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Pinpoint High Spatial Resolution Analysis Technique for Material Surfaces Using FIB[†]

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Abstract:

Focused ion beam (FIB) is a powerful technique for nano-level analysis on local structures of material surfaces, because it allows us to make a sample of the specific point on sample surfaces. In this paper, the results of cross-sectional analysis of steel surfaces using FIB are presented. It is revealed that the promotion in galvannealing reaction on the thiourea treated P-added steel is due to the formation of fine grain structures in surface region caused by a pinning effect of (Mn, Fe)S particles formed during annealing. It is found that initial alloys formed in the galvanizing processes on Si-added steel have partly peculiar shape and phase. It is suggested that these initial alloys prevent the following galvannealing reaction.

1. Introduction

If the surfaces of steel materials appear homogenous in macroscopic level, inhomogeneties can frequently be seen in the microstructure, morphology, and surface composition with observation at the order of several microns or less. When discussing the relationship between the surface and related properties, an understanding of the actual condition of the surface, including these microscopic inhomogeneities, is necessary. Moreover, although the term "surface" is commonly used in an unqualified sense, it is almost always necessary to consider not only the substances which can be observed on the surface, but also a region of a certain depth, like surface grain structure or internal oxides. Thus, in addition to observation of the surface as such, cross-sectional observation of the surface region is indispensable.

In recent years, there have been numerous cases in which the surface components and morphology are controlled at the microscopic level, extending to thicknesses or sizes of several tens of nanometers or less, heightening the importance of cross-sectional observation and analysis of the surface region using the transmission electron microscope (TEM). However, as mentioned previously, when viewed microscopically, the surface of steel materials is not always homogeneons, and in some cases, observational results will differ greatly depending on what position on the surface is observed. In observation of random positions using TEM, which has a narrow field of view, one "cannot see the forest for the trees." This means that the researcher can proceed with a detailed analysis of the region of interest only after first investigating the surface as a whole at comparatively low magnification.

Methods of preparing samples for cross-sectional observation include mechanical polishing, ion polishing, ultra-microtome, and others. In contrast to these, the most important feature of the focused ion beam (FIB) technique discussed in this paper is its suitability for fabricating and sampling of specific positions on the material surface. This paper briefly explains the method of using the FIB technique in analysis of the steel surfaces and presents examples of its application to analysis of practical materials.

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2. FIB Technique

2.1 FIB Processing for Analysis of Material Surfaces

The FIB technique was originally used as a microfabrication method for analysis of defects in semiconductor devices, but subsequently, application as a TEM sample preparation technique expanded into the field of materials science. JFE Steel uses the FIB technique in analysis of the steel surfaces. Employing FIB, it is possible to make samples for cross-sectional observation of the surface region using the scanning ion microscope (SIM) and scanning electron microscope (SEM) and prepare samples for cross-sectional TEM observation at specific positions of interest on the surface.

When observing cross section of the surface region by SIM or SEM using the FIB technique, microfabrication in box shape is performed. **Photo 1** shows an example of microfabrication for a 45° cross sectional observation. The ion beam is irradiated from the left at a 45° to the surface and, for example, observation is performed from above the sample. Other processing angles are also used in some cases, including processing perpendicular to the surface or at some arbitrary angle, depending on the sample and the purpose of observation.

2.2 Micro-Sampling Method

In cases where spatial resolution is inadequate in SEM observation and observation and analysis of a finer structure or crystal structure analysis by electron diffraction is necessary, analysis is performed by cross-sectional TEM. When TEM samples were prepared by FIB processing using apparatus released in the ealy days, preprocessing prior to FIB processing was necessary in order to reduce the size of the sample to some extent. However, with the development of the micro-sampling method, it is now possible to perform direct sampling from the position of interest by introducing the sample into the device without preprocessing. Because the micro-sampling method has already been explained numerous times,[1)] a detailed explanation will be omitted here, and this report will present only an outline of the processing process, as follows:

(1) A carbon protective layer is deposited on the area of interest (sampling region) by vapor deposition.
(2) The area around the sampling region is removed, leaving one point supporting the sample.
(3) After fixing the manipulator probe to the sample, the sample is cut away from the base material.
(4) The sample taken in this manner is transferred to a TEM sample mesh (3 mmϕ) and mounted.
(5) The sample is finished to a thickness (up to approximately 100 nm) suitable for TEM observation.

3. Examples of Analysis of Steel Materials

3.1 Analysis of Thiourea Treated Steel

As an example of cross-sectional analysis of the surface region of a steel using FIB, this section presents an example of analysis[2,3)] of a high strength steel sheet with a surface modified by thiourea treatment, which was carried out for the purpose of accelerating the galvannealing reaction for a P-added steel substrate.

Photo 2 is a secondary electron image of the surface of a high strength steel sheet which was annealed after coating the surface with thiourea. A fine structure which could not be seen without thiourea treatment was observed in this material[3)]. **Photo 3**(a) shows the microfabrication by FIB performed for cross-sectional observation of the surface region. Photo 3(b) shows an SIM image of the cross section parallel to the rolling direction, which was obtained with the sample shown in Photo 3(a). The SIM image shows that fine grain structure extends to a depth of approximately 1 μm, and the region below this consists of large grains which have

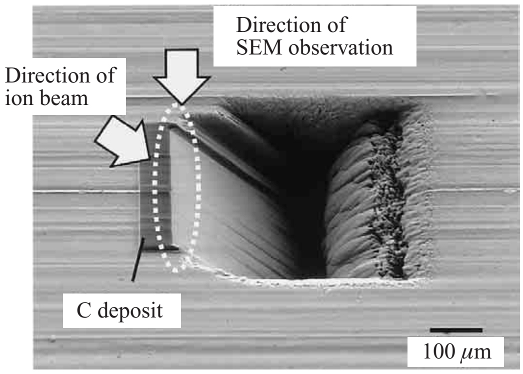

Photo 1 Example of micro-fabrication with FIB for cross sectional observation

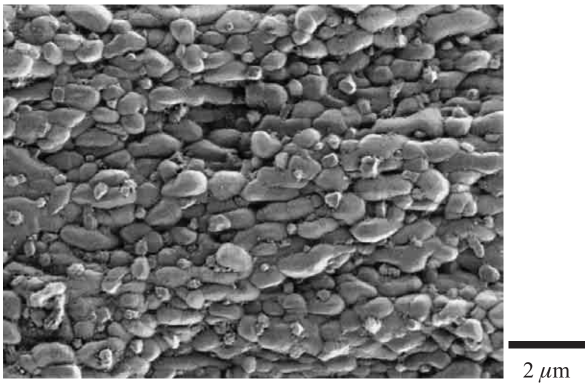

Photo 2 SEM image of surface of thiourea treated steel showing the presence of fine-grain at the surface

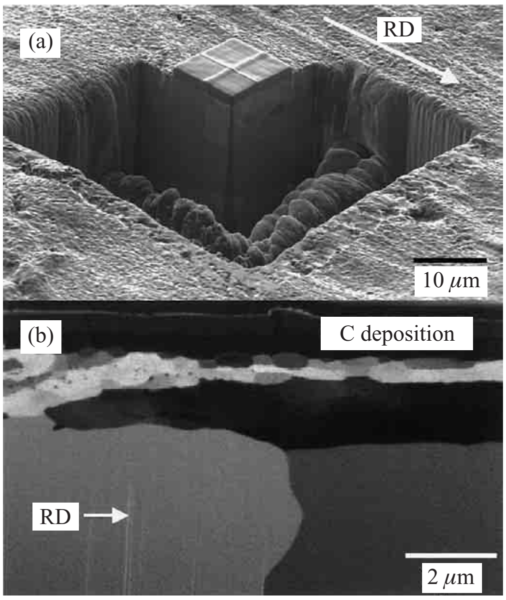

Photo 3 Cross-sectional scanning ion microscopy image of thiourea treated steel[2)] (RD: Rolling direction)

grown by recrystallization during annealing.

After the observation described above, a thin specimen for TEM observation was prepared by micro-sampling method from the same region. The prepared specimen was observed using an FE-TEM (Philips CM20ST-FEG). A TEM image is shown in **Photo 4**. TEM observation revealed a high density of dislocations in the fine grains. In addition, large numbers of fine particles with sizes of $<$100 nm exist at the boundaries of fine grains could be seen. These particles were identified as (Mn, Fe)S by energy dispersive X-ray spectroscopy. From the results of this series of analyses, it is assumed that formation of fine grain structure in the thiourea treated surface was due to the pinning effect of (Mn, Fe)S, which had formed during annealing. It is concluded that this increased diffusion paths of Fe and Zn, thereby accelerating the galvannealing reaction.

3.2 Analysis of Initial Alloys in Galvannealing

This section presents the results[4)] of an investigation of initial alloying behavior which was carried out to elucidate the factors that retard galvannealing reaction of Si-added steel.

After a hot-dip Zn coating was applied to Si-added steel (0.5%Si-1.5%Mn) in a vertical-type coating apparatus, the η-Zn phase was dissolved to remove, and the Fe-Zn initial alloy at the coating/substrate interface was observed. An SEM image of the specimen surface is shown in **Photo 5**. It can be understood that the entire surface is covered with coarse columnar crystals and granular crystals with a size on the order of several micrometers. In contrast to this, when coating was performed under identical conditions using a non-Si-added steel substrate, only the columnar crystals formed, and the granular crystals did not form, demonstrating that the granular crystals which can be seen in Photo 5 are peculiar to Si-added steel.

Using the micro-sampling method, a specimen for cross-sectional TEM observation was prepared so as to include both columnar crystals and granular crystals. **Photo 6**(a) shows the actually-sampled part; Photo 6(b) shows a cross-sectional TEM image. The results of an analysis by TEM revealed that the columnar Fe-Zn alloy crystals are ζ phase and the granular crystals consist of δ_1 phase and Γ_1 phase. The ζ phase melts at the galvannealing temperature, but in contrast, the δ_1 and Γ_1 phases remain as solid phases even at the galvannealing temperature. It is assumed that these phases act as a barrier to the diffusion of Zn and Fe during the galvannealing reaction. This suggests that the galvannealing reaction in Si-added steel is retarded by the formation of particulate δ_1 and Γ_1 phases.

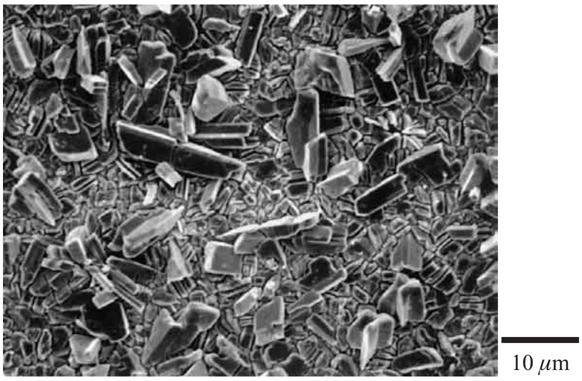

Photo 5 SEM image of initial alloy of Si-added steel

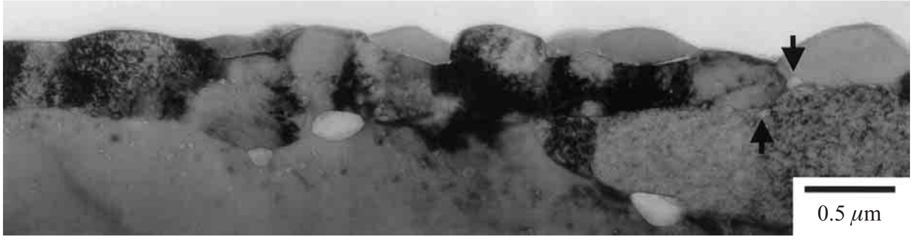

Photo 4 Cross-sectional TEM image of surface of thiourea treated steel showing the presence of fine-grained region at the surface[2)] (Arrows show the fine particles in grain boundaries.)

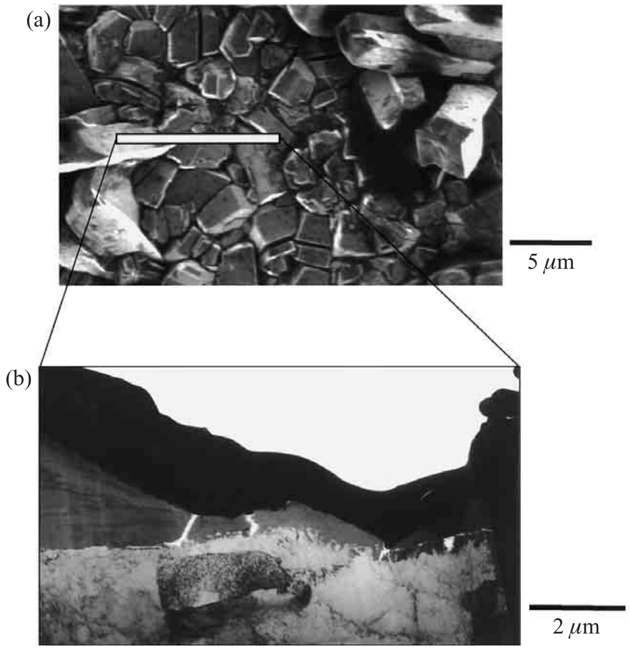

Photo 6 (a) SEM image of initial alloy (White line shows the region for micro-sampling with FIB for TEM observation.) and (b) Cross-sectional TEM image of initial alloys

4. Methods of Using FIB

As described above, the greatest advantage of FIB is the fact that it is possible to perform sampling from any specific region of interest on the material surface. This is an indispensable function for analyses of surfaces with microscopic inhomogeneities, steel materials be a typical example. In this case, how to grasp the actual condition of the surface before processing and select the sampling position is important.

The authors have employed ultra-low voltage SEM in evaluating inhomogeneity of material surfaces[5,6]. SEM observation with the ultra-low accelerating voltage region makes it possible to determine the distribution of substances on the material surface and the microscopic structure of the surface at the order of several 10 nm or less, which is impossible with ordinary accelerating voltages (>10 kV). In particular, ultra-low voltage SEM is effective when the intention is to perform cross-sectional TEM observation of the top-most surface layer is performed, as the surface morphology cannot be grasped adequately with ordinary SEM, making accurate selection of the sampling position difficult. With ultra-low voltage SEM, it is possible to obtain sufficiently detailed information for discussion having a correspondence with high spatial resolution cross-sectional observation by TEM, and as a result, gain a continuous, uninterrupted understanding of the material surface, from an overall sense to its nano-level structure.

Apparatus in which an electron gun for SEM observation is incorporated in an FIB apparatus (and apparatus in which the FIB column is incorporated in an SEM) are released by sevelal makers. The authors believe that apparatus of this type will enable more efficient analysis of the surface regions of the materials introduced in this paper, and these techniques can also be expanded to 3-dimensional analysis.

As discussed above, maximum use of the functions of FIB is possible with methods which closely combine FIB with other observation techniques. From this viewpoint, FIB should be considered not simply as a processing method, but as an integral part of material observation.

5. Conclusion

This report has presented an outline of methods of using the FIB technique in analyses of the surface of steel. The findings in the following two cases were presented as examples of application of FIB to actual material analysis.

(1) In P-added high strength steel, the galvannealing reaction is accelerated by thiourea treatment of the substrate. Cross-sectional observation utilizing FIB revealed that a fine grain structure formed due to the pinning effect of (Mn, Fe)S promote galvannealing reaction.

(2) With an Si-added steel, a pinpoint analysis by the micro-sampling method found that initial alloys with a partly peculiar phase of Zn-Fe alloy formed during hot-dip Zn coating. It was suggested that the presence of these phases, which are high-melting point alloy, prevent the following galvannealing reaction of Si-added steel.

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