IN-SITU OBSERVATION OF THE REACTION BETWEEN IRON AND CARBON IN TEM[1]

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Abstract
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 823K as the precipitation from the boundary between iron and carbon and the precipitates grew into the carbon layer. The concentration of the iron in the precipitates became lower with the increase of distance from the boundary. The growth rate of the precipitates was 100-200nm/min at 873K. The images of the precipitates and the results of EDS indicated the precipitates were transformation of the carbon from amorphous to crystal promoted by the diffusion of the iron atoms.
Key words: In-situ analysis; TEM; Carbon/ iron interface; Carburization.

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1 INTRODUCTION

The reduction of iron oxides has been one of the most frequently studied topics in iron smelting. The in-situ namely the dynamic analysis of the iron-making process is also studied by many researchers. The transmission electron microscope (TEM) is unique facility which possesses one of the highest resolution among the facilities for microscopic analysis. But the reductants were 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 such as CO or H to investigate the reduction process.[1-5] The coke i.e. solid state carbon is used as a reductant in iron industry. 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 state carbon applying the deposit of carbon.[6-7]. The carbon is also important resource of carburization. The in-situ TEM observation of the reaction among carbon and other solids were not applied because of the difficulty of preparation of TEM specimen. But it is expected that application of carbon deposition on other materials will enable the in-situ TEM observation. We tried to carry out the in-situ analysis of the reaction between the carbon and iron applying the carbon-deposition in TEM.

2 SPECIMEN PREPARATION

The preparation of the TEM specimen is most important in this study. The samples were cut from the bulk pure iron by means of the diamond sawing. The size of the specimen was about 1×2 mm with the thickness of 0.5 mm. The thin foils were polished to attain the thickness of approximately 10μm using emery papers. The clean surface of iron is necessary to contact with carbon. The fracture surface was used as clean surface using iron oxides because of the brittleness of oxides in the previous study. But it is impossible to get the clean surface to break the iron keeping out the deformation with a great many cracks and dislocations because the iron is metal. We applied ion polishing to get the flat and clean surface. The dislocations due to the damage of ion bombardments are also induced into the specimen but the transformation to amorphous such as using oxides were avoided. The focused ion beam (FIB) was used to polish the surface and the ions were implanted parallel to the surface 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 surface of iron.

The specimens were removed to the deposition apparatus as soon as possible after polishing to keep the surface clean. The carbon was deposited on the polished surface with the thickness of 0.5-1μm. The final thinning was carried out using FIB. The drawing of TEM specimen for FIB is shown in Fig.2.

The advantages of using FIB are as follows. (1) The necessary volume of the specimen is much smaller than that of typical TEM specimen with 3mm in diameter. The electron beam in TEM is controlled by magnetic field. The iron is ferromagnetic material and the size of the specimen should be as small as possible. (2) The secondary electron image of the specimen can be observed during polishing and the location of polishing area can be easily decided . (3)It is easy to prepare the specimen which includes the boundary to observe from the cross sectional direction.

TEM observation was performed using JEM-2000FX with the accelerating voltage of 200kV which affects almost no change in the specimen. The Heating holder was used in this study and the photographs was taken at periods of heating time. The video recording was also carried out simultaneously. Energy dispersive X-ray spectroscopy (EDS) was carried out using a JEM- 2100F with field emission gun after heat treatment.

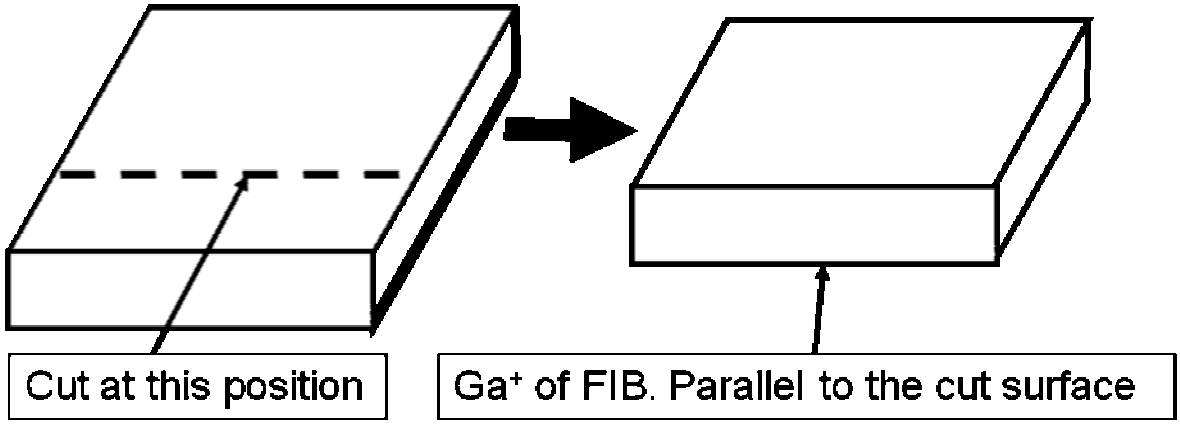

Figure 1. Schematic drawing of the specimen to reveal the clean surface for carbon deposition.

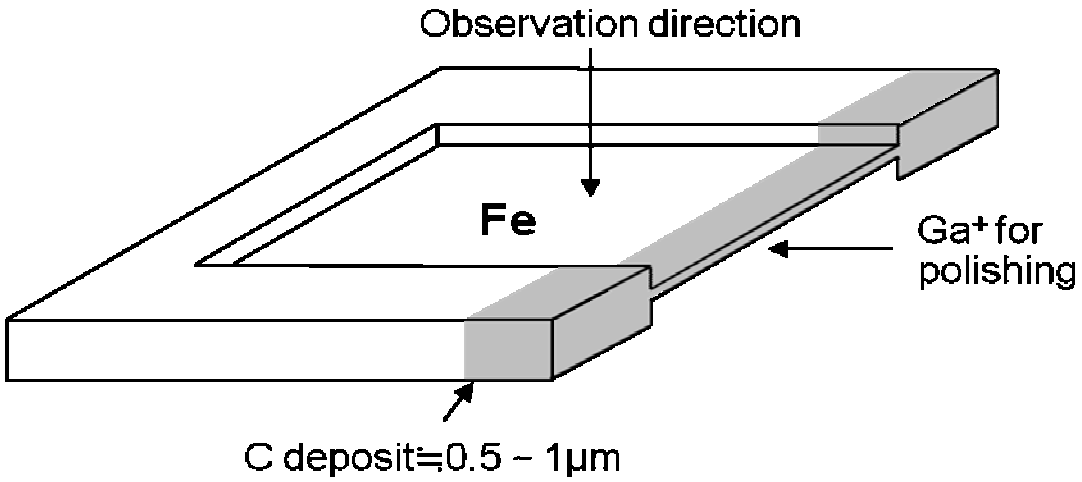

Figure 2. Schematic drawing of the TEM specimen after carbon deposition by FIB.

3 RESULTS AND DISCUSSION

At first, the rate of raising temperature and the temperature of the observation had to be considered. About 50-100K/min was adopted to raise the temperature because the velocity of the drift of the specimen due to heating was limited to keep in sight. The observable reaction was happened beyond the 773K approximately. The reaction became faster with increasing the temperature and it means if the endless observation was possible, the reaction would be able to be observed at lower temperature.

Figure 3 shows the bright field image of the structural change of the boundary between the iron and carbon which was kept at 823K. The deposited carbon was

amorphous. The boundary was not flat even after ion polishing but the contact with carbon was smoothly. The photos are a) Before heating, (b) after 10 minutes, (c) after 30minuites and (d) after 60min respectively. 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. The precipitates were identified as the mixture of iron and carbon obtained by EDS analysis after heat treatment. The internal structure of iron was also changed but the component was not changed. The detachment between carbon and iron was sometimes observed and the reaction stopped after the detachment. This result indicates the gas emission from the boundary. But vacuum level was not changed and there was almost no affection to the condition of TEM observation.

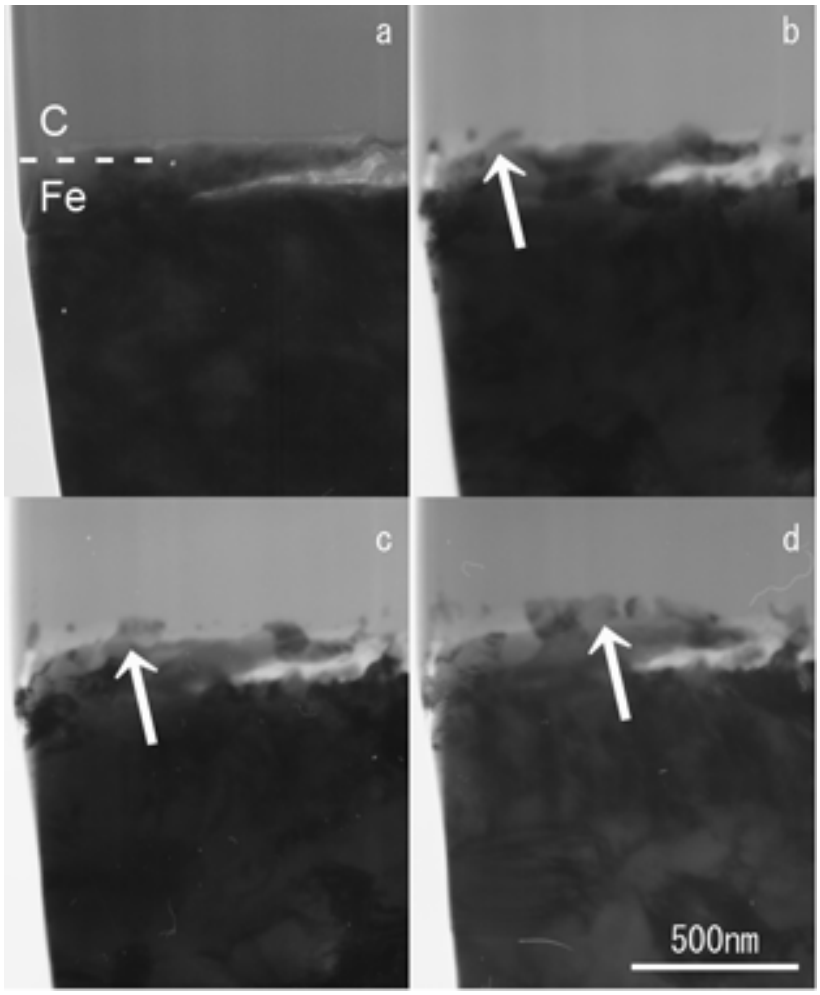

Figure 3. TEM photographs of the change of boundary between a iron and a carbon kept at 823K up to 60min. (a) before heating, (b) after 10 minutes, (c) after 30 minutes and (d) after 60 minutes. The precipitates are pointed by arrows.

Figure 4 shows the continuous images captured from DVD recording at 873K. The reaction became faster as the temperature rising and it became impossible to follow the image by photographs. The elapsed time were a) just reached 873K, b) 8s, c) 22s, d) 36s, e) 59s, f) 104s, g) 135s, h) 217s. The contrast of the iron and carbon was so different that only the reaction inside the carbon was recorded. The growth rate of the precipitates become much faster and it reached the end of carbon layer within several minutes. First precipitate generated before 8 seconds passed and it is pointed by arrow in b). The precipitation were also started at other places after

several seconds passed and first precipitate was pointed by arrows in c) and d). The shape of the precipitates were changed very quickly and stuck together like liquid. The change of the configuration of the precipitates induced some holes in the carbon layer and the growth was stopped. There were interference fringes inside the precipitates and it indicates that the precipitates were crystal. The image of the precipitates was a little darker than that of carbon but much brighter than iron layer. EDS showed the concentration of the iron in the precipitates come down with increasing distance from the boundary. These results indicates that the precipitates were generated by the transformation of carbon from amorphous to crystal and it was promoted by the invasion of iron atoms to the carbon layer. Figure 5 is an example of the EDS peaks measured by EDS. The growth rate of the precipitates was approximately 100-200nm/min. The temperature of the experiments is much lower than the carburization used in the industry. But the precipitates were not generated by the carburization but the diffusion of the iron into the carbon. The square of carbon layer reduced by heating and it may diffuse to iron layer.

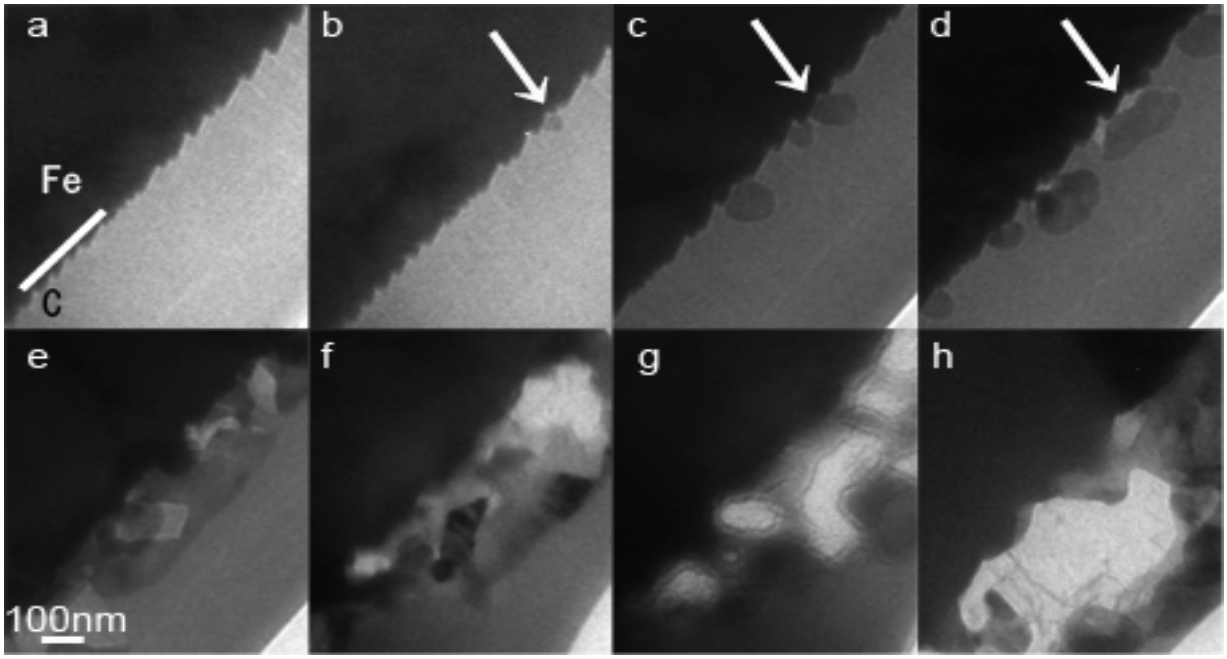

Figure 4. The capture images from DVD recording kept at 873K up to 60min. a) just reached 873K, b) 8s, c) 22s, d) 36s, e) 59s, f) 104s, g) 135s, h) 217s. The first precipitate is pointed by arrows in b), c), and d).

4 CONCLUSION

(1) The in-situ transmission electron microscopy of the reaction of solid state carbon and iron was developed.

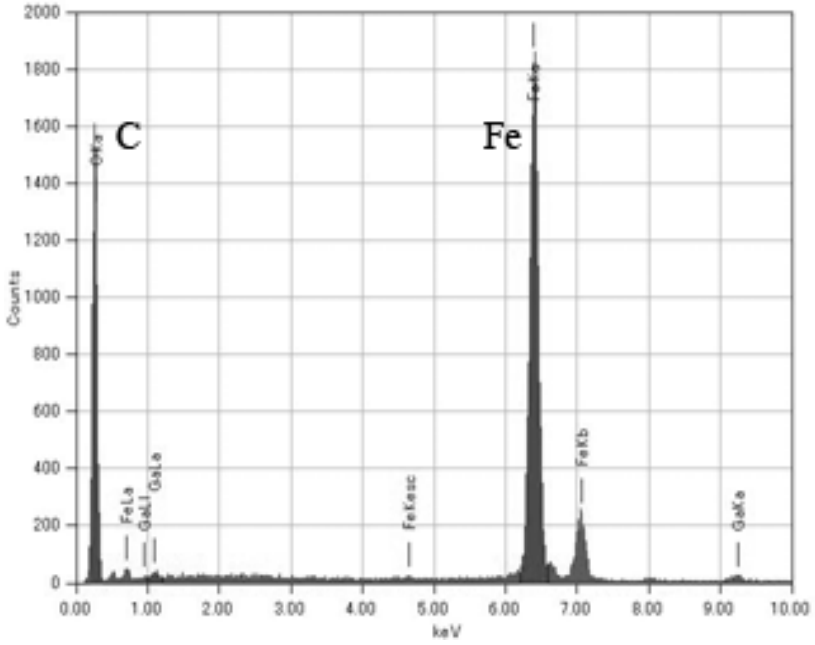

Figure 5. EDS spectrum in the precipitates induced by iron and carbon.

5 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 beyond the 773K and growth rate was 100-200nm at the 873K.
(4) The concentration of the iron in the precipitates decreased with the distance from the boundary.
(5) The generation of the precipitates occurred not by the carburization but the diffusion of iron atoms into the carbon.

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