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Development of *In situ* Microstructure Observation Technique in Steel

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Abstract

In situ observation of microstructure change at high temperature is valuable technique to investigate the phase transformation, grain growth, and precipitation phenomenon in steels. Although scanning and transmission electron microscopes are utilized for the in situ observation, these techniques have some serious problems represented by a surface diffusion effect and a thin foil effect. A new technology based on the focused ion beam system has been developed to overcome these subjects. A bulk microstructure required was newly obtained at high temperature by the FIB fabrication, and the microstructure changes with annealing were observed, in which a considerable surface artificial effect seems to be decreased. Using this technique, the intra-granular ferrite transformation process has been investigated, resulting in a strong proof supporting the Mn depletion effect model for the transformation.

1. Introduction

The metallographic microstructure of steels is controlled by heat treatments and rolling process taking advantage of various metallurgical phenomena such as recrystallization, phase transformation and precipitation; most of these phenomena occur at high temperatures. If it is possible to observe the changes of the metallographic microstructure at high temperatures dynamically as they take place, successively to identify, for example, from which point a phase transformation starts, or what hinders the migration of a grain boundary, then one will have a better chance not only of validating proposed models but also of finding new governing factors of such metallurgical phenomena.

Conventionally, the *in situ* observation of the microstructure of steel at high temperatures has been done, in most cases, employing either a scanning or transmission electron microscope equipped with a heating stage[1,2]. However, there have been intrinsic problems with both methods: in the case of the scanning electron microscope, the size of a sample is often too large to heat to a high temperature more than 1,073K, and also it is difficult to eliminate various surface effects originated from a surface diffusion of a sample. In the case of the transmission electron microscope, on the other hand, a sample observed is as thin as 0.2 μm in thickness, so the very phenomenon observed is inevitably a thin-foil phenomenon, which is represented by an appearance of the lower transformation temperature than the bulk one. Owing to these difficulties, no significant technical innovations have taken place in the field of the high-temperature, *in situ* observation of the microstructure changes in steels.

In view of the above, attention was directed by the authors to the micro machining technique that employed a focused ion beam (hereinafter abbreviated as FIB)[3], the use of which rapidly expanded in the material science filed over the last few years. In combination with a heating stage for the FIB, the approach would make it possible to identify such surface effects, which had been difficult to distinguish by conventional techniques. This finding pointed to the viability of a new technique for observing the microstructure of steel *in situ* at high temperatures. Applying the technique, success was achieved by the authors in directly observing the pinning event of a crystal grain boundary by a precipitate and also the dynamic observations for an intra-granular ferrite transformation from an austenite

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phase, triggered by a precipitate that served as a starting point of the transformation. The intra-granular ferrite transformation phenomenon was utilized as one of the means to refine the microstructure of a heat affected zone in a material portion such as a welded joint. In addition, through the observation of the intra-granular ferrite transformation and comparison of observation conditions, it was obtained that the change in the Mn concentration at the interface between a precipitate and an austenite matrix was involved in the transformation as an important governing factor. This paper reports examples of these observations and findings.

2. Establishment of *In situ* Microstructure Observation Technique for Steel Applying FIB Technology

Since the FIB technology is discussed in a separate paper in the present special issue, this section outlines a special heating stage for the *in situ* observation.

In order to heat a sample up to 1,400°C, a sample is machined to a size of 1 mm × 3 mm × 0.1 mm and placed between two spiral heaters of ceramics. For the observation and fabrication of the sample in the FIB at a high temperature, there is a hole approximately 1 mm in diameter at the center of the upper heater. The sample was heated by electrothermal heating, and its temperature was measured with a thermocouple attached to it. **Photo 1** is a photograph of the tip portion of a heating stage, and **Fig. 1** is a schematic illustration of the mounting of a sample on the stage. The heating stage can be used in an FIB and also a transmission electron microscope if the sample is sufficiently thinned.

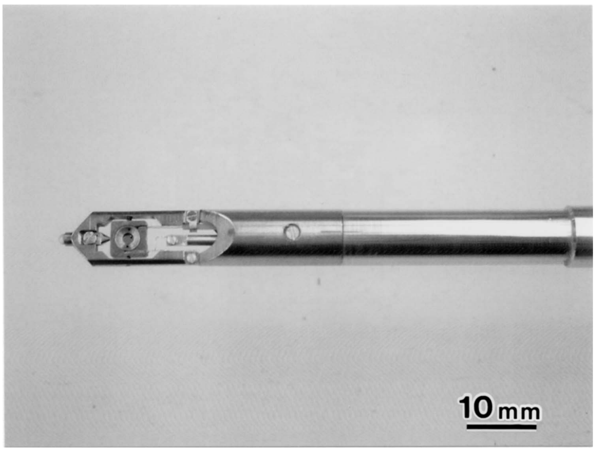

Photo 1 Top view of a heating stage developed for FIB observation

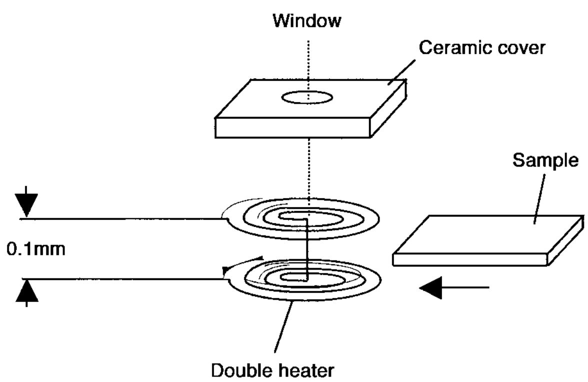

Fig. 1 Schematic illustration showing a sample mounting procedure at heating stage

For clarifying the temperature characteristics of the heating stage, the temperature of the heater was measured with a radiation thermometer at different heater current values from 0.2 to 0.6 A, with and without a sample therebetween. Further, for the purpose of defining the relationship between the heater temperature and the sample temperature, the austenite transformation start (As) and its finish (Af) temperatures of a carbon steel sample were determined through a thermal expansion measurement, then the reverse transformation of the sample from ferrite to austenite was observed using the present heating stage in FIB, and the current values of the heater at the As and Af points of the transformation were measured.

Fig. 2 shows an example of scanning ion microscope observation of the reverse transformation, before and after. The white lines near the upper and left ends of the micrographs are marking lines engraved by the FIB machining to help observe the same position. Part (a) of Fig. 2 shows a ferritic structure at room temperature, and part (b) the same position after heating to 900°C; it is clearly seen here that a reverse transformation into austenite occurred and crystal grains coarsened. As a result, there was only a relative temperature difference of approximately 20°C between the measurements with the radiation thermometer and the thermocouple, and the gradients of the calibration curves of the two measurements were substantially the same. A Ga ion beam having an acceleration voltage of 30 kV, a current density of approximately 0.14 A/mm^2 and a diameter approximately of 60 nm was used for the observation.

With regard to the coarsening of crystal grains as a consequence to the reverse transformation as seen in Fig. 2, if there is a precipitate or the like in the path of the grain boundary migration during the grain coarsening, the grain boundary motion is pinned there. This has long been known and the force and other characteristics of the pinning have been calculated, but its actual occurrence has scarcely been observed by *in situ*. **Fig. 3** shows a series of *in situ* observation of the pinning of a grain boundary by a precipitate of an Fe-O system that was intentionally introduced into a steel sample. The temperature was approximately 1,100°C. The processes in which a grain boundary that had been pinned by the precipitate shifted and then broke away from it are seen clearly in parts (a) to (c) of Fig. 3. It is possible to approximate the pinning force of a precipitate from the spread angle of the grain boundary.

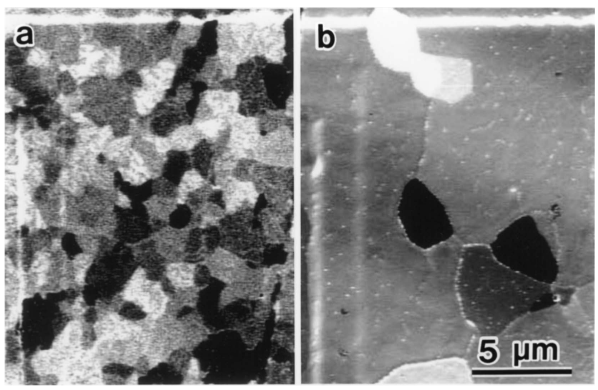

Fig. 2 Scanning ion micrographs showing a change of microstructure during a reverse transformation from ferrite to austenite (a) Ferrite at room temperature, (b) Austenite at 900°C.

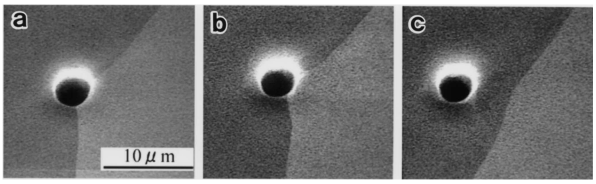

Fig. 3 *In situ* observation at 1,100°C of a grain boundary pinning motion by a precipitate in steel
(a) Pinning of grain boundary, (b) Further pinned by the precipitate, (c) The grain boundary broke away from the pinning precipitate.

3. Application of *In situ* Observation to Intra-granular Transformation

3.1 Technical background

The intra-granular ferrite transformation of steel means the phase transformation from austenite (γ), which is a high-temperature phase, into ferrite (α), wherein non-metallic inclusions and/or precipitates dispersed within austenite grains serve as the starting points. Usually, the transformation from austenite into ferrite starts from an austenite grain boundary or the pre-eutectoid ferrite grain forming at the grain boundary. It is possible to make many ferrite grains with different crystal orientations from each other form within an austenite grain by introducing a great number of particles that serve as transformation starting points into the inside of an austenite grain, and by so doing, a fine microstructure in ferrite is obtained after the transformation. This is the technology that Nippon Steel has often used for purposes such as the refining of the solidification structure of welded joints[4,5].

The mechanism of the intra-granular ferrite transformation is studied principally from the following three viewpoints: firstly, the good lattice coherency between the non-metallic inclusions and the transformed ferrite, then the interface serves as the starting point of the transformation; secondly, the local strain during cooling due to the difference in the coefficients of thermal expansion between austenite and the non-metallic inclusions and/or precipitates; and finally, the formation of Mn-depleted portions that is expected to take place near the interface with MnS precipitates, a typical kind of precipitate in steel.

With respect to the effect of the formation of Mn-depleted zone, Nippon Steel has measured the distribution of the Mn concentration near MnS precipitates employing a focused ion beam method and transmission electron microscopy, and clarified that the formation of the Mn-depleted portions has a significant role in the intra-granular ferrite transformation[6]. At present, it is considered that all the above three factors have influence on the intra-granular ferrite transformation. However, it is important to clarify which of them is the most dominant.

3.2 Test method

A steel having the chemical composition shown in **Table 1** was machined into the size specified in section 2 and used as the samples for heating and *in situ* observation. Each of the samples was mounted on a heating stage, subjected to one of the two heating patterns shown in **Fig. 4** in a FIB, and observed with a scanning ion microscope. In the case of the heating pattern of part (a) of Fig. 4, a non-metallic inclusion appearing at a surface of a sample was spotted beforehand at room temperature, the sample was heated to 1,400°C, held at the temperature for 60 s, cooled to 1,100°C, held there for 30 s, then cooled to 600°C, and the phase transformation around the non-metallic inclusion was observed. The holding at 1,100°C was curried out because of the growth of MnS precipitates and the Mn-depleted portions formed as a result of the diffusion and precipitation of Mn into MnS in ferrite.

Table 1 Chemical composition of samples used for *in situ* observation of intragranular ferrite transformation

(mass%, *ppm)

C	Si	Mn	S	Al	Ti	N
0.08	0.2	1.47	40*	0.03	0.01	40*

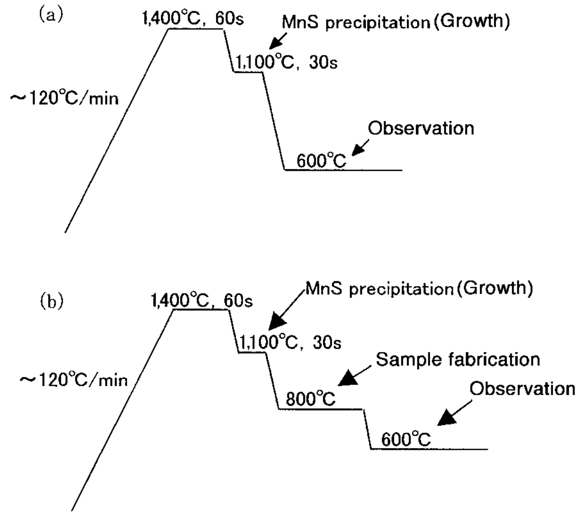

Fig. 4 Heating patterns for observing intra-granular ferrite transformation.
(a) Conventional heating pattern, (b) heating pattern with sample fabrication step by FIB.

In the case of the heating pattern of part (b) of Fig. 4, on the other hand, a sample was held at 1,100°C for 30 s, cooled to 800°C, a little higher than the transformation temperature, tilted by 45° and machined at an end at the temperature until a non-metallic inclusion appeared at the machined surface, cooled to 600°C, and the transformation around the inclusion that had been brought to the surface at 800°C was observed.

3.3 Results and discussion

In the case of the heating pattern of Fig. 4 (a) where a non-metallic inclusion appearing at a surface of a sample was spotted at room temperature, then the sample was subjected to the heating pattern of part (a) of Fig. 4, and the transformation around the non-metallic inclusion was observed at 600°C, what was seen was not the intra-granular ferrite transformation but only the grain-boundary ferrite transformation starting from austenitic grain boundaries, as shown in **Fig. 5**. The time (s) at the bottom of each of the micrographs indicates the holding time after setting the heater current at the value corresponding to a sample temperature of 600°C. During the process from part (b) to part (c) of Fig. 5, the ferrite phase having developed from a grain boundary was not pinned despite the presence of the precipitate, but the phase continued to develop swallowing it. Note that because the crystal orientations of the original austenite and the product ferrite phases are different, the two phases appear in a clearly distinguishable contrast in the scanning ion micrograph. Since the contrast results from the difference in the amounts of sec-

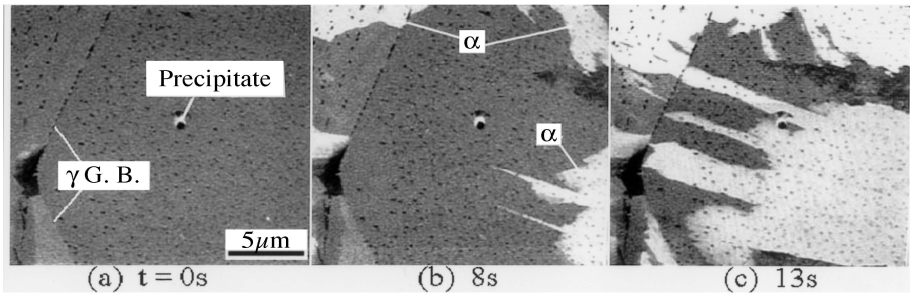

Fig. 5 ***In situ*** **observation of ferrite transformation in condition of heating pattern (a). The ferrite transformation occurred at a grain boundary.**

ondary electrons, which are emitted depending on the angle between the incident Ga ion beam and the orientation of a steel crystal grain, different ferrite crystals show different hues depending on their crystal orientations.

On the other hand, in the case of the samples that were subjected to the heating pattern and the high-temperature fabrication shown in part (b) of Fig. 4, the authors observed the area around the precipitate brought to the surface by the machining of an end of a sample at 800°C, and as a result, succeeded in observing the phase transformation starting from a precipitate, namely the intra-granular ferrite transformation, *in situ* as shown in **Fig. 6**. That is to say, the precipitate that had been dug out from the bulk of the sample to the surface served as a starting point of the phase transformation. It took approximately 20 min to machine the end of the sample at 800°C until a precipitate was brought to the machined surface. The time (s) at the bottom of each of the micrographs indicates the holding time after setting the heater current at the value corresponding to a sample temperature of 600°C; one can see from the indications that the intra-granular ferrite transformation began after elapsing approximately 10 s.

Observations were repeated several times under each of the above conditions. As a result, whereas the intra-granular ferrite transformation was not observed with the samples in which a precipitate appearing at the surface of a sample was spotted before the heat treatment. In contrast, the occurrence of the austenite-to-ferrite transformation around the precipitate was observed, that is, the intra-granular ferrite transformation was observed, with a probability of 75 to 80%, with the samples in which a precipitate was brought to a surface through the machining at 800°C on the heating stage of FIB. It must be pointed out here that an elementary analysis for the precipitate brought to the surface was not performed under the FIB fabrication, resulting in not confirmation of the composition of the precipitate, where is really consisted of MnS. In fact, what the authors did at the observations was to select the precipitates based on the empirical knowledge about the shape of the precipitates that could serve as the starting points of the intra-granular transformation. Judging from the fact that the intra-granular ferrite transformation was reproduced with a probability of 75 to 80%, the authors believe that the following conclusion can be drawn: the occurrence of the intra-granular transformation starting from a precipitate depends on whether the precipitate is at a sample surface when the temperature is 800°C or higher, or it was buried in the bulk of the sample before it is brought to a surface.

Now, let us consider the behavior of MnS at high temperatures.

MnS is considered to dissolve in steel partially according to its solubility product during reheating in the austenitic zone and precipitate during subsequent cooling. Aihara et al. have analyzed the equations of the diffusion of Mn and S at high temperatures in a system having the same chemical composition as that of the samples of the authors' tests, and calculated the Mn concentration near the interface of MnS precipitates; the results are reported in a separate paper in this special issue. According to the paper, when the steel temperature is 1,250°C, the calculated fall in the Mn concentration near the interface becomes the largest, approximately 0.1 mass %, after holding for roughly 50 s, but when the steel is held at the temperature for a longer time period, the fall in the Mn concentration decreases; on the other hand, when the steel is held at 1,100°C for roughly 100 s, the fall in the Mn concentration near the interface increases to approximately 0.3 mass % at the maximum.

Their calculation results indicate, further, that at 1,100°C the Mn-depleted portions do not disappear quickly after a longer holding time: even after a holding time of 1,000 s, the fall in the Mn concen-

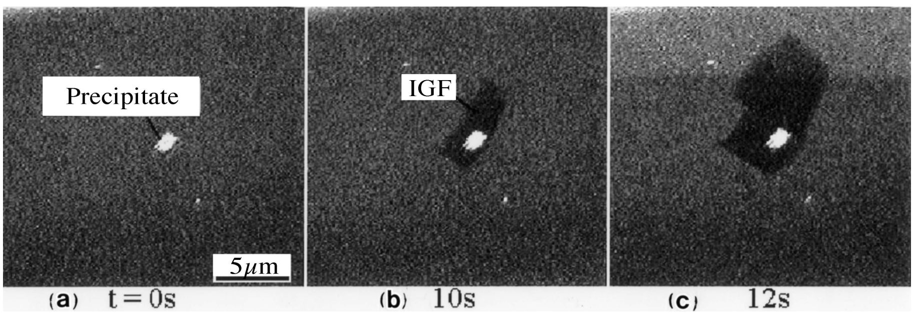

Fig. 6 ***In situ*** **observation of ferrite transformation in condition of heating pattern (b). The ferrite transformation occurred at a precipitate.**

tration is still approximately 0.2 mass %, although the very Mn-depleted portions near the interface decrease in volume. This means that, under the condition of the *in situ* observation of the authors, wherein the samples were cooled from 1,400 to 1,100°C and held there for 30 s, portions having a sufficiently low Mn concentration are expected to form near the interface with MnS precipitates. At 800°C or lower, on the other hand, the diffusion rate of Mn in steel is so low that the FIB fabrication at 800°C for 20 min does not exert any substantial influence on the formation of the Mn-depleted portions.

Reorganizing the results of the authors' tests in the light of the above, one can conclude that, since the condition of the local strain at the interface of a precipitate appearing at a surface is presumed to be the same as that of a precipitate at the inside, there is no difference in local strain energy between a precipitate appearing at a surface from the beginning and a one dug out to a surface from inside. There is no difference, either, in the lattice matching of the interface between a precipitate and ferrite whether the precipitate appears at a surface from the beginning or it is dug out to a surface as in the authors' tests. The only conclusion that can be drawn from the above is that the remarkable difference in the transformation behavior seen in Figs. 5 and 6 is attributable to some governing factor resulting from surface effects. The results of the authors' *in situ* observation indicate that, among the governing factors of the intra-granular ferrite transformation, the only one influenced by the surface diffusion of Mn and S at high temperatures is the formability of the Mn-depleted portions near the interface with a precipitate, and that this is one of the governing factors of the intra-granular transformation.

4. Closing

By applying the focused ion beam fabrication technique at high temperatures, the adverse influences of surface effects to understand the phenomenon have been successfully avoided. Instead of the conventional *in situ* observation with a scanning or transmission electron microscope, the scanning ion microscope equipped with the FIB becomes a useful technique in the field of material science. In addition, the authors obtained observation results indicating that intra-granular ferrite transformation was strongly influenced by the surface diffusion phenomenon, and therefore, the existence of the Mn-depleted portions near the interface with a precipitate is one of the principal governing factors of the intra-granular ferrite transformation.

The establishment of the *in situ* microstructure observation technique is meaningful in two aspects. One is the technological impact of the fact that it enables the *in situ* microstructure observation of bulk materials at high temperatures, which was considered impossible by conventional techniques, and makes it possible to clarify the governing factors of high-temperature phenomena by actually "seeing" them. The other is the fact that the use of a Ga ion beam makes it possible to work even a hard material such as steel into a desired shape at a high temperature of 800°C or so. Although Ga is liquid at room temperature, a beam of ionized Ga causes sputtering at the surface of a sample at high temperatures as well as at room temperature, and thus a sample can be machined as desired.

Finally, what requires consideration in the high-temperature, *in situ* observation of the microstructure of steel is the behavior of Ga ions at high temperatures. It has been known that the penetration depth of Ga ions at the surface of a sample is different at room temperature and 700°C or above[7]. Luckily, this did not adversely affect the observation of intra-granular ferrite transformation. However, when other phenomena are observed, Ga dissolved in the material of a sample may change the phase transformation temperature and other properties of the sample, and for this reason, it is necessary to continue to further study the details of the sputtering phenomenon by Ga ions at high temperatures.

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