

# Phase Transformation of Oxide Scale and Its Control

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## Abstract

*The detachment of oxide scale may cause surface defects of steel product. Therefore, it is important to understand the adhesion property of oxide scale. This study focused on the relationship between the adhesiveness and phase transformation structure of scale, and investigated the effects of initial scale structure on the phase transformation behavior of scale. The bilayer scale of  $\text{Fe}_3\text{O}_4$  and  $\text{FeO}$  transforms from the  $\text{Fe}_3\text{O}_4/\text{FeO}$  interface, while the monolayer scale of  $\text{FeO}$  alone generates  $\text{Fe}_3\text{O}_4$  precipitates at the scale/steel interface preferentially. These results indicate that the phase transformation behavior of  $\text{FeO}$  can be controlled by the initial scale structure.*

## 1. Introduction

During hot rolling, steel is oxidized and a scale of iron oxides forms on the surface. In general, a scale comprises layers of wustite ( $\text{FeO}$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), and hematite ( $\text{Fe}_2\text{O}_3$ ), from the base metal side to the surface. Of these, according to the Fe-O phase diagram<sup>1)</sup> given in Fig. 1,  $\text{FeO}$  undergoes eutectoid transformation and turns into  $\text{Fe}_3\text{O}_4$  and ferrite at  $560^\circ\text{C}$  or below during the cooling after rolling. Therefore to study the adhesion and pickling characteristics of scale, it is necessary to understand its phase transformation behavior.

There have been many study reports on the phase transformation of  $\text{FeO}$ . Fisher, Hoffman et al. demonstrated that the phase transformation of steel scale advances with  $\text{Fe}_3\text{O}_4$  precipitating in the first place, and the eutectoid structures of  $\text{Fe}_3\text{O}_4$  and ferrite form thereafter.<sup>2,3)</sup> Here, the  $\text{Fe}_3\text{O}_4$  that precipitates at the beginning sometimes appears from the interface between the base metal and  $\text{FeO}$ ; this layer of  $\text{Fe}_3\text{O}_4$  is called a magnetite seam. Baud et al. maintained that the formation of magnetite seams increased significantly when  $\text{FeO}$  underwent isothermal transformation at a temperature range of  $375$  to  $475^\circ\text{C}$ .<sup>4)</sup> Hayashi et al. closely observed the phase transformation of scale that formed on pure iron, found that the transformation advanced through stages of nucleation and nuclear growth, and clarified the forming mechanism of magnetite seams.<sup>5)</sup> In addition, Kobayashi et al. reported that the structure of magnetite seams arising from the interface with steel was highly coherent with the base metal, which makes them adhere firmly to the base metal.<sup>6)</sup> This indicates that it is possible to strengthen the adhesion of scale by adequately controlling its microstructure.

Focusing on the structure of scale before phase transformation,

this paper deals with the phase transformation of  $\text{FeO}$ , particularly its influence over the formation of magnetite seams. The scale structure changes readily depending on the atmosphere and temperature, and what results from the structural change is likely to affect the phase transformation behavior of  $\text{FeO}$ . There have been few studies, however, on the way in which the structure of scale before transformation influences the phase transformation of  $\text{FeO}$ . The findings of the present study, therefore, are both academically and industrially important. In the present study, the scale was held at a set temperature as a pretreatment to cause the scale structure change before

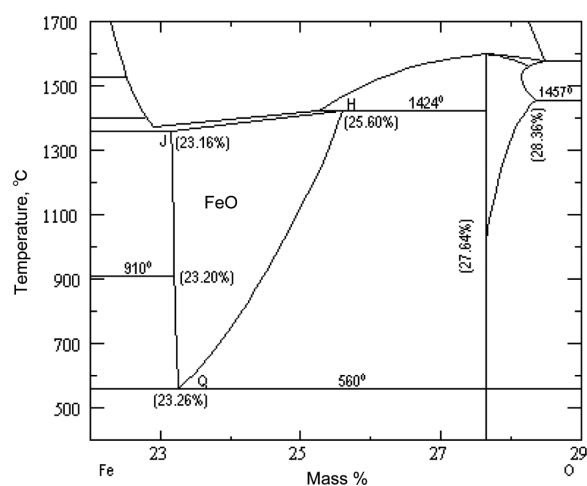


Fig. 1 Fe-O phase diagram<sup>1)</sup>

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phase transformation, and then, its isothermal transformation behavior was observed.

**2. Experimental**

**Table 1** shows the chemical composition of the specimen sheets used for the present test. Sample sheets, 50×60×3 mm<sup>3</sup> in size, with thermocouples fixed onto the surface, were treated as follows: they were heated for 5 min to 750°C in a nitrogen atmosphere in an infrared furnace; an air atmosphere was then introduced to the furnace to oxidize the sheets for 40 s; the furnace was returned to a nitrogen atmosphere; and the sample sheets were held at 550 or 700°C for 30 min to have scale of different structures form before phase transformation.

At the end of the oxidizing at 750°C, the scale comprised FeO, Fe<sub>3</sub>O<sub>4</sub>, and Fe<sub>2</sub>O<sub>3</sub>, but by holding at 550°C in a nitrogen atmosphere, the Fe<sub>2</sub>O<sub>3</sub> layer at the surface was changed into Fe<sub>3</sub>O<sub>4</sub>, and the scale came to comprise two layers of FeO and Fe<sub>3</sub>O<sub>4</sub>. In contrast, through holding at 700°C, since FeO exists stably under this condition as seen in the phase diagram, the Fe<sub>3</sub>O<sub>4</sub> and the Fe<sub>2</sub>O<sub>3</sub> layers changed into a single FeO layer, and thus, the scale comprised one FeO layer. Two-layer (bilayer) scale made up of FeO and Fe<sub>3</sub>O<sub>4</sub> and single-layer (monolayer) scale of FeO only were thus obtained before phase transformation.

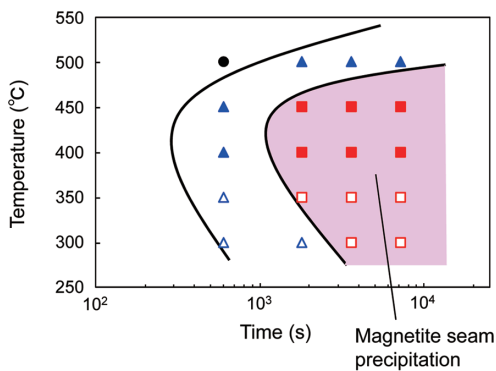
The specimen sheets that were held at 550 or 700°C were then soaked at 300 to 500°C for 10 to 240 min to cause the scale to undergo phase transformation, and then, after cooling, the structure of the scale after the transformation was observed at sections through a scanning electron microscope (SEM).

**3. Results**

Isothermal transformation diagrams, or time-temperature-transformation (TTT) diagrams, for bilayer scale of formed of FeO and Fe<sub>3</sub>O<sub>4</sub> and monolayer scale of FeO only were prepared based on their respective structures. A TTT diagram and a typical example of the bilayer structure are given in **Figs. 2** and **3**, respectively. In the

**Table 1** Chemical compositions of the specimens (wt%)

C	Si	Mn	P	S	Bal.
0.0021	0.04	0.12	0.009	0.006	Fe

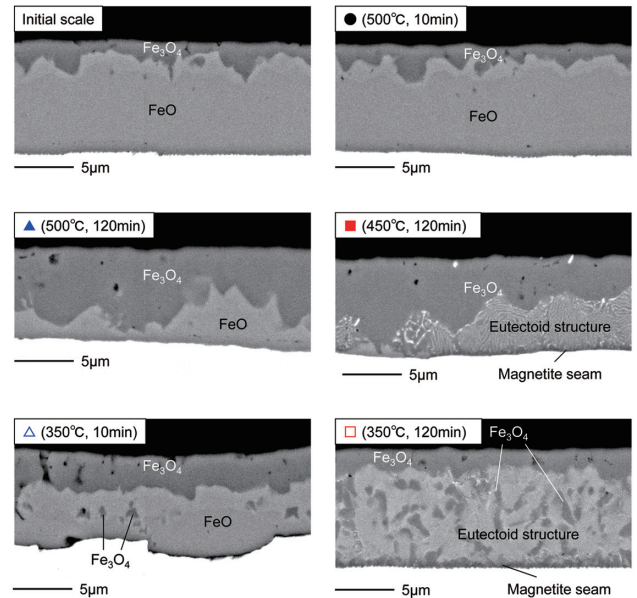


**Fig. 2** TTT diagram for FeO/Fe<sub>3</sub>O<sub>4</sub> bilayer scale

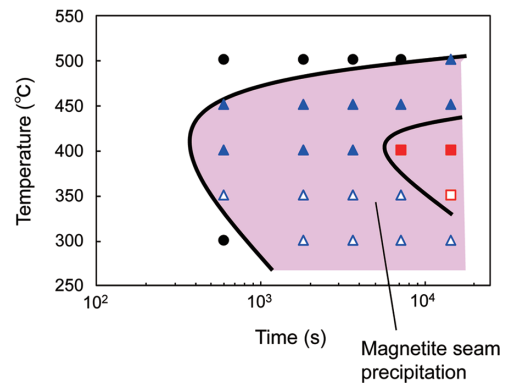
● : Scale in initial structure, ▲ : Precipitation of Fe<sub>3</sub>O<sub>4</sub> from Fe<sub>3</sub>O<sub>4</sub>/FeO interface, ■ : Eutectoid transformation into Fe<sub>3</sub>O<sub>4</sub> and ferrite, △ : Precipitation of granular Fe<sub>3</sub>O<sub>4</sub> in FeO layer, □ : Precipitation of granular Fe<sub>3</sub>O<sub>4</sub> and eutectoid transformation

case of soaking at 500°C, Fe<sub>3</sub>O<sub>4</sub> precipitated from the interface between Fe<sub>3</sub>O<sub>4</sub> and FeO and grew in the depth direction. In the cases of soaking at 400 and 450°C, Fe<sub>3</sub>O<sub>4</sub> precipitated from the Fe<sub>3</sub>O<sub>4</sub>/FeO interface, and then a layer of Fe<sub>3</sub>O<sub>4</sub> precipitated in a small amount from the interface between the FeO and the base metal. Thereafter, the remaining FeO changed into a eutectoid structure of Fe and Fe<sub>3</sub>O<sub>4</sub>. In the case of soaking at 350°C or below, on the other hand, Fe<sub>3</sub>O<sub>4</sub> precipitated in small particles in the layer of FeO.

Next, the TTT diagram for the monolayer scale of FeO and typical examples of its structure are given in **Figs. 4** and **5**, respectively. In the case of soaking at 500°C, Fe<sub>3</sub>O<sub>4</sub> was not seen to precipitate, but in the cases of soaking at 450 and 400°C, it did precipitate markedly from the interface between FeO and the base metal, which indicates that magnetite seams form more easily with FeO monolayer scale than with FeO/Fe<sub>3</sub>O<sub>4</sub> bilayer scale. The eutectoid structure appeared in the end, but the time before its appearance was longer with the monolayer scale than with the bilayer: with the former, it



**Fig. 3** Typical SEM images of cross sections of the scale in **Fig. 2**



**Fig. 4** TTT diagram for FeO monolayer scale

● : Scale in initial structure, ▲ : Precipitation of Fe<sub>3</sub>O<sub>4</sub> from FeO/metal interface, ■ : Eutectoid transformation into Fe<sub>3</sub>O<sub>4</sub> and ferrite, △ : Precipitation of granular Fe<sub>3</sub>O<sub>4</sub>, □ : Precipitation of granular Fe<sub>3</sub>O<sub>4</sub> and eutectoid transformation

appeared after as long as 4 h of holding at 400°C. In the case of soaking at 350°C or below, Fe<sub>3</sub>O<sub>4</sub> was seen to precipitate in small particles as seen with the bilayer scale. The phase transformation patterns of FeO starting from different scale structures are summarized in Fig. 6.

4. Discussion

4.1 Precipitation of Fe<sub>3</sub>O<sub>4</sub>

Now, let us focus on the difference in the precipitation behavior of Fe<sub>3</sub>O<sub>4</sub> depending on the scale structure before the phase transformation of FeO. The FeO phase transformation is considered to progress through nucleation and nuclear growth.<sup>5)</sup> It follows, therefore, that at a temperature of 500°C or higher, the degree of super cooling is small, the driving force for nucleation is insufficient, and the phase transformation is driven forward by nuclear growth. In the case of bilayer scale formed of FeO and Fe<sub>3</sub>O<sub>4</sub>, since there is a layer of Fe<sub>3</sub>O<sub>4</sub> at the surface, this layer grows thicker, and no other Fe<sub>3</sub>O<sub>4</sub> layer appears. At 450 and 400°C, the phase transformation takes place in the nose zone of the TTT diagram, and it proceeds either by nucleation or by nuclear growth.

The precipitation of Fe<sub>3</sub>O<sub>4</sub> is possible with a certain degree of super cooling, which acts as the driving force, and a magnetite seam can form from the FeO/metal interface only when such a driving force is given; the surface Fe<sub>3</sub>O<sub>4</sub> layer also grows at the same time. When phase transformation takes place at 350°C or below, the degree of super cooling is large and, while nucleation occurs preferentially, the temperature is insufficient for nuclear growth. Fe<sub>3</sub>O<sub>4</sub>, therefore, precipitates in small particles in the FeO layer, and small amount of magnetite seam also precipitates.

Similarly, with a monolayer scale of FeO only, at temperatures of 500°C or higher, there is no Fe<sub>3</sub>O<sub>4</sub> layer at the surface, and nuclear growth does not take place. Nucleation hardly occurs in this situation because of insufficient driving force, and phase transformation advances very slowly. When the sample is soaked at 450°C or below, on the other hand, the degree of super cooling, or the driving force, is sufficiently large, and as a result, nucleation takes place preferentially, and magnetite seams easily arise from the interface between FeO and base metal.

4.2 Rate of phase transformation

Attention is focused here on the slow rate of the phase transformation of FeO monolayer scale. FeO is sometimes expressed, in a precise manner, as Fe<sub>x</sub>O (0.87 ≤ x ≤ 0.92).<sup>2)</sup> Iron atoms are a little less in number than oxygen atoms. Because the phase transformation of FeO advances by means of the diffusion of Fe ions, if the Fe concentration in FeO (the value of x in Fe<sub>x</sub>O) changes as a result of heat treatment before phase transformation, such a change is likely to affect the rate of the phase transformation. In consideration of this, to examine the influence of the change in Fe concentration in FeO, the authors conducted high-temperature X-ray diffraction (XRD) measurement to follow how the detection intensity and inter-atomic distance of FeO would change during the course of the heat treatment and the phase transformation.

Here, the same ultra-low-C steel sheets as those specified in Section 2 were oxidized at 750°C to obtain scale 10 μm in thickness on their surfaces and then subjected to high-temperature XRD. The specimens were placed inside the facility in a nitrogen atmosphere at 550, 700 or 900°C for 30 min as the heat treatment before phase transformation, and then held at 400°C for 120 min to have the scale undergo the transformation. The XRD measurement was conducted during the above process under the conditions of a 2θ measurement range of 25 to 50° and a rate of 2.7°/min. A typical example of the measurement result is given in Fig. 7. Here, the authors focused their attention on the changes in the integral intensities in the peaks of FeO (200) and Fe<sub>3</sub>O<sub>4</sub> (400), and that of the 2θ value. The change

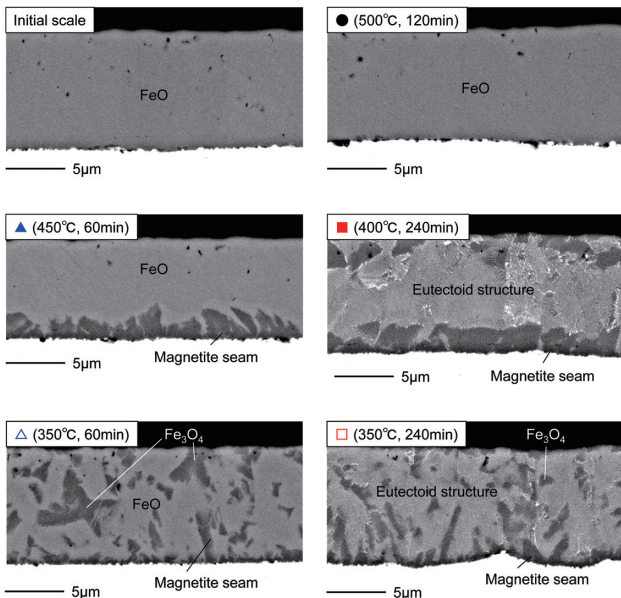


Fig. 5 Typical SEM images of cross sections of the scale in Fig. 4

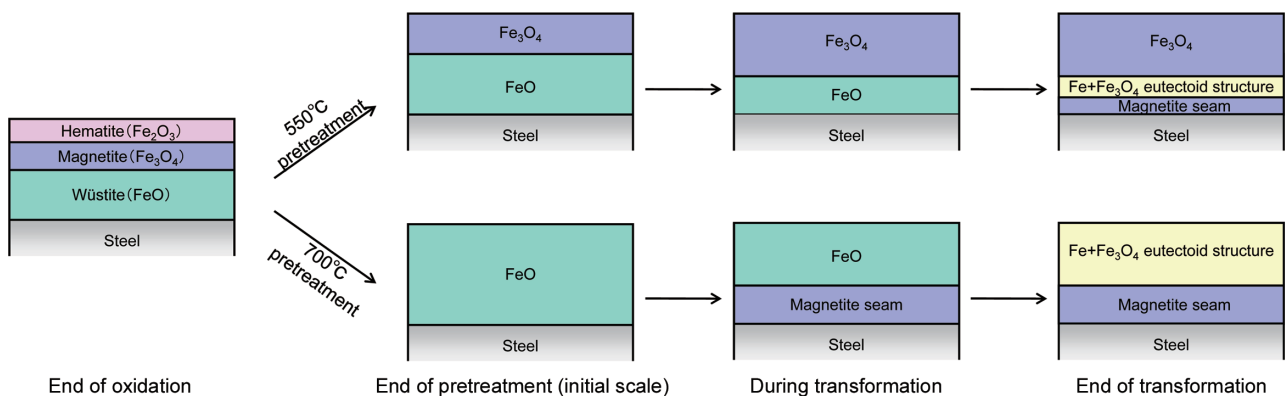


Fig. 6 Patterns of structural change of scale after heating to different temperatures

in the peak intensity corresponds to the change in the structure of scale, and the change in the  $2\theta$  value to that in the interatomic distance. It has been reported that the interatomic distance of FeO is substantially linearly related to the Fe concentration in FeO.<sup>7)</sup>

**Figure 8** shows the change in the integral intensities of FeO (200) and Fe<sub>3</sub>O<sub>4</sub> (400). The point 0 of the horizontal axis corresponds to the start of the holding at 400°C. The negative zone represents the treatment period before the phase transformation, and the positive zone the time during the transformation. When the specimens were held at 550°C before the transformation, FeO and Fe<sub>3</sub>O<sub>4</sub> were detected, and only FeO when they were held at 700 or 900°C; this agrees with that which was stated in Section 2. During pretreatment at 400°C, the peak intensity of FeO decreased with every specimen while that of Fe<sub>3</sub>O<sub>4</sub> increased, and the rates of the changes tended to be moderate at higher pretreatment temperatures, which means that the transformation speed slows down as the pretreatment temperature becomes higher.

**Figure 9** shows the change in the interatomic distance of FeO (200) calculated from the  $2\theta$  values; note here that the effects of

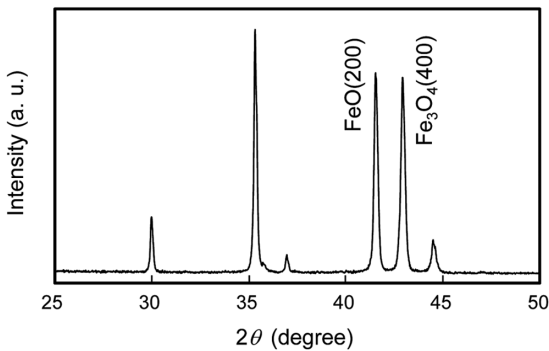


Fig. 7 Typical XRD spectrum

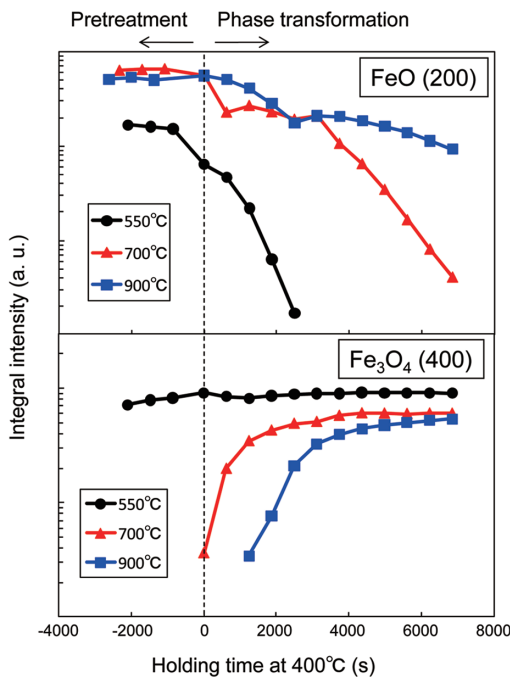
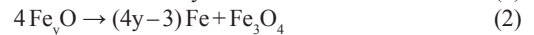
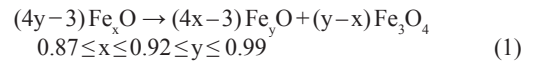


Fig. 8 Change in integral intensities of FeO (200) and Fe<sub>3</sub>O<sub>4</sub> (400)

temperature change is adjusted, and the graph does not include thermal expansion. The solid curve of **Fig. 10** shows the relationship between the interatomic distance of FeO and the Fe concentration. Based on this relationship, plotted in the graph of Fig. 10 are the Fe concentrations in FeO of specimens pretreated at different temperatures given in Fig. 9 before and after the phase transformation. The higher the temperature of the pretreatment, the higher the Fe concentration in FeO before the phase transformation; this is presumably because Fe ions diffuse from base metal into FeO more easily as the pretreatment temperature becomes higher. In contrast, the Fe concentration after phase transformation is substantially the same regardless of the pretreatment temperature.

The increase in the interatomic distance of FeO during soaking at 400°C given in Fig. 9, and the increase in the peak intensity of Fe<sub>3</sub>O<sub>4</sub> given in Fig. 8 take place almost at the same time, which indicates that the interatomic distance of FeO, or the Fe concentration in FeO, increases as a result of the phase transformation. This agrees with the two formulae below relating to the phase transformation of FeO.



It became clear through the high-temperature XRD measurement that, as has been stated herein, the higher the temperature of the heat treatment before the transformation, the higher the Fe concentration in FeO before the transformation occurs, and as a result, the slower the transformation progresses. The phase transformation of FeO advances together with the diffusion of Fe ions through Fe ion voids. It seems reasonable to assume, therefore, that, when the Fe concen-

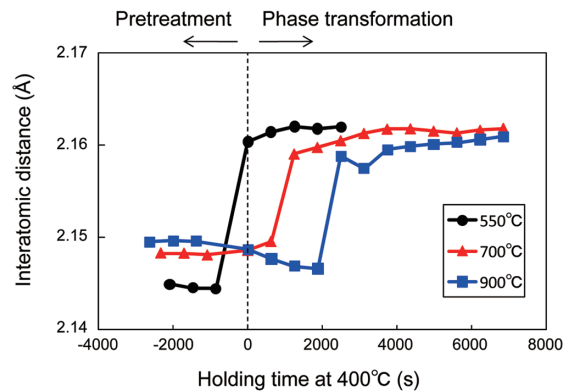


Fig. 9 Change in interatomic distance of FeO (200) calculated from  $2\theta$  values of corresponding peaks

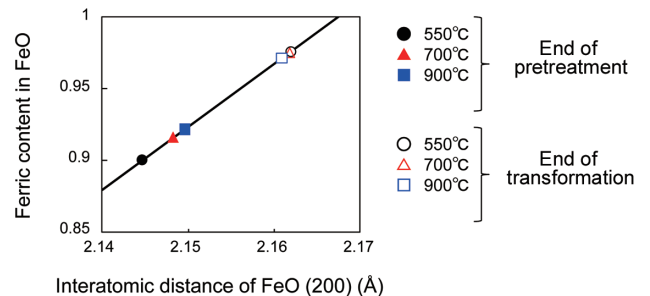


Fig. 10 Relationship between interatomic distance of FeO (200) and ferric content of FeO

tration in FeO before the phase transformation is high, the number of ion voids decreases, making it more difficult for Fe ions to diffuse, and that therefore the advance of the phase transformation becomes slower.

## 5. Conclusion

The phase transformation behavior of FeO in oxidized scale on steel surfaces has been studied with attention focused on the structure of scale before the transformation. In the case of bilayer scale of FeO and Fe<sub>3</sub>O<sub>4</sub>, the Fe<sub>3</sub>O<sub>4</sub> layer at the surface grows preferentially, and the precipitation of FeO hardly occurs at the interface with the base metal. In the case of monolayer scale of FeO only, in contrast, since the outermost Fe<sub>3</sub>O<sub>4</sub> layer is nonexistent, Fe<sub>3</sub>O<sub>4</sub> nucleates preferentially at the FeO/metal interface, and magnetite seams form in substantial quantities.

It also became clear that the rate of the phase transformation is slower with monolayer scale formed of FeO. Further, through high-temperature XRD measurement it has been made clear that, by holding steel at high temperatures before the phase transformation to ob-

tain FeO monolayer scale, the Fe concentration in FeO increases. This is presumably because the number of the Fe ion voids in FeO decreases, restricting the diffusion of Fe ions and slowing the rate of phase transformation.

As has been stated herein, the present study has made it clear that the phase transformation behavior of FeO can be controlled by adequately preparing the scale structure before the transformation. By intentionally having magnetite seams precipitate in substantial quantities, it will be possible to improve the adhesion of scale.

## References

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