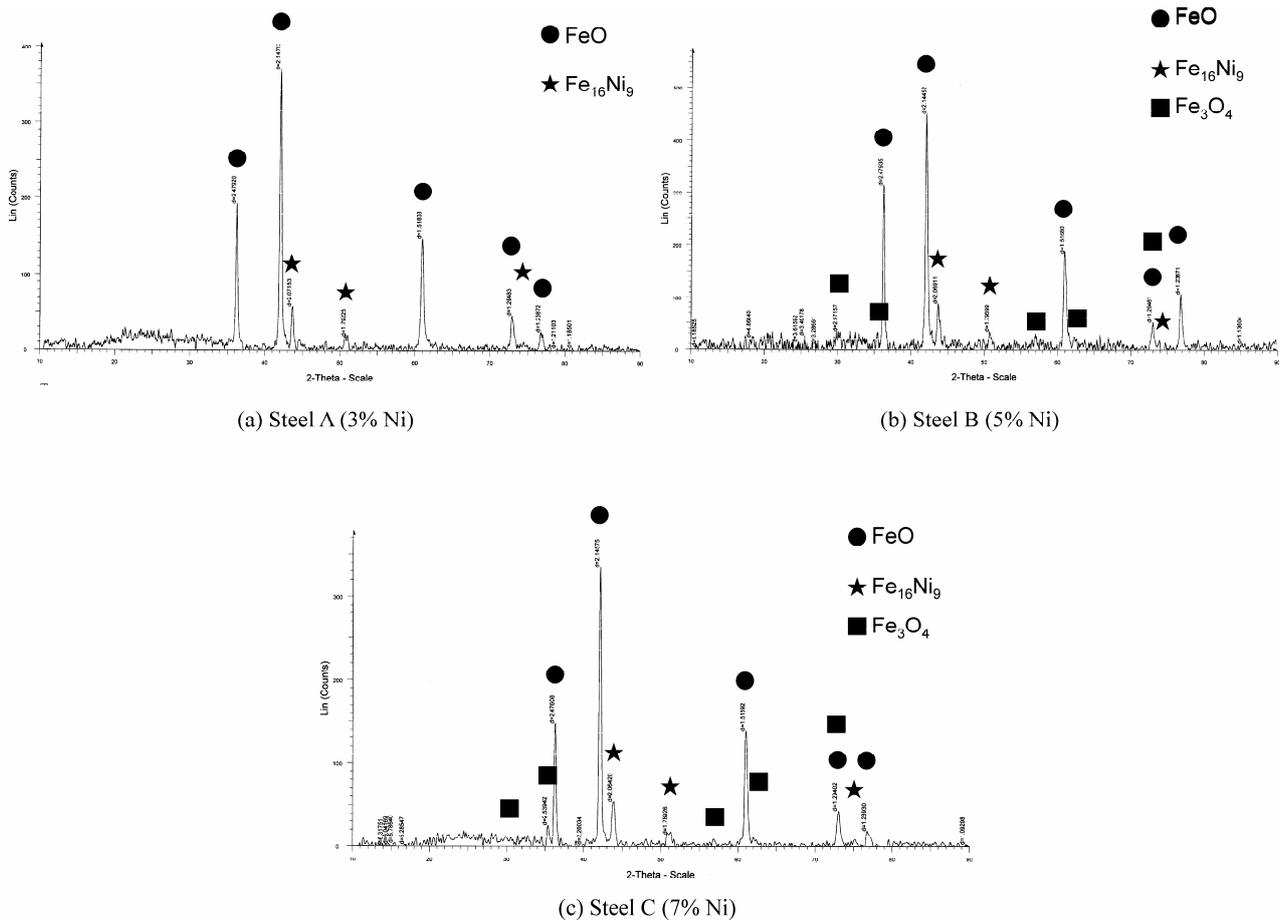


Fig. 4. Results of XRD analyses of the remaining oxide scales.

Table 2 The Species Identified from XRD Analyses of the Oxide Scales

Steel	Spalled Oxide		Remaining Oxide	
	Major Species	Minor Species	Major Species	Minor Species
A	FeO	Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>16</sub> Ni <sub>9</sub>
B	FeO	Fe <sub>3</sub> O <sub>4</sub>	FeO	Fe <sub>16</sub> Ni <sub>9</sub> , Fe <sub>3</sub> O <sub>4</sub>
C	FeO	Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>16</sub> Ni <sub>9</sub> , Fe <sub>3</sub> O <sub>4</sub>

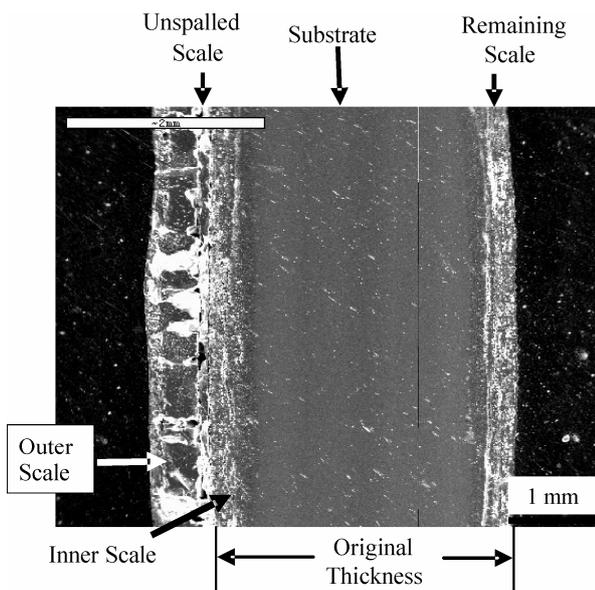
Table 3 The Estimated Ratio  $I_{2.07\text{\AA}} / (I_{2.15\text{\AA}} + I_{2.53\text{\AA}} + I_{2.07\text{\AA}})$  of the Remaining Oxide

Steel	A (3%Ni)	B (5%Ni)	C (7%Ni)
Ratio	0.12	0.15	0.15

### 3.3 Metallographic Analyses

A cross sectional SEM image of Steel C after oxidation and quenching is shown in Fig. 5 in which the morphology through the whole specimen thickness

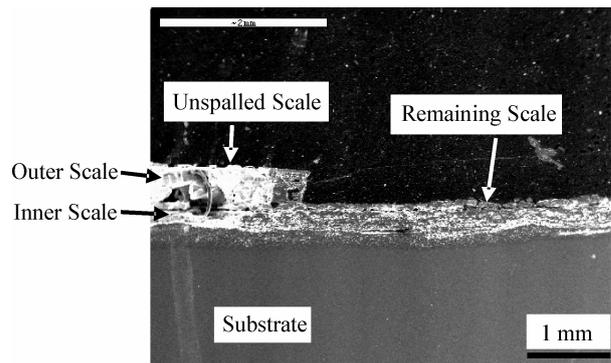
can be revealed. The scale on the left surface is the unspalled oxide which contains inner scale and outer scale, while that on the right surface is the remaining inner scale after quenching. Comparison of the size with the specimen before oxidation demonstrated that the surface of the specimen before oxidation was exactly at the inner/outer scale interface. This observation suggests that the oxidation mechanism included the inward transport of oxygen to react with the metal substrate to form inner scale and the outward transport of metal to react with oxygen in the environment to form outer scale.



**Fig. 5.** A cross sectional SEM image of Steel C after oxidation and quenching.

A cross sectional SEM image of Steel B after oxidation and quenching is shown in Fig. 6 in which the morphology from the portion of spalled scale to that of unspalled scale can be revealed. The remaining scale possessed a similar morphology to the inner scale in the unspalled portion. This observation confirmed that the remaining scale after quenching was the original inner scale.

Figure 7 is SEM/EDS analysis of the remaining scale of Steel A after oxidation and quenching, and reveals that a number of white particles containing Fe and Ni only were immersed in the iron oxide scale. These particles were demonstrated to be  $\text{Fe}_{16}\text{Ni}_9$  in XRD analysis (Fig. 4). Figure 8 is the SEM image of

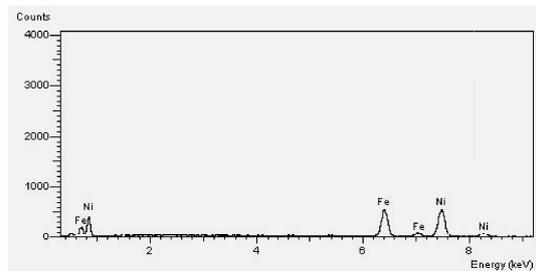
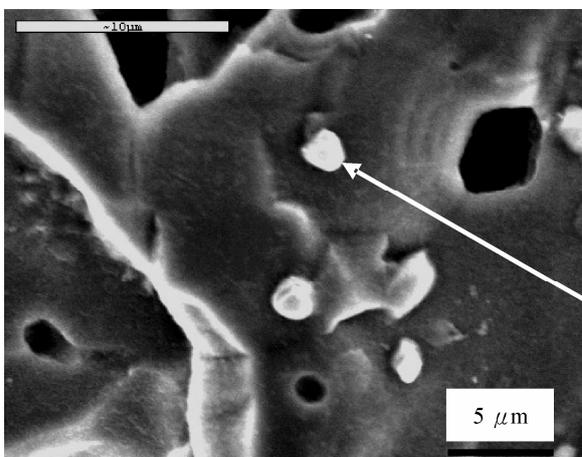


**Fig. 6.** A cross sectional SEM image of Steel B after oxidation and quenching.

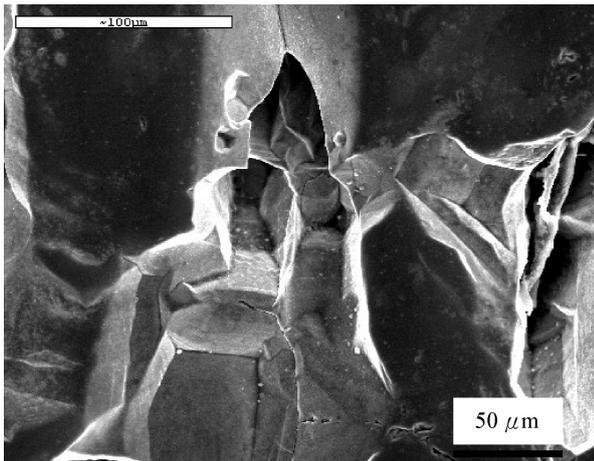
the outer scale of Steel B after oxidation and quenching. In contrast to the image in Fig. 7, no white  $\text{Fe}_{16}\text{Ni}_9$  particles were observed at all. Similar results were also obtained on the remaining scales and the outer scales of the other two steels. The fact that the outer scales were composed of iron oxides only was consistent with the XRD analyses described above (Table 2). Furthermore, it is apparent that the morphology of the scale in Fig. 7 was more coherent than that in Fig. 8, and it can be predicted that the scale in Fig. 8 was easier to remove by the thermal shock of quenching.

#### 4. DISCUSSION

It was reported that in high temperature oxidation of Ni-containing low alloy steels, Fe is preferentially oxidized and Ni is enriched at the iron oxide/substrate interface to act as a mechanical bonding, and the adherence of the scale to the substrate is promoted.<sup>(1)</sup> Further oxidation caused the metallic nickel to be dispersed in the inner scale to reduce its porosity<sup>(4)</sup> which might have a detrimental effect on hydraulic descaling.



**Fig. 7.** SEM/EDS analysis of remaining scale of Steel A after oxidation and quenching.



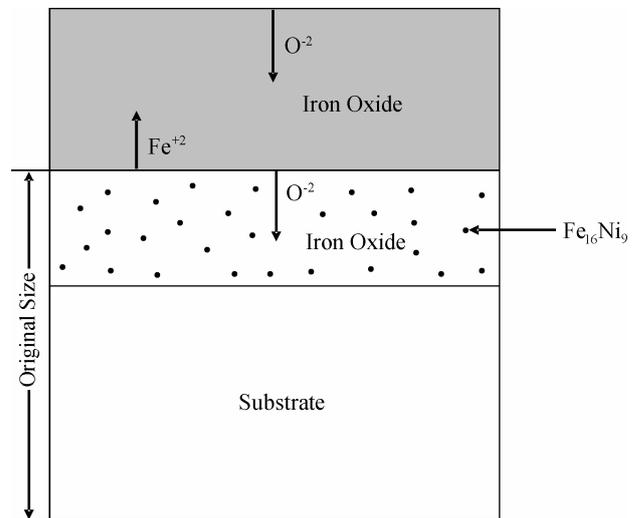
**Fig. 8.** SEM image of the outer scale of Steel B after oxidation and quenching.

Kato et al.<sup>(5)</sup> also reported that the dispersed Ni in the subscale deteriorated the descaling ability. According to Tuck and Barlow,<sup>(2)</sup> the oxide scales produced in the heating furnace of a steel mill contain four types. The first type is coherent scale, normally single-layered, without fractures or cracks. Evidently separation of this scale from the metal is difficult. The second type is layered scale. The inner layer is separated from the outer layer. The third type is porous scale and the fourth type is transversely cracked scale. Obviously the scales in Fig. 5 and Fig. 6 in this investigation contained smooth outer layers and wrinkled inner layers, probably belonging to the second type. Water quenching in this investigation demonstrated that the outer layer was easier than the inner layer to spall off. This phenomenon might be due to the dispersed  $\text{Fe}_{16}\text{Ni}_9$  particles in the inner scale. On the contrary, the outer scale was smooth and might be easy to fracture via the thermal shock of water quenching.

Concerning the difference in weight loss between the steel with 3% Ni (Steel A) and that with 5% Ni (Steel B), the steel with higher Ni content of course possessed higher oxidation resistance resulting in lower weight loss. Furthermore, the steel with higher Ni content had more  $\text{Fe}_{16}\text{Ni}_9$  particles in the inner scale (Table 3). This might affect the amount of unspalled outer scale resulting in higher adherence.

Because the inner/outer scale interface was exactly at the location of the surface of the specimen before oxidation, an oxidation mechanism has been proposed and is shown in Fig. 9. Fe is preferentially oxidized to iron oxide as outer scale on the surface.  $\text{O}^{2-}$  continues diffusing inward in the scale. Some of the  $\text{O}^{2-}$  ions combine with the outward diffusing  $\text{Fe}^{+2}$  in the scale to thicken the iron oxide. Other  $\text{O}^{2-}$  ions diffuse to the

subscale of the steel to react with Fe in the substrate to iron oxide. However, Ni is not oxidized. It combines with unoxidized Fe to form  $\text{Fe}_{16}\text{Ni}_9$  particles and is dispersed in the iron oxide matrix.



**Fig. 9.** Schematic diagram of high temperature oxidation mechanism of Ni-containing steel proposed in this investigation.

## 5. CONCLUSION

In conclusion, each Ni-containing steel after high temperature oxidation contained inner scale and outer scale, and the surface of the substrate before oxidation was exactly at the inner/outer scale interface. After water quenching, some portion of the outer scales spalled off and all the inner scales remained on the substrate. The spalled oxides included iron oxides only, while the remaining oxides included  $\text{Fe}_{16}\text{Ni}_9$  particles dispersed in iron oxide. As the Ni content in the steel substrate increased from 3% to 5%, the adherence of the scale increased significantly due to the increased amount of  $\text{Fe}_{16}\text{Ni}_9$  in the inner scale. A further increase in the Ni content to 7% did not initiate further significant change. Furthermore, an oxidation mechanism has been proposed in this investigation. It includes the inward diffusion of oxygen to react with the substrate to form inner scale and the outward diffusion of iron to react with external oxygen to form outer scale. Water quenching made some outer scales to spall off, while the inner scales still remained on the substrate.

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