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Three-dimensional atom probe analysis of boron segregation at austenite grain boundary in a low carbon steel - Effects of boundary misorientation and quenching temperature

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ABSTRACT

Segregation of boron at random austenite grain boundaries with known misorientation angle in a boron-added low carbon steel quenched from austenite state at different temperatures was investigated quantitatively using three-dimensional atom probe. Boron segregation is reduced at low angle boundaries or low quenching temperatures. The latter result indicates that non-equilibrium boron segregation plays an important role and is enhanced at higher quenching temperature due to more excess vacancies and longer diffusion distance during quenching from higher temperature.

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Addition of small amount of boron (B) can significantly improve hardenability of steels and are widely used in the production of high strength thick steel plates having martensite or bainite structures [1]. It has been considered that segregation of B atoms at austenite grain boundary lowers austenite grain boundary energy and delays nucleation of ferrite at austenite grain boundary [2]. Therefore, understanding of B segregation at austenite grain boundary is a key issue in microstructure control by B addition.

B segregation at austenite grain boundaries has been investigated extensively using secondary ion mass spectroscopy (SIMS), one dimensional atom probe tomography (APT) and alpha-particle track etching (ATE) [3–6]. Those studies have revealed that B segregation depends on a temperature before cooling, a cooling rate and other alloying elements and also influenced by precipitation of borides. One peculiar behavior of B segregation detected by ATE is a reduction of B segregation after cooling from lower temperature [6]. This temperature dependency, inconsistent with equilibrium segregation predicted by the McLean model, was understood in terms of non-equilibrium segregation where annihilation of excess vacancies at austenite grain boundaries induces a vacancy-B complex flow toward grain boundaries and results in accumulation of B atoms at grain boundaries [7]. However, spatial resolution of ATE is far poorer compared with a grain boundary thickness and is not sufficient to investigate B segregation quantitatively.

Recently, scanning transmission electron microscopy equipped with electron energy loss spectroscopy (STEM-EELS) or three dimensional atom probe (3DAP) have been applied to quantitatively measure B segregation at austenite grain boundaries [8–10]. Takahashi et al. [10] systematically investigated effects of cooling rates from 950 °C on B segregation using 3DAP and found that B segregation increases at slower cooling rate if boride precipitation is avoided. They also reported that a diffusion limited equilibrium segregation model can reproduce observed B segregation and concluded that an effect of non-equilibrium B segregation is small in cooling from 950 °C due to low vacancy concentration at such low temperature. However, different B segregation behavior is expected in cooling from higher temperature where vacancy concentration is high although effects of a temperature before cooling on B segregation is unknown.

Furthermore, as summarized in a textbook [11], boundary segregation of solute strongly depends on grain boundary character such as misorientation angle and boundary plane. Recent correlative 3DAP and TEM analyses of carbon (C) segregation to ferrite boundaries clearly show that segregation behavior to low angle boundaries differs significantly from that for high angle grain boundaries [12]. However, there is almost no investigation on boundary character dependence of B segregation.

Therefore, in this study, we aim to investigate B segregation at austenite grain boundaries in the specimens quenched from various

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temperatures using 3DAP together with characterization of austenite grain boundaries in order to clarify B segregation mechanism.

Fe-0.19C-1.99Mn-0.015Ti-0.0018N-11ppmB (mass%) alloy was used in this study. Ti is added to scavenge nitrogen in order to prevent from consumption of B by the formation of BN. After an annealing at 1150 °C for 24 h to homogenize Mn segregation, $3 \times 5 \times 10$ mm^3 rectangular specimens were cut, and heat-treated in three different conditions as shown in Fig. 1(a). One specimen was austenitized at 1200 °C for 10 min, and subsequently quenched into water. In order to investigate effects of quenching temperature on B segregation without changing a austenite grain size, two-steps heat treatment was conducted; the specimens were held at 1050 °C or 900 °C following to austenitization at

Fig. 1. (a) Heat treatment conditions used in this study, (b) orientation map of martensite, (b) austenite orientation map reconstructed from (a). θ represents misorientation angle of austenite grain boundary.

1200 °C, and water-quenched as shown in Fig. 1(a). Longer annealing periods in the second step were applied to ensure similar diffusion distances for all the annealing temperatures for segregation. Those specimens are denoted as Q1200 °C, Q1050 °C and Q900 °C, respectively. Average prior austenite grain size is about 80 μm in the three specimens. Average cooling rates between 1100 and 400 °C during water-quenching were measured several times by a thermocouple welded inside of a rectangular specimen and vary from 980 to 1340 °C/s.

Orientation of martensite was measured by electron backscattering diffraction (EBSD: OIM ver. 7 produced by EDAX) equipped with a field emission scanning electron microscope (SEM: JSM-7001F produced by JEOL and operated at 15 kV) and orientation of prior austenite was reconstructed using a method developed by some of the present authors as shown in Fig. 1(b) and (c) [13]. Then, several needle specimens for 3DAP measurement were prepared from multiple prior austenite grain boundaries (PAGBs) with known misorientations using focused ion beam (FIB) method. It should be noted that only random PAGBs, which does not satisfy Brandon's criteria [14], were selected for the analysis of high angle boundaries. B segregation was quantified using three-dimensional atom probe (3DAP: LEAP-4000HR produced by CAMECA). Measurement temperature, pulse fraction and pulse rate for 3DAP analysis were 80 K, 20% and 200 kHz, respectively. Although loss of Fe ions in detection of 3DAP measurement is known to cause overestimation of composition measurements [15], measured composition was not corrected because expected overestimation is as small as 10% in this measurement condition and detection loss of Fe ions inside of a grain boundary is unknown. Macroscopic B distribution and boride precipitation were analyzed by secondary ion mass spectroscopy (SIMS: TOF-SIMS5-100 produced by ION-TOF) with Bi$^+$ as a primary ion. Signals originated from B atoms are detected as BO_2^- in SIMS while its mass (m) is very close to other ions, AlO^- and $C_2H_3O^-$, $\Delta m/m <$ 0.0005. Accordingly, mixing of signals from those ions makes understanding of SIMS data not-straightforward. Therefore, first, we optimized the observation condition using high mass-resolution mode so as signals of BO_2^- ion to be much higher than the other two ions. Then total signals of the three ions were acquired to make a map in high spatial resolution mode where mass resolution is not sufficient to distinguish signals of those three ions. The map will be denoted as BO_2^- map, hereafter.

Before quantitative measurement of B segregation, precipitation of boride in three specimens was investigated using SIMS because solubility of B in austenite is quite small and depends greatly on a temperature [16]. Fig. 2(a) shows a vertical section of a phase diagram of an Fe-0.2C-2Mn-B system calculated using ThermoCalc with a TCFE9 database. 1200 °C and 1150 °C are within austenite single phase region while 900 °C is slightly below solubility of Fe$_2$B. Fig. 2(b) and (c) shows BO_2^- maps taken from the Q1050°C and Q900 °C specimens, respectively. B segregation at PAGB is clearly seen in both specimens. In addition, boride precipitation is detected within austenite grain in the Q900 °C specimen.

To investigate B segregation without an influence by boride precipitation, the Q1200 °C specimen was selected and B segregation were measured at several PAGBs with different misorientation angles (θ). Fig. 3(a) and (b) shows 3DAP results measured from low angle (θ = 10°) and high angle PAGBs (θ = 45°), respectively. Three dimensional maps in Fig. 3(a) and (b) clearly display B and C segregation at the PAGBs. Element profiles across the PAGBs shows both B and C are enriched at the PAGBs and segregation is enhanced at higher θ. It should be noted that carbon atoms forms cluster as indicated as red arrows, which may correspond to defects in martensite such as dislocations or lath boundaries, in accordance with previous 3DAP measurements [9,10]. The formation of C clusters strongly indicates that C diffusion after martensite transformation changes C distribution in austenite. Since solubility of C in ferrite is much lower than that in austenite, C atoms are probably further segregated to prior austenite grain boundaries after martensite tran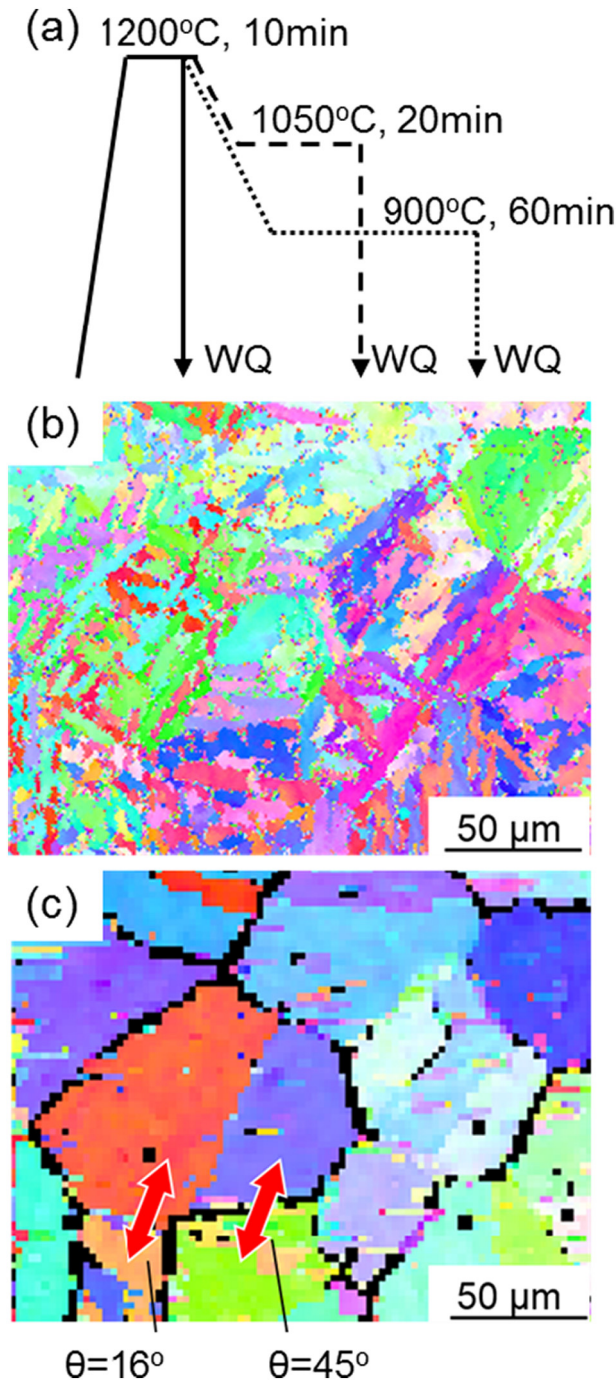sformation, which makes quantitative