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3DAP Analysis on Solute Segregation of Nb and Mo during Primary Recrystallization of α-Fe

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Abstract

Atomic-scale interface segregation behavior of Nb and Mo during different stages of recrystallization of α-Fe was investigated using a three-dimensional atom probe (3D AP). Solute segregation of Nb or Mo was found at cell boundaries and subgrain boundaries in the early stage of recovery and recrystallization, and also at recrystallization interfaces, implying that the retardation of recovery and recrystallization by the addition of Nb or Mo can be caused by solute drag (SD) effect. Atom probe analysis also revealed that stronger solute-interface interaction is the main reason for the larger retardation effect of recrystallization by Nb addition. The comparison of measured solute profiles with calculated solute profiles showed that Cahn's SD model gives a reasonable fit to solute profiles for migrating interfaces.

1. Introduction

It is well known that microalloying elements in steels, contained as impurities or added on purpose, are known to often segregate to lattice defects in materials during manufacturing. Among such defects, grain boundaries and phase interfaces are the typical sites of segregation. The elements segregating at these sites affect the mechanical properties of steels directly through embrittlement or strengthening of grain boundaries, or indirectly through the evolution of microstructure typically by retarding recrystallization, grain growth and phase transformation. It is, therefore, very important to understand solute segregation behavior and the contribution of solutes to the metallurgical phenomena.

When the solute atoms move with the interfaces or lag behind the interfaces, the solutes exert a dragging force. The dragging is often called "solute drag (SD)," and there have been a lot of theoretical and experimental reports on the SD effect[1-8]. However, in spite of a considerable number of investigations, there is still doubt about the actual distribution of solute atoms on migrating interfaces, although it is one of the most important features for evaluating the proposed SD models. This is because experimental techniques for studying solute distributions with sufficient spatial resolution have been lacking.

The three-dimensional atom probe (3DAP) technique[9] is one of the promising methods for the quantification of the atomic scale solute distribution behaviour in the vicinity of interfaces, since it enables quantification of solute distribution in materials with a spatial resolution of a few Angstroms. Moreover, 3DAP has an advantage in that there is no restriction in the analysable elements in materials. In addition to the study of substitutional alloy elements, this technique enables quantification of the local chemistry of light elements such as C, N and B, which play a very important role in the microstructural evolution in steels. The difficulty in bringing the interfaces to the apex region of needle-shaped specimens has long been known as a serious practical problem in applying an atom probe technique to the study of particular interfaces. However, the problem has been largely solved, as will be shown later, by recent application of ion beam milling to the preparation of atom probe specimens.

The main objective of this paper is to quantify the distribution of solute Mo or Nb at recrystallization interfaces in α-Fe, by using the 3DAP. The comparison between measured solute profiles and calculated solute profiles by using Cahn's SD model[2] is also shown.

2. Experimental Procedure

Cylindrical test specimens (8 mm in diameter and 12 mm in length) of Fe and Fe-0.09%Nb and Fe-0.18%Mo alloys (in at%) were

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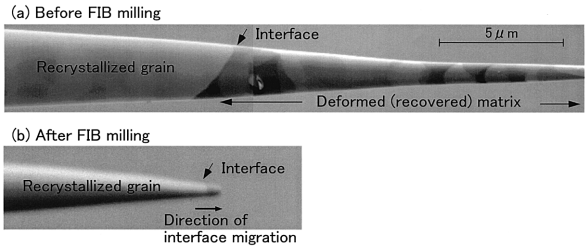

Photo 1 FIB secondary electron images of an atom probe field ion specimen (a) before and (b) after FIB milling. The specimen is Fe-0.09Nb alloys held for 1,000 s at 725°C.

heated to 650, 725 or 800°C, and subsequently hot-compressed at a strain rate of 10 s^{-1} and a reduction ratio of 75%, and held for different periods at the temperatures, and finally gas-quenched to room temperature, in order to prepare various recrystallization stages. Specimens for atom probe were cut out from the center of the compressed specimens, and then polished by a standard two-step electropolishing procedure. The needle-shaped specimens were then inserted into a focused ion beam system and the microstructure was observed. In FIB (focused in beam), interfaces are clearly recognized as boundaries of light and dark contrast, so that we could easily bring the interfaces of interest to the apex of the specimens by using an annular milling pattern[10] (**Photo 1**). The specimens were subsequently inspected by conventional transmission electron microscopy to make sure that they were sufficiently sharp for atom probe analysis and to determine the misorientation of the interfaces by Kikuchi pattern analysis.

3. Atom Probe Results

Fig. 1 shows the change of recrystallization fraction with isothermal holding after hot-compression at 650, 725, and 800°C. As seen in Fig. 1 and **Photo 2**, recrystallization was retarded by the addition of Nb or Mo, with the effect much larger for Nb. During isothermal holding, recovery occurred at first, and then certain crystal grains (recrystallized grains) began to grow preferentially (**Photo 3**), and finally the microstructure was entirely covered with recrystallized grains. Provided that the recrystallization is retarded by the solute dragging by Nb or Mo, solutes accumulation to the recrystallization interfaces (the interfaces between the recrystallized grains and the recovered matrix) or the subgrain boundaries in the matrix should be expected.

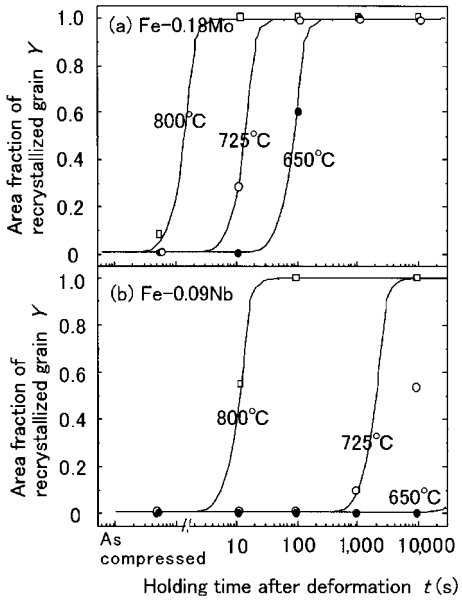

Fig. 1 The change of recrystallization fraction with holding time *t* determined by optical micrographs and the fitted curves.

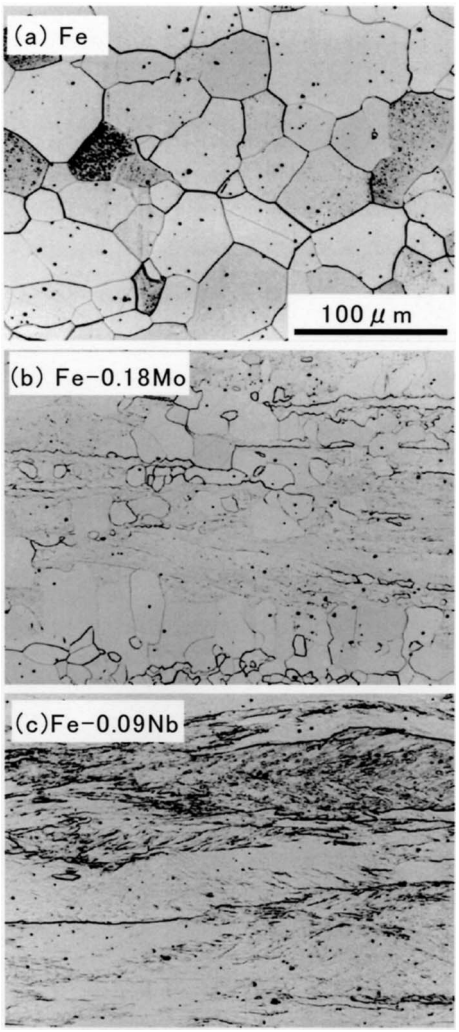

Photo 2 Optical micrographs showing the microstructure after hot compression and holding for 100 s at 725°C in (a) pure Fe, (b) Fe-0.18Mo and (c) Fe-0.09Nb binary alloys.

Fig. 2 shows a ladder diagram and a 3D atom map of Nb across the cell boundary in the Fe-0.09Nb alloy quenched just after hot-compression at 725°C, and across the subgrain boundary in the same specimen held for 100 s[11]. Nb atoms were found to segregate on the cell boundary and on the subgrain boundary, although the segregation on the cell boundary was broad. The Gibbsian interfacial excess of Nb (Γ^{Nb}) on the subgrain boundary was approximately 1.2 [atoms/nm^2]. **Fig. 3** shows a ladder diagram and a concentration profile of Nb across a recrystallization interface with a large-angle misorientaion[11], and **Fig. 4**(a) a concentration profile of Mo across a recrystallization interface. The arrows in the figures indicate the

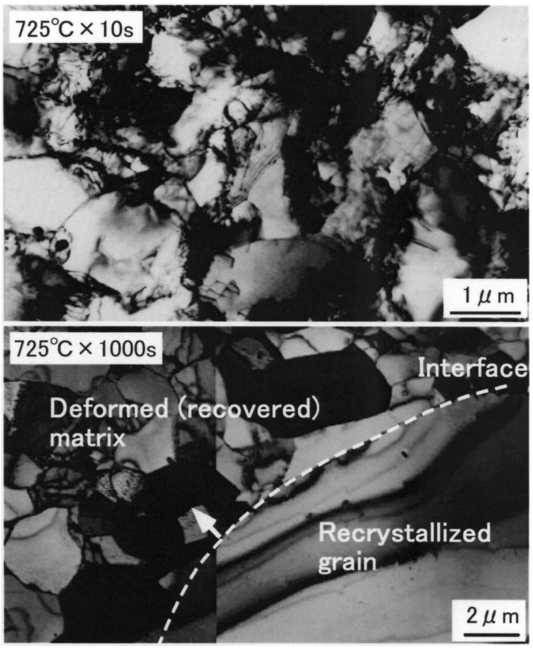

Photo 3 TEM micrographs on the (a) early stage (725°C × 10 s) and (b) later stage (725°C × 1,000 s) of recrystallization in Fe-0.09Nb alloy.

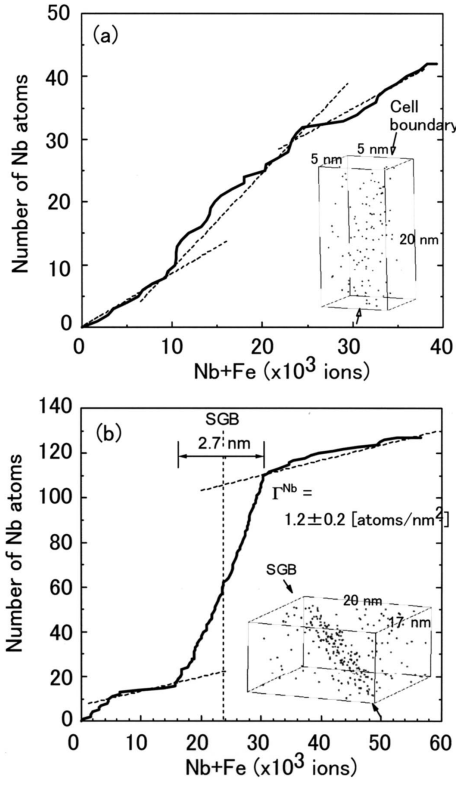

Fig. 2 A ladder diagram across (a) cell boundary in Fe-0.09Nb alloy quenched just after hot-compression at 725°C, and (b) across subgrain boundary with misorientation of 10° in Fe-0.09Nb alloy held for 100 s at 725°C. Inset in the figures shows a 3D atom map of Nb.

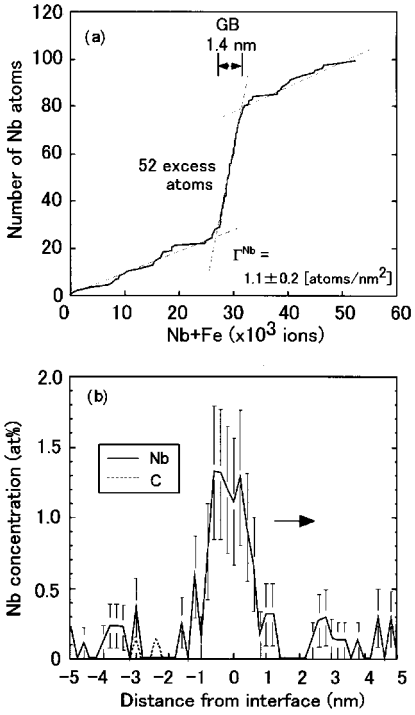

Fig. 3 (a) A ladder diagram of Nb and (b) concentration profiles of Nb and C across recrystallization interface with a misorientation of 10° in the Fe-0.09Nb alloy held for 1,000 s at 725°C, measured by the 3D AP. The error bar in (b) was taken to ± σ for the measured number of solute atoms (only for Nb).

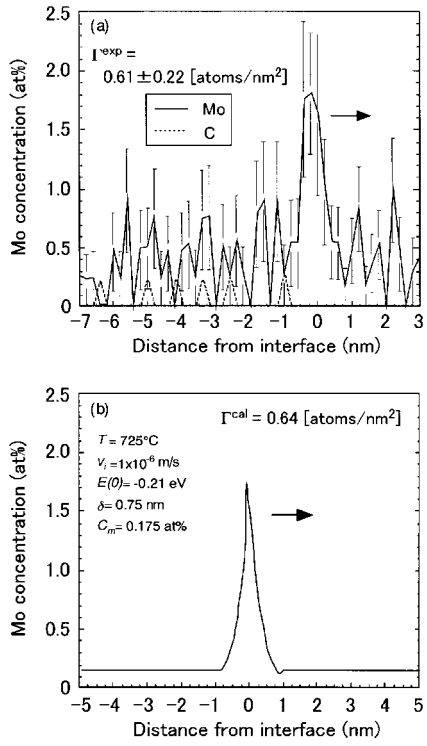

Fig. 4 (a) Measured concentration profiles of Mo and C across recrystallization interface with a misorientation of 13° in Fe-0.18Mo alloy held for 10 s at 725°C, and (b) a concentration profile of Mo calculated from Cahn's solute drag model.

migration direction of the interface, which was judged from the secondary electron images of the specimens before the FIB milling (Photo 1). It looks reasonable to conclude from the 3DAP analysis that the migration of subgrain boundaries during recovery and the recrystallisation interfaces is retarded by solute Nb and Mo which have segregated to the boundaries or interfaces.

The Gibbsian interfacial excess for Nb on the recrystallisation interfaces was larger than that of Mo, and the tendency was the same in fully recrystallized specimens[12]. This indicates that the interaction between Nb and the interfaces is stronger than Mo, and may imply that the stronger retardation effect of recrystallization by Nb is due to the stronger solute-interface interaction. The width of the solute segregation on the interfaces was 1 to 2 nm, which corresponds to several atomic layers of matrix Fe. In the concentration profiles of Figs. 3 and 4, the distribution of C, containing in the steels by approximately 20 at-ppm as an impurity, is also shown. No evidence of C segregation on the interfaces was observed, implying that the retardation effect could be caused by solute Nb or Mo alone without any aids of C.

4. Comparison with Calculated Solute Profile on Cahn's SD Model[11]

Cahn[2] provides an approximate equation for the available total driving pressure P which yields a velocity of migrating interface v_i, as a function of solute-interface interaction energy with a potential $E(x)$, the diffusion coefficient for motion normal to the interface $D(x)$, and the solute concentration C_m in matrix.

$$P = P_{int} + P_{SD} = \frac{v_i}{M_{int}} + \frac{\alpha C_m v_i}{1+\beta^2 v_i^2} \quad (1)$$

where, P_{int} and P_{SD} are the intrinsic driving pressure required for interface migration in a pure material without solutes and the driving pressure required for solute dragging, respectively, and M_{int} is the intrinsic mobility of an interface in a pure material, C_m is the average solute concentration in the matrix, and α and β are parameters of the model, which are given as a function of v_i, $E(x)$ and $D(x)$.

A solute profile at a moving interface is calculated by considering the flux of atoms across the boundary. If the interface moves with a steady velocity v_i, the relationship between $D(x)$, $E(x)$, $C(x)$ and v_i is expressed as

$$D\frac{\partial^2 C}{\partial x^2} + \left[\frac{\partial D}{\partial x} + \frac{D}{kT}\frac{\partial E}{\partial x} + v_i\right]\frac{\partial C}{\partial x} + \frac{1}{kT}\left[\frac{\partial D}{\partial x}\frac{\partial E}{\partial x} + D\frac{\partial^2 E}{\partial x^2}\right]C = 0 \quad (2)$$

By solving this equation, a composition profile of solute across the migrating interface at steady state can be obtained.

Fig. 4(b) shows the concentration profile for Mo at a migrating interface calculated from Cahn's model under the condition of T = 725°C[11]. In our calculation, a wedge-shaped function with a maximum at the plane of the interface and a half width of 0.75 nm was assumed for solute-interface interaction $E(x)$ and solute diffusion coefficient $D(x)$ across the interface. Diffusion coefficients of solute just on the interfaces $D(0)$ were assumed to be 300 times of those in the matrix far away from interfaces. Solute-interface interactions just on the interfaces $E(0)$ were determined from the amount of segregation at grain boundaries in the well-annealed specimens; –0.32 eV for Nb and –0.21 eV for Mo. Migration velocity of interfaces was estimated from the change of a fraction of recrystallized grains vs. annealing time, based on the Avrami equation assuming site-saturated nucleation[12]. Solute diffusion coefficients for Nb and Mo in α-Fe, and intrinsic mobility of pure α-Fe were taken from ref. (13) and ref. (12), respectively.

As shown in Fig. 4(b), the calculated solute profile shows a reasonable agreement with the 3DAP measurement (Fig. 4(a)) with respect to any of the maximum concentration, the width of segregation and the calculated Mo-excess (Γ^{Mo}). A similar result was obtained for Nb. Thus, it may be concluded that the segregation behavior of solutes on migrating interfaces is reasonably represented by Cahn's SD model. One may expect a depression of solute in front of the migrating interface, but the expected small depression is unfortunately within the statistical error of this 3DAP measurement. The collection of more extensive data with minimized analytical artifacts[14] at several different conditions, and the discussion of the solute segregation behavior including small spike in the vicinity of the migrating interfaces would be a subject of further study.

5. Summary

Atomic-scale interface segregation behavior of Nb and Mo during different stages of recrystallization of α-Fe has been investigated for the first time by a 3DAP with the aid of FIB milling for the preparation of needle-shaped specimens with interfaces of interest. The investigation revealed that recrystallization is retarded by the SD effect of Nb or Mo, and that the stronger retardation of recrystallization by Nb than Mo is due to the strong solute-interface interaction. The comparison of measured solute profiles at migrating recrystallisation interfaces with calculated solute profiles show that Cahn's solute drag model gives a reasonable fit to solute profiles for migrating interfaces, although further study is necessary. Since it is possible to discuss the solute distribution in the vicinity of interfaces of an interest at the atomic level with links to crystallographic information of the interface, 3DAP is a valuable tool for the interface segregation study.

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