The Effect of Grain Boundaries on the Surface Rearrangement during Wüstite Reduction within its Range of Existence

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Dense polycrystalline wüstite samples equilibrated with 50%CO–CO₂ gas mixture for 432 ks has been reduced at 1 073 K using 60%CO–CO₂ gas mixture to study the effect of grain boundaries on the surface rearrangement process. Orientations of surface grains on the wüstite specimens are measured by applying electron backscattering pattern technique. The development of the surface arrangement away from grain boundaries is significantly larger than that near grain boundaries. Quick establishment of the equilibrium with the reacting gas in the region near grain boundaries at the early stage of the reduction makes it difficult to continue the transportation of Fe²⁺ ions into deep interiors of wüstite by the volume diffusion process. As a result, the surface rearrangement is retarded at the surface near grain boundaries after the equilibration of the surface. The transportation of Fe²⁺ ions at the surface layer away from grain boundaries by volume diffusion is small but not negligible so that the surface rearrangement away from the grain boundary is possible to continue until almost the whole sample is equilibrated.

KEY WORDS: grain boundary; surface rearrangement; wüstite reduction; grain orientations; electron backscattering pattern technique.

1. Introduction

Due to nonstoichiometric properties of wüstite, the reduction of wüstite within its range of existence can occur. Many researchers observed the development of surface rearrangement of wüstite during reduction process before iron nucleation occurred. The surface rearrangement is related to wüstite reduction within its existence. Most of studies for wüstite reduction have been focused on iron nucleation, and very few works for the reduction of wüstite within its existence were carried out.

The reduction mechanism of wüstite based on its non-stoichiometric property was investigated by Wagner. From the Wagner’s mechanism, it is noted that migrations of cation vacancies and holes from the interiors of sample to the reacting sites are required for wüstite reduction. These migrations are carried out by volume, surface and grain boundary diffusion processes. The grain boundary diffusion rate is significantly faster than that of volume diffusion so that the grain boundary is expected to have a critical role for wüstite reduction. For iron nucleation process, it was confirmed in the previous study that the iron nucleation dominantly occurred at the area near the grain boundary.

In the present study, wüstite reduction within its existence has been carried out to investigate the effect of grain boundaries and the grain orientation on the surface rearrangement. The rearranged surface is observed by using a field emission scanning electron microscope (FE-SEM). The grain orientation is evaluated by using electron backscattering diffraction (EBSD) method.

2. Experimental

2.1. Apparatus and Material Preparation

The experimental arrangement was basically similar to that described previously except the composition of reducing gas mixtures. A piece of wüstite samples (about 0.1 g) was put in a platinum boat and the boat was at the closed end of silica reaction tube (400 mm long and inside diameter of 14 mm). The sample was positioned within the isothermal zone of a resistance furnace. Gas delivery was performed through a high purity transparent silica tube of 500 mm length and 4 mm inside diameter, which was held by 10 mm above the surface of the sample. The furnace temperature was controlled by Almel–chromel thermocouple while the sample temperature was measured by Pt-13%Rh alloy thermocouple. Reducing gas was dried by passing through a silica gel column while traces of CO₂ in the CO gas were removed by soda lime. The gas flow rates were controlled by mass flow controllers. All reduction processes were carried out at 1 073 K.

Wüstite samples were prepared by melting reagent grade Fe₃O₄ powder in a heavy iron crucible and quenching on a steel plate. The wüstite block was cut into pieces of about 5×5×2 mm. In the previous study, it was confirmed that...
equilibration time of more than 432 ks was necessary to equilibrate the whole wüstite sample. Therefore, all pieces of wüstite were equilibrated at 1 073 K for 432 ks using 50%CO–CO₂ gas mixture with total flow rate of \(8.33 \times 10^{-6} \text{ m}^3/\text{s}\) (0.5 L/min) for the equilibrium accomplishment. The surface of equilibrated wüstite sample was polished to serve for EBSD and SEM analysis.

2.2. Reduction Procedure
The wüstite specimen of about 0.1 g was heated with flowing 50%CO–CO₂ gas mixture of total flow rate \(8.33 \times 10^{-6} \text{ m}^3/\text{s}\). After temperature reached to 1 073 K the samples were kept at the same temperature for 900 s with the same gaseous ratio. Then, surface rearrangement experiments were started by changing the gas ratio to 60%CO–CO₂ with total flow rate of \(8.33 \times 10^{-6} \text{ m}^3/\text{s}\) for different reduction times of 30, 300, 900 and 1 800 s. In this experiment, the time at changing the gas ratio is defined as the starting time of reaction. From the nominal volume of the experimental system, the actual reaction time may be about 5 s less than the nominal time. After particular reaction time, the sample was quenched by opening the upper separable part of the furnace without moving the samples with flowing the reaction gas.

2.3. Orientation Measurement
For EBSD analyses, the surface of wüstite samples were polished by using silicon carbide wet polishing papers, then diamond paste and finally colloidal silica (0.1 μm) suspended solution. Polished wüstite samples were subject for carbon coating. An selected area for measuring was identified by the traces of Vickers indenter. All wüstite samples were subject to EBSD system to measure surface grain orientations before reduction reaction. Surfaces of various grains with different orientations were observed before and after reduction reaction by using a FE-SEM. In this study, we adopt conventions of referring to the crystallographic orientation of the grain by the direction of the normal to it and Miller index was used to present the orientation.

3. Results
3.1. Surface Rearrangement
Surface rearrangements due to the reduction by 60%CO–CO₂ were investigated by varying reaction time of 30, 300, 900 and 1 800 s. For the reaction time of 30 s, no macroscopic surface rearrangement was observed while it might take place in atomic scale. For the reaction time of more than 300 s, the surface rearrangement was found to start and gradually developed. The surface rearrangement was observed for all observed grains with different orientations.

The surface rearrangement occurs dominantly in an area away from grain boundaries as shown in Fig. 1. A dark area along with grain boundaries represents weak surface rearrangement in these areas. White color area observed in the area away from boundaries reflects the presence of very developed surface rearrangement. This tendency is clearly observed in Figs. 2(a) and 2(b) with high magnification. The surface structures along the grain boundary between the grains with (11 3 13) and (8 1 8) orientations, and that between those with (9 5 15) and (7 1 8) are shown. The dominant surface rearrangement away from the grain boundary is clearly recognized. The surface rearrangement occurs in the area of about 10 μm away from grain boundaries and do not seem to change with grain orientations. The change of the observed width of the surface rearrangement band for various grains with reaction time is shown in Fig. 3. The width seems to be almost constant of about 20 μm.

The rearranged surface structures of grains with (7 1 8), (3 2 5) and (11 3 13) orientations after 900 s reduction are
shown in Fig. 4 respectively. The appearance of each grain surface after the surface rearrangement is quite different depended on their initial grain orientations.

4. Discussion

4.1. Role of Surface and Grain Boundary Diffusion

Wüstite reduction within its existence is driven by an oxygen removal reaction before it reaches to equilibrium condition. The oxygen removal reaction on wüstite with CO gas is generally expressed by

\[ \text{CO(g)} \rightarrow \text{CO(ad)} \]  

\[ \text{CO(ad)} + 2h + V_{\text{Fe}}^{\text{Fe}^2+} + O_{\text{O}}^{\text{Fe}^2+} \rightarrow \text{CO}_2(\text{ad}) \]  

\[ \text{CO}_2(\text{ad}) \rightarrow \text{CO}_2(\text{g}) \]  

where $O_{\text{O}}^{\text{Fe}^2+}$ is a doubly charged oxygen ion occupying a normal lattice site, $h$ is an electron hole, and $V_{\text{Fe}}$ is a Fe divalent cation vacancy. The notation of defects in the present study is based on the method by Kröger et al.\(^7\) From reaction (2), $h$ and $V_{\text{Fe}}$ must be consumed to accomplish the oxygen removal reaction, otherwise the oxygen removal reaction cannot succeed. Namely, once an oxygen ion at the surface is removed, $\text{Fe}^{3+}$ ions in the lattice accept the electrons released from the removed $O_{\text{O}}^{\text{Fe}^2+}$ ion and are converted to $\text{Fe}^{2+}$ ions, namely $h$ is consumed. It is noted that not only oxygen ions but also unpaired $\text{Fe}^{2+}$ ions on the surface are subsequently eliminated by the oxygen removal reaction. This elimination of the “FeO” unit promotes the surface rearrangement. This process is schematically shown in Fig. 5. The flows of $\text{Fe}^{2+}$ takes place along with the counter flow of $h$ to keep electrical neutrality. Thus, flows of $\text{Fe}^{2+}$ ions from the surface to the cation sub-lattice and the counter flow of vacancies and holes driven by diffusion process should have a critical role for surface rearrangement.

With the progress of wüstite reduction, produced $\text{Fe}^{2+}$ is transported into the surface layer by volume diffusion so that the Fe/O ratio in the surface layer gradually increases. The produced $\text{Fe}^{2+}$ ions at the surface near the grain boundary can be transported into interiors not only by the volume diffusion but also by the aid of the surface and grain boundary diffusions, since the surface area near the grain boundary is convenient for the surface and grain boundary diffusion processes. The surface and grain boundary diffusion rates are 'significantly faster' than the volume diffusion rate so that $\text{Fe}^{2+}$ ions at the surface close to the grain boundary is effectively transported from the surface to the interior along the grain boundary, and the transported $\text{Fe}^{2+}$ ions in the grain boundary diffuses vertically into the interiors by the volume diffusion. This diffusion process is schematically illustrated in Fig. 6. For the surface layer A, $\text{Fe}^{2+}$ ions are transported not only from the surface but also from the grain boundary. Consequently Fe/O ratio is more quickly increased compared with that in the surface layer B where $\text{Fe}^{2+}$ is supplied only from the surface. Therefore, Fe/O ratio in the surface layer near grain boundaries approaches
to the equilibrium value more quickly than that away from grain boundaries. Once the equilibrium state is established at the surface layer, the oxygen removal reaction cannot progress so that the surface rearrangement must be halted. The near-equilibrated zone after some reaction time is schematically shown in Fig. 7 as a hatched area. Even the surface layer is equilibrated, \( \text{Fe}^{2+} \) ions in the surface layer at the surface away from the grain boundary can diffuse downwards into interiors so that the interiors are not saturated with \( \text{Fe}^{2+} \). Thus the \( \text{Fe}^{2+} \) concentration in that surface layer is able to decrease and the oxygen removal reaction at the surface can continue. However, this mechanism does not work for the surface layer near the grain boundary. It is noted that the near-equilibrated zone is not only in the surface layer but also along the grain boundary due to the fast transportation of \( \text{Fe}^{2+} \) ions by the surface rearrangement.

The diffusion flux of \( \text{Fe}^{2+} \) from the surface to the interiors due to the volume diffusion is expressed by

\[
J_{\text{Fe}^{2+}} = D_v \frac{\partial C_{\text{Fe}^{2+}}}{\partial y}
\]

(4)

where \( D_v \) is the volume diffusion coefficient of wüstite, \( C_{\text{Fe}^{2+}} \) is the \( \text{Fe}^{2+} \) concentration. After the establishment of the near-equilibration of the surface, the downwards diffusion flux of \( \text{Fe}^{2+} \) in the surface layer \( A \) by the volume diffusion is negligibly small, since the concentration gradient \( \partial C_{\text{Fe}^{2+}}/\partial y \) in the surface layer \( A \) is essentially zero as indicated in Fig. 7. Consequently \( \text{Fe}^{2+} \) ions cannot be transported from the surface to the interiors so that the \( \text{Fe}^{2+} \) concentration in the surface layer near the grain boundary does not decrease, or the equilibrium state is maintained. Therefore, the oxygen removal reaction cannot continue at the surface near grain boundaries. Namely the surface rearrangement at that area continuously halts after the surface layer has reached to the equilibrium at the early stage of the reduction.

For the surface layer \( B \), however, the interior region beneath the surface area is still far from the equilibrium state even if the surface layer is in near-equilibrium state. Namely the concentration gradient \( \partial C_{\text{Fe}^{2+}}/\partial y \) at the surface layer \( B \) shown in Fig. 7 is small but not negligible. Subsequently \( \text{Fe}^{2+} \) in the surface layer \( B \) can be transported into the deep interiors by the volume diffusion process. By this volume diffusion process of \( \text{Fe}^{2+} \) ions, the oxygen removal reaction or the surface rearrangement at that surface is possible to continue until the whole wüstite sample converted to the equilibrium state.

Namely, the degree of the surface arrangement near the grain boundary may be larger than that away from the grain boundary until the surface near the grain boundary reached to the near equilibrium state. After that, however, the development of the surface arrangement at the surface near the grain boundary has ceased but that away from the grain boundary can continue. As a result, the degree of the surface arrangement at the surface away from the grain boundary finally surpasses that near the grain boundary after some time. This is the reason that the development of the surface rearrangement away from grain boundaries is significantly larger than that near grain boundaries.

5. Conclusions

By using very homogeneous and highly dense wüstite, the effect of grain boundaries on the surface rearrangement developed during wüstite reduction has been investigated. It is found that grain boundaries have a strong effect on the surface rearrangement process as follows:

(1) The surface rearrangement dominantly occurs away from grain boundaries.

(2) The grain boundary effect on the surface rearrangement is observed all over grains with various orientations.

(3) Establishment of the equilibrium in the region near grain boundaries at the early stage of the reduction makes it difficult to continue the transportation of \( \text{Fe}^{2+} \) ions into deep interiors of wüstite by the volume diffusion process. This retardation of \( \text{Fe}^{2+} \) ion transportation by the volume diffusion process is the reason that the surface rearrangement is less significant at the surface near grain boundaries.

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REFERENCES

1) C. Wagner: *J. Met.*, 4 (1952), 214.
2) M. Bahgat, Y. Sasaki, S. Hijino, M. Iguchi and K. Ishii: *ISIJ Int.*, 44 (2004), 2023.
3) S. I. Wright: Electron Backscatter Diffraction in Materials Science, ed. by A. J. Schwartz, M. Kumar and B. L. Adams: Kluwer Academic/Plenum Publishers, New York, (2000), 51.
4) S. I. Wright and B. L. Adams: *Metall. Trans. A*, 23A (1992), 759.
5) B. L. Adams, S. I. Wright and K. Kunze: *Metall. Trans. A*, 124A (1993), 819.
6) N. Birks and G. H. Meier: Introduction to High Temperature Oxidation of Metals, Edward Arnold, London, (1983), 38.
7) F. A. Kröger and H. J. Vink: Solid State Physics, Vol. 3, ed. by F. Seize and D. Turnbull, Academic Press, New York, (1956), 29.