Ultramicroscopy ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Observation of co-segregation of titanium and boron at the interface between recrystallized and unrecrystallized grains in cold-rolled interstitial-free steel sheets

J. Takahashi *, J. Haga, K. Kawakami, K. Ushioda

Advanced Technology Research Laboratories, Nippon Steel & Sumitomo Metal Corporation, 20-1 Shintomi, Futtsu-city, Chiba 293-8511, Japan

ARTICLE INFO

Article history:
Received 27 August 2014
Received in revised form
17 February 2015
Accepted 14 March 2015

Keywords:
Atom probe
Interface
Grain boundary
Segregation
Boron
Titanium
Solute drag

ABSTRACT

It has been reported that the addition of ppm levels of B strongly retarded the growth of recrystallized grain into unrecrystallized grains in the process of cold-rolling and annealing of Ti-added interstitial-free (IF) ferritic steels. This phenomenon was explained by solute drag effect based on the assumption that, during annealing, B atoms segregate at the interface between recrystallized and unrecrystallized grains where they interact with Ti atoms. To verify this, atom probe tomography analysis of the interface was performed in Ti-added IF steels with and without B addition. Needle tips containing the interface identified from electron backscattering diffraction analysis, were produced by focused ion beam milling with the lift-out method. To increase the experiment reliability, the misorientation angle of the aimed interface was compared with that estimated by field ion microscopy analysis. Considerable amount of Ti segregation was observed at the interface in the steel without B addition, which increased with increasing amount of B segregation in the steel with B addition. The results suggest that the retardation of the interface migration was caused by solute drag effect based on the simultaneous co-segregation of Ti and B due to their attractive interaction.

1. Introduction

The addition of ppm levels of B produces various influences on microstructure and mechanical property in steel. One of the influences is that the segregation of B atoms at the grain boundary prevents ferrite grain nucleation caused by the decrease in the interfacial energy of austenite grain boundaries [1]. Another influence is that the segregation of B atoms at the grain boundary decreases the ductile-to-brittle transition temperature (DBTT) by strengthening the grain boundary [2,3]. These phenomena are solely an effect of B at the grain boundary. The multiple effect of B addition with other elements has been also investigated. Haga et al. reported that B addition of several mass ppm significantly retarded the growth of recrystallized grains in the presence of solute Ti in Ti-added interstitial-free (IF) ultra low C steels [4,5]. They proposed a hypothesis that, during the recrystallization process, B atoms segregating at the interface between recrystallized and unrecrystallized grains attractively interact with solute Ti atoms [5,6].

In steels, the interaction between interstitial and substitutional solute atoms plays a major role in the formation of microstructures and the appearance of mechanical properties. Atomic scale analysis techniques were required to observe them directly. Atom probe tomography (APT) is a powerful tool to observe segregation at the grain boundary, since it enables observation of every element with sufficiently low detection limit [7,8]. For the observation, it is necessary to fabricate the needle specimen tip containing the aimed grain boundary in the apex. Furthermore, it is essential to characterize the boundary from a crystallographic viewpoint, since the segregation state strongly depends on the crystallographic character of the boundary [9,10].

In this study, quantitative APT analysis of the interface between recrystallized and unrecrystallized grains was performed in Ti-added IF steels with and without B addition in order to verify the hypothesis proposed by Haga et al. [5,6]. The interface was identified and characterized from electron backscatter diffraction (EBSD) analysis and field ion microscopy (FIM) analysis, and needle tips containing the aimed interface were produced by focused ion beam (FIB) milling with lift-out method. The interaction between segregating elements at the interface is discussed in terms

* Corresponding author.
E-mail address: takahashi.3ct.jun@jp.nssmc.com (J. Takahashi).

http://dx.doi.org/10.1016/j.ultramic.2015.03.019
0304-3991/

of the influence on the interface migration.

2. Materials

In this study, Ti-added IF ferritic steels containing B ranging from 1 to 14 mass ppm were used. Table 1 presents the chemical composition of the steels. The 1B steel is the reference without B addition, where 1 mass ppm B existed as an unintentional residual impurity. The 20 mm-thick slabs were reheated at 1240 °C for 30 min and hot-rolled to 5 mm-thick bands, where finishing temperature was above 920 °C. The hot bands were immediately cooled to 700 °C by water spray and kept for 30 min, then slowly cooled at a rate of 20 °C/h to simulate coiling. In the coiling process, C and N were scavenged completely by Ti, which was confirmed by the aging index test [6]. Based on the hypothesis that Ti precipitates as Ti(C, N) and TiS, the content of solute Ti (sol.Ti) was estimated to be approximately 0.03 mass% for these steels. After removing scale by machining, the 4 mm-thick hot bands were cold-rolled to 0.8 mm thickness with 80% reduction. The isothermal annealing was conducted in salt bath at 650 °C.

Fig. 1 shows the evolution in Rockwell superficial hardness as a function of annealing time in cold-rolled steels. Gradual decrease in hardness indicates the progress of recovery, while rapid decrease indicates the progress of recrystallization. It revealed that the addition of small amounts of B considerably retarded recrystallization, as reported by Haga et al. [4–6]. Both the apparent recrystallization start (R_s) and the finish (R_f) were delayed by B addition. The delay of R_s, i.e., the increase in incubation period for the nucleation of recrystallized grains suggested that the nucleation rate of recrystallized grains decreased by B addition. The delay of R_f indicates that the growth of recrystallized grains was also retarded by B addition [5,6]. Haga et al. considered that such a significant retardation of the growth of recrystallzated grains was not caused by the solute drag effect of B atoms because B diffuses too fast to retard the interface migration at high temperature. Therefore, they proposed the hypothesis that B atoms segregating at the interface attractively interacts with solute Ti atoms, causing the segregation of Ti at the interface, and Ti atoms retards the interface migration by solute drag effect. If the hypothesis is true, Ti and B atoms are expected to co-segregate at the moving interface. Note that co-segregation is not the simultaneous segregation of the two elements, but it is the subsequent segregation due to an attractive interaction between the two elements.

For APT analysis, the steels in the early stage of recrystallization with a recrystallized fraction of 0.05–0.35 were used, since recrystallized grains in these materials are not considered to impinge each other to any significant degree. The 1B steel annealed for 4 min (1B-4 min) without B addition, and the 14B steels annealed for 60 min (14B-60 min) and 120 min (14B-120 min) with B addition were used, which were represented by the arrows in the Fig.1.

Fig. 2 shows EBSD orientation maps observed from the transverse direction in 1B-4 min, 14B-60 min, and 14B-120 min steels, where solid lines indicate large angle boundaries with misorientation of more than 15°. The depth position corresponding to 1/4 of the sheet thickness (0.8 mm) was observed on the lightly etched sectional surface of the steel sheets. Recrystallized grains can be identified as the area with homogeneous contrast, while unrecrystallized grains have inhomogeneous contrast. This is because unrecrystallized grains contain large strains and local crystal rotations even if recovery proceeded. Conversely, recrystallized grains hardly have such strains and local crystal rotations, resulting in homogeneous contrast. Note that most of the interfaces between recrystallized and unrecrystallized grains are large angle boundaries because the high angle interfaces can migrate. Sub-boundaries formed by recovery were also observed in unrecrystallized grains, but most of the sub-boundaries were small angle boundaries with misorientation of less than 15°, except for the region in the vicinity of prior hot band grain boundaries.

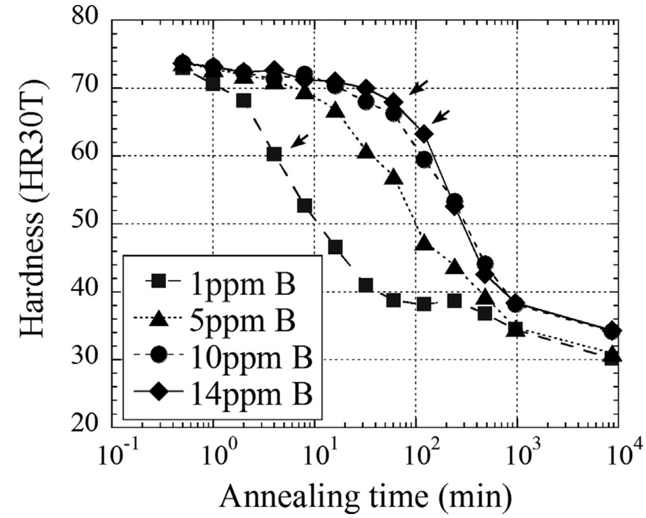

Fig. 1. Evolution in Rockwell superficial hardness with time during isothermal annealing at 650 °C in cold-rolled Ti-added IF steels with various B contents.

3. Reliable needle tip preparation for the recrystallized/unrecrystallized interface

3.1. Needle tip fabrication

We employed a FIB (FB2000A, Hitachi) for fabricating needle specimen tips. Gallium ion beams accelerated with 30 kV were used for milling materials. Scanning ion microscopy (SIM) was used for observing microstructures of the materials. We also employed a transmission electron microscope (H8000, Hitachi) for observing the boundary position in the needle specimen tip.

The steels have several types of boundaries (Fig. 2); sub-boundaries within unrecrystallized grains, grain boundaries between unrecrystallized grains, grain boundaries between recrystallized grains, and interfaces between recrystallized and unrecrystallized grains. Therefore, needle tip fabrication through

Table 1
Chemical compositions of the sample steels used, together with the expected content of solute Ti (sol. Ti*), which was estimated by the inserted formula.

Steel	C	Si	Mn	P	S	Al	N	Ti	B	sol.Ti* (mass%)
1B	0.0023	< 0.01	0.10	0.008	0.005	0.039	0.0017	0.052	0.0001	0.029
5B	0.0018	< 0.01	0.10	0.011	0.005	0.033	0.0018	0.050	0.0005	0.029
10B	0.0019	< 0.01	0.10	0.009	0.005	0.032	0.0016	0.050	0.0010	0.029
14B	0.0018	< 0.01	0.10	0.010	0.005	0.033	0.0014	0.051	0.0014	0.032

sol.Ti* = Ti - (48/14N + 48/32S + 48/12C).

Please cite this article as: J. Takahashi, et al., Observation of co-segregation of titanium and boron at the interface between recrystallized and unrecrystallized grains in cold-rolled..., Ultramicroscopy (2015), http://dx.doi.org/10.1016/j.ultramic.2015.03.019