Effects of Initial Scale Structure on Transformation Behavior of Wüstite

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(Received on August 3, 2011; accepted on September 8, 2011)

This study clarifies that the initial scale structure affects the transformation behavior of wüstite. The initial scale structure is controlled by limiting the temperature of nitrogen gas before the transformation of wüstite. The bilayer scale of magnetite and wüstite transforms from the magnetite/wüstite interface, while the monolayer scale of wüstite alone generates magnetite precipitates at the scale/steel interface preferentially. Furthermore, the monolayer scale takes longer to transform compared with the bilayer scale. These results indicate that the transformation behavior of wüstite can be controlled by the initial scale structure.

KEY WORDS: scale; wüstite; magnetite; phase transformation.

1. Introduction

Oxidized steel generally includes surface oxide scale, consisting of an outermost hematite layer (Fe₂O₃), an intermediate magnetite layer (Fe₃O₄), and a wüstite layer (FeO) in contact with the steel. Because the wüstite is unstable below 560°C as shown in Fig. 1 of the Fe–O phase diagram,1) it transforms to a mixture of magnetite and ferrite during cooling of the hot-rolled steel making it important to understand transformed scale structure on cooled steel products with scale adhesion and acid-pickling performance in mind.

Several studies concerning wüstite phase transformation have been reported.2–6) For wüstite phase transformation formed on steel, magnetite precipitations are initially generated, whereupon the magnetite-ferrite eutectoid structure appears. The morphology of the proeutectoid magnetite depends on the transformation temperature;7–9) at temperatures between 370 and 470°C, the magnetite precipitation forms a continuous layer at the scale-steel interface, known as a magnetite seam.

It has been reported that the scale with a magnetite seam shows high adhesion because of the high coherency with the substrate steel.10) This indicates that controlling the scale microstructure can be proposed as an alternate technique, e.g. by controlling extra elements.11,12)

Conversely, few studies have considered the effects of the initial scale structure, which is prone to change based on temperature and atmospheric factors. For example, at temperatures above 560°C in a non-oxidizing atmosphere, the scale consists of only a wüstite layer.

Here, we investigate and attempt to control the transformation behavior of wüstite for two types of initial scale structures.

2. Experiments

Super-ultra low carbon steels are used and the chemical composition of the specimen is shown in Table 1. The specimens are cut into rectangular shapes of 50 mm × 60 mm × 3 mm, whereupon surface polishing is performed.

The specimens with surface thermocouples are heated in an infrared heating furnace. Firstly, they are oxidized for 40
sec at 750°C in air, and then maintained at a temperature of 550 or 700°C in nitrogen gas for 30 min as pretreatment, in order to change the scale structure before transformation and prevent extra oxidation. We here describe the scale at the end of pretreatment as an initial scale.

At the end of 750°C oxidation, the scale structure consists of hematite, magnetite and wüstite, as mentioned above. After 550°C pretreatment, the hematite layer at the surface changes to a magnetite layer, hence the scale structure consists of magnetite and wüstite. Conversely, for 700°C pretreatment, the hematite and magnetite layer at the surface changes to wüstite, due to its ability to exist stably at temperatures exceeding 560°C. Accordingly, for 550°C pretreatment, the initial scale structure is a magnetite/wüstite bilayer, and for 700°C pretreatment, the initial scale structure is a single layer of wüstite.

Finally, the specimens are kept for between 10 and 240 min at temperatures of 350, 400, 450, 450 or 500°C in nitrogen gas, whereupon rapid cooling is performed. The final scale structure is observed by a scanning electron microscope (SEM) on the cross sections.

3. Results

The time-temperature-transformation (TTT) diagrams for each initial scale structure are obtained based on the scale microstructure observed by SEM. Figures 2 and 3 show the diagram and typical examples of SEM images for 550°C pretreatment, i.e. for bilayer initial scale structures, respectively. When the scale is kept at 500°C, magnetite precipitations appear from the interface of magnetite and wüstite, and grow in the direction of thickness. At temperatures of between 400 and 450°C, magnetite precipitations from the magnetite/wüstite interface are initially observed, followed by a small magnetite layer at the wüstite/steel interface. Finally the eutectoid magnetite/ferrite structure appears for transformation times exceeding 30 min. At temperatures below 400°C, the granular magnetite precipitations appear from the inside of wüstite.

Next, the diagram and corresponding SEM images for 700°C pretreatment, i.e. the monolayer scale of wüstite alone, are shown in Figs. 4 and 5, respectively. When the scale is kept at 500°C, no magnetite precipitations appear, but they do emerge from the wüstite/steel interface at temperatures of between 400 and 450°C, which suggests that the monolayer scale can easily generate a magnetite seam at the wüstite/steel interface compared with the bilayer scale. Finally, the eutectoid structure appears, but it takes about 240 min, which is longer than the case of the bilayer struc-
ture. At temperatures below 400°C, the granular magnetite precipitations appear from inside the wüstite layer, which is same as for 550°C pretreatment. Figure 6 shows typical differences of the changes in scale structure during heating between the bilayer and monolayer initial scale.

4. Discussions

4.1. Precipitation Behavior of Magnetite

Initially, we discuss the differences in terms of the precipitation behavior of magnetite, limiting comparison to the bilayer scale of magnetite and wüstite, and the monolayer scale of wüstite alone. For the bilayer scale, the surface magnetite layer can be nuclei of magnetite precipitations, which means the latter can easily grow in the direction of thickness, despite the small driving force for nucleation at temperatures exceeding 500°C, while the magnetite seam at the wüstite/steel interface is only slightly evident at temperatures below 450°C.

Conversely, for the monolayer scale, there is no magnetite layer at the surface. At temperatures above 500°C, therefore, there is no magnetite nucleation due to the lack of driving force, although below 450°C, there is sufficient undercooling for the driving force for nucleation, which can generate magnetite precipitation at the wüstite/steel interface.

4.2. Phase-transformation Rate

Secondly, we discuss why the monolayer scale takes longer to transform. Wüstite is a p-type semiconductor with metallic deficiencies, and is technically represented as Fe$_{(0.87 \leq x \leq 0.92)}$O at temperatures above 560°C (see Fig. 1). Because wüstite phase transformation progresses by the diffusion of ferric ions, pre-existing ferric ions in the initial wüstite may affect the speed of phase transformation. A high-temperature X-ray diffraction (XRD) measurement is performed to confirm this possibility. The specimens are 10-μm thick scale on steels with chemical composition as shown in Table 1. They are heated in high-temperature XRD equipment with nitrogen gas and initially kept at 550, 700 or 900°C for 30 min as pretreatment, and 400°C for 120 min for the phase transformation. During the heating, XRD measurement is performed iteratively with 2θ ranging from 25 to 50 degrees. A typical example of the measured XRD spectrum is shown in Fig. 7. We here focus on the transition of integral intensity and the interatomic distance obtained from 2θ value of wüstite (200) and magnetite (400) peaks. The transition of peak intensity corresponds to the change of scale composition, and the interatomic distance is known to be related to the ferric content of wüstite. Figure 8 shows the transition of the integral intensity of

![Fig. 5. Typical SEM images of cross sections of the scale in Fig. 4. The dark gray and light gray areas representatively indicate magnetite and wüstite.](image)

![Fig. 6. Typical differences shown in scale structure changes during heating between the pretreatment temperatures. For 550°C pretreatment, the initial scale consists of a magnetite and wüstite layer and generates little magnetite seam at the scale/steel interface. For 700°C pretreatment, the initial scale consists of the wüstite layer alone and it generates a distinguished magnetite seam.](image)

![Fig. 7. Typical example of an XRD spectrum. The focus here is on wüstite (200) and magnetite (400) peaks.](image)
wüstite (200) and magnetite (400). The transverse axis represents the elapsed time since the onset of 400°C holding, while the negative and positive areas are representative of the pretreatment and phase transformation. During the pretreatment, the wüstite and magnetite peaks are detected for only 550°C pretreatment, which is consistent with the above discussion. As soon as 400°C holding commences, the wüstite intensity declines and that of magnetite increases in all cases, although increasing the pretreatment temperature leads to the pace of change slowing, which indicates a slower phase transformation.

Figure 9 shows the interatomic-distance transition of wüstite (200) obtained from 2θ values of corresponding peaks. The effects of thermal expansion are eliminated in Fig. 9, while Fig. 10 shows the relationship between the interatomic distance and ferric content of the wüstite,13) the ferric contents of which are calculated from the interatomic distances in Fig. 9. At the end of the pretreatment, the ferric content increases with rising pretreatment temperature. The high-temperature pretreatment is considered to make ferric-ion diffusion active. Conversely, at the end of 400°C holding, the interatomic distances rise and become virtually equal.

During 400°C holding in Fig. 9, the interatomic distance increases at almost the same time as the increase in intensity of the magnetite in Fig. 8, indicating that the phase transformation increases the interatomic distance or the ferric content of the wüstite. This result is consistent with the following well-known reactions involved in wüstite phase transformation:

\[(4y-3)Fe_xO \rightarrow (4x-3)Fe_y + (y-x)Fe_3O_4, \quad 0.87 \leq x \leq 0.92 \leq y \leq 0.99 \] ........................ (1)

\[4Fe_2O_3 \rightarrow (4y-3)Fe + Fe_3O_4 \] .................. (2)

Accordingly, the high-temperature XRD measurement clarifies that high-temperature pretreatment increases the ferric content in wüstite before phase transformation, making it takes longer to transform. It is considered that the ferric-ion cannot diffuse sufficiently for the phase transformation because the initial iron-rich wüstite has scarce metallic vacancies.

5. Conclusions

Wüstite phase transformation is investigated focusing on the initial scale structure. When the initial scale structure is a magnetite/wüstite bilayer, magnetite precipitations appear from the magnetite/wüstite interface, while scarcely any magnetite seam forms at the wüstite/steel interface. Because the surface magnetite layer can be a magnetite nucleation site, the magnetite layer can be easily grown without requiring any magnetite nucleation catalyst. Conversely, when the initial scale structure is a wüstite monolayer alone, the magnetite seam preferentially forms at the wüstite/steel interface because the monolayer scale lacks the magnetite layer as a
nucleation site. It takes longer for the monolayer scale to transform. High-temperature XRD measurement clarifies that the monolayer scale with high-temperature pretreatment becomes iron-rich wüstite, in other words, the wüstite has few metallic vacancies, which hampers ferric diffusion for phase transformation.

Accordingly, in this study, we suggest that the wüstite phase transformation can be controlled by the initial scale structure.

REFERENCES
