In-situ Observation of the Reaction between Iron and Carbon in TEM

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The in-situ observation of the reaction between iron and carbon in TEM was carried out. The contact between iron and carbon was realized utilizing the carbon deposition on the surface of iron and FIB enabled to prepare TEM specimens. The reaction occurred beyond 773K as the precipitation from the boundary between iron and carbon and the precipitates grew into the carbon layer. The growth rate of the precipitates was 100-200nm/min at 873K. EDS and EELS showed that the concentration of the iron in the precipitates was almost 100% and carbon was seldom detected. Only the diffusion of iron into the carbon layer was clarified. The images of the precipitates and the results of EDS and EELS indicated the precipitates were as the result of exchange of iron and carbon.

1. Introduction

The reduction of iron oxides has been one of the most frequently studied topics in iron smelting. The dynamic analysis of the iron-making process is also studied by many researchers. Transmission electron microscope (TEM) is unique facility which possesses one of the highest resolution among the apparatus for microscopic analysis. But the study of reductant was limited to gases such as CO or H using TEM. For example, environmental cells that is the capsule enclose specimens with gas-atmosphere or ion-implantation into the iron oxides to investigate the reduction process [1-5] The coke i.e. solid state carbon is used as a reductant in iron industry and direct reduction by solid carbon was also proceeded with gas reduction in the blast furnace. The difficulty of TEM observation for solid/solid reaction is to realize the contact of plural materials inside the observation area and the usable matters were very limited. We developed the making TEM specimen to realize the in-situ analysis of the reduction of the iron-oxides by solid carbon applying the deposition of carbon [6-7].

The carbon is also used in industry for making steel as carburization. But microstructure of the carburization process is not clear in spite of frequency usage of carbon. It is also difficult that the contact of iron and carbon is necessary to prepare the TEM specimen like in case of reduction of iron oxides then it is expected to realize in-situ TEM observation of the reaction between carbon and iron in the similar way of TEM specimen preparation. The purpose of our study is to carry out the in-situ analysis of the reaction between carbon and iron in TEM applying the carbon-deposition.

2. Experiments

The preparation of TEM specimen is most important in this study. The samples were cut from the bulk pure iron by means of the diamond sawing with the size of 1×2 mm square and the thickness of 0.5 mm. The thin foils were polished to attain the thickness of less than 50μm using emery papers. The clean surface of iron is necessary to contact with carbon. The fracture surface was used in the case of oxides because of the brittleness of oxides in the previous study. But it was impossible to get the clean surface by break of iron keeping out the deformation with many cracks and dislocations due to the metallic structure. FIB was used to get the flat and clean surface because it is easy to find the polishing area. The dislocations due to the damage of ion bombardments are also induced into the specimen, but the transformation to amorphous using such as oxides were avoided. Ion beam was used to polish the surface and the ions were implanted parallel to the surface of the polishing area to minimize the radiation damage. Schematic drawing of the specimen to get the clean surface is shown in Fig.1. Then the carbon was deposited on the polished surface of iron. The specimens were

removed to the deposition apparatus in air as soon as possible after polishing to minimize the surface contamination. The thickness of carbon was 0.5-1μm. Final thinning was carried out also using FIB to get the thin area locally. The drawing of TEM specimen for final polish is shown in Fig.2. The in-situ experiment at elevated temperature was carried out in the JEM-2000FX. EDS and EELS which installed in JEM-2100F and JEM-3000F respectively were also used for analysis of the component

3. Results and Discussion

The rate of raising and observation temperature had to be considered at first because it was necessary that the observation area had to be kept in site and to find the suitable temperature for in-situ observation. Finally about 100 degree/min of heating rate was adopted. The observable reaction was happened beyond the 773K approximately. The reaction became faster with increasing the temperature.

Figure 3 shows bright field images of continuous observation of the structural change at the boundary between iron and carbon which was kept at 823K up to 90min, a) before heating, b) after 10minutes, c) after 30minutes and after 90 minutes in d). During heating, the precipitation of small particles which was observed in b) occurred and they grew into the carbon layer. The internal structure of iron was also changed but the component was not changed.

Digital image recording was also done because taking photos needs a little interval for continuous observation and it became difficult to catch the initial stage of precipitation especially at higher temperature. Figure 4 shows the capture of images those successive image recording at 873K a) before heating, b) after 8 seconds, c) after 22 seconds, d) after 36 seconds, e) 59 seconds and after 217 seconds in f). The reaction became faster and precipitates attained at the edge of carbon layer within several minutes. The growth rate of the precipitates was approximately 100-200nm/min. The contrast of the iron and carbon was so different due to the atomic volume that only the reaction inside the carbon layer was recorded. First precipitate generated before passing of 8 seconds and it is pointed by arrow in b). The precipitation were also started at many places after passing several seconds. The shape of the precipitates were changed very quickly and stuck together like liquid. The precipitates also formed some holes in the carbon layer. There were interference fringes inside the precipitates and it indicated the precipitates crystal. The image of the precipitates was a little darker than that of carbon but much brighter than iron layer. The growth of the reaction stopped in the place of formation of detachment between carbon and iron or coming at the edge of carbon layer as shown in fig.3.

EDS was used for identify the component of precipitates. Figure 5 showed that one of the example of spectrum profiles in the precipitates. The EDS spectrum showed that the precipitates were nearly iron and very low concentration of carbon was detected. There also found almost no carbon inside the iron layer.

EELS was also used to confirm the results of EDS. Figure 6 shows mapping of EELS around the precipitates. The images of mapping was same as the result of EDS and there found no signal of carbon but iron in the precipitates.

These result indicated that iron diffused into the carbon layer and exchanged with carbon. But it was unclear destination of exchanged carbon because the solubility of carbon in iron is extremely low at the range of observed temperature. The observation was done at much lower temperature than the common industrial way for carburization. It is cleared that the phenomenon of iron precipitation into the carbon is much different from the carburization. The higher temperature analysis needs to clarify the carburization process directly.

4. Concluding Remarks

(1) The in-situ analysis of the reaction of iron and carbon in TEM was carried out.
(2) The precipitates were generated at the boundary between iron and carbon.
(3) The precipitation started above about the 773K and growth rate was 100-200nm at 873K.
(4) The shape of the precipitates changed easily during heating and growth was stopped by the attainment of the precipitates to the end of carbon layer.
(5) The concentration of the iron in the precipitates was almost 100%.
(6) Only the diffusion of iron atoms into the carbon was clarified.

5. References

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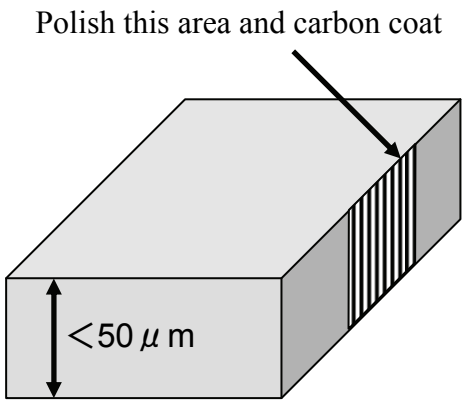

Fig. 1 Drawing of the polishing position on iron bulk specimen.

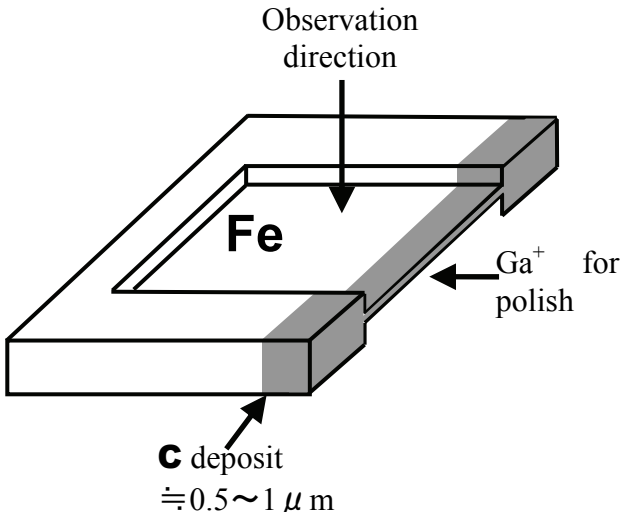

Fig. 2 Drawing of the final polishing of the TEM specimen by FIB.

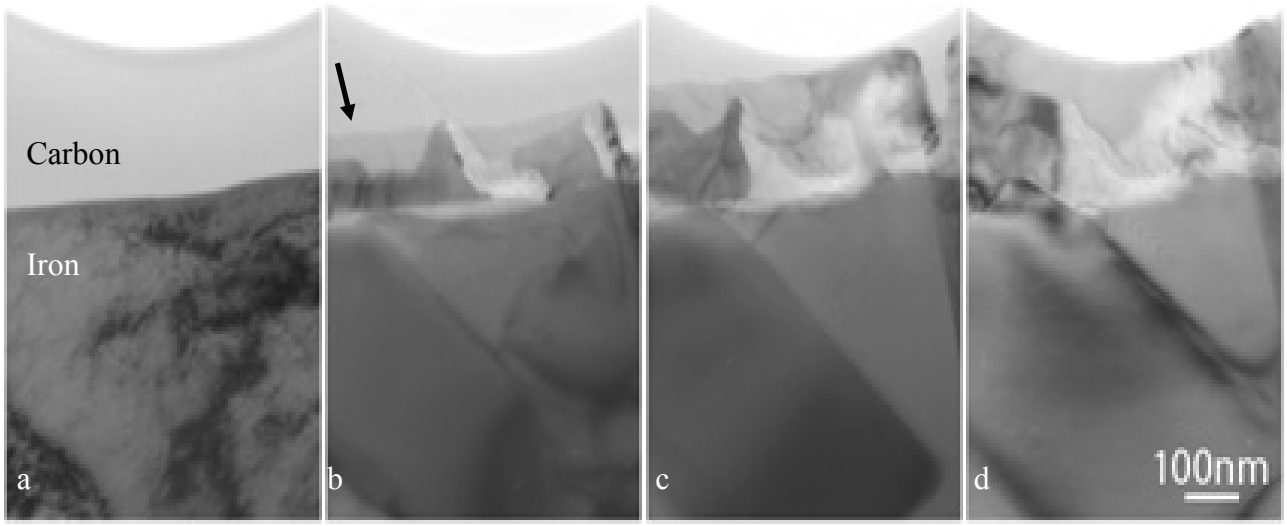

Fig. 3 TEM photograph of the change of boundary between a iron and a carbon kept at 823K up to 90min. a) just reached 823K, b) after 10minutes, c) after 30 minutes and (d) after 90 minutes. The precipitates were pointed by an arrow in b).

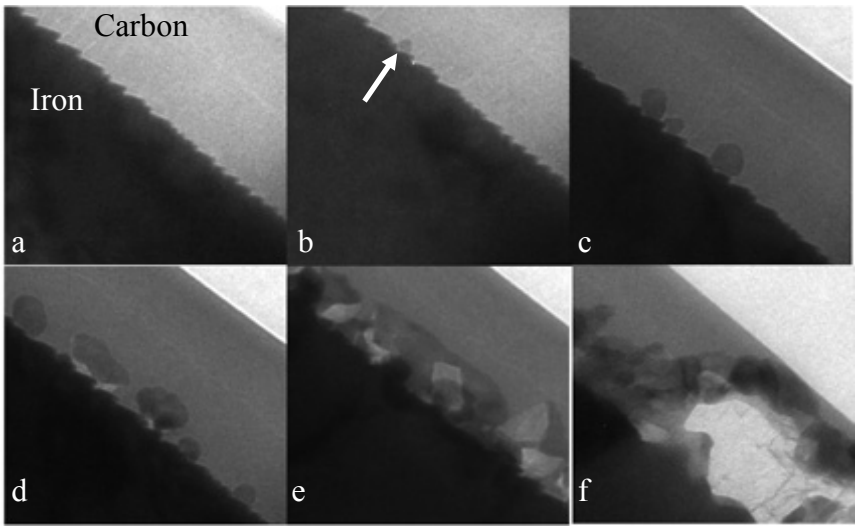

Fig. 4 The continuous images captured from digital image recording at 873K. The elapsed time is a) just reached 873K, b) 8 seconds, c) 22 seconds, d) 36 seconds, e) 59seconds, f) 217 seconds. The precipitate at the initial stage is pointed by an arrow in b).

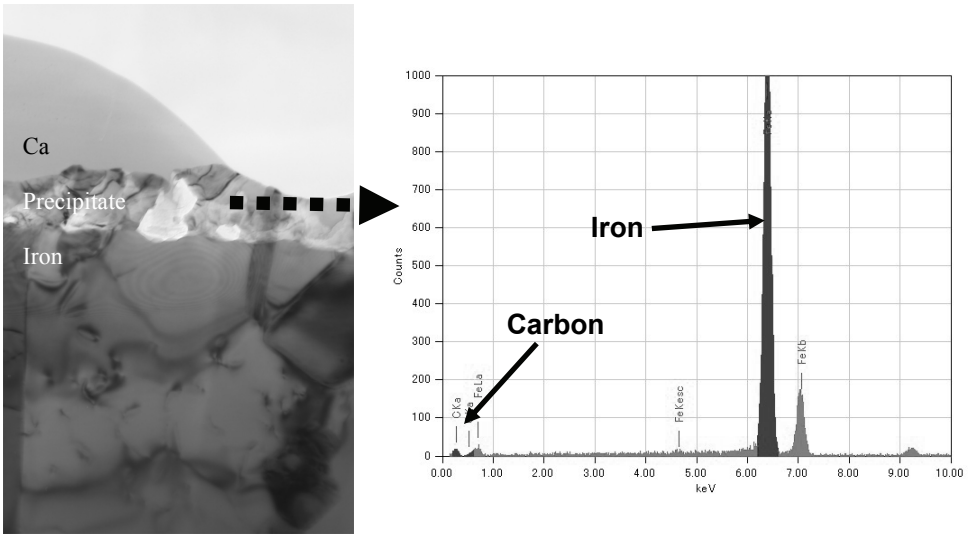

Fig. 5 EDS spectrum inside the precipitates formed in carbon layer.

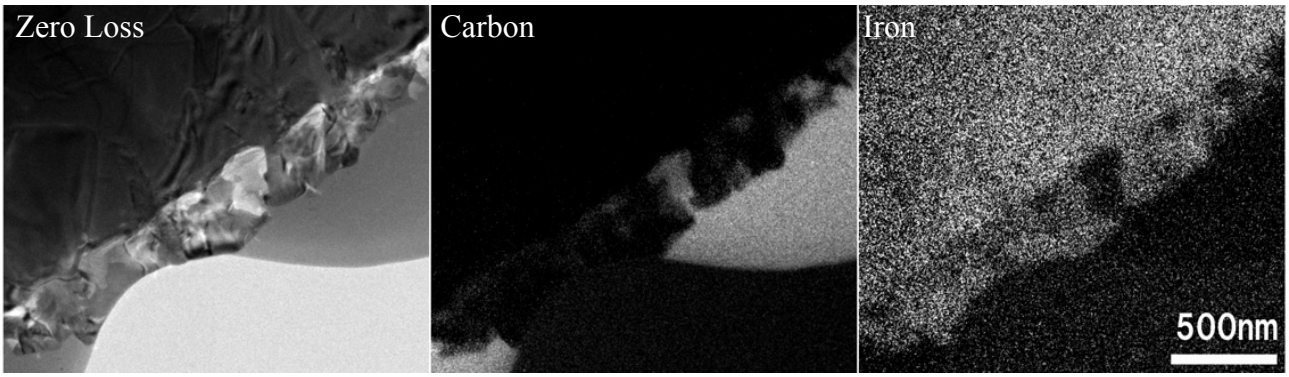

Fig. 6 EELS mapping of carbon and iron.