Effect of Cooling Rate after Recrystallization on P and B Segregation along Grain Boundary in IF Steels

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Many researchers revealed that the addition of small amount of boron (B) significantly suppresses the intergranular fracture (IGF) induced by segregated phosphorous (P) along grain boundaries in iron and steels. However the details of this suppression have not been clarified yet. In the present study, the behavior of B and P during heat treatment and the mechanism of toughening caused by B in interstitial free (IF) steels containing P was examined using alpha-particle track etching (ATE), tensile testing, Auger electron spectroscopy (AES) and scanning electron microscopy (SEM). The results of ATE exhibit that the degree of grain boundary segregation of B depends on the cooling rate from 850°C and shows maximum at about 10°C/s for high B–low P steel while it shows maximum at about 555°C/s for high B–high P steel. The results of ATE also reveal that low P steel shows higher B segregation than high P steel at all cooling rates, while the difference is reduced by increasing the cooling rate. It was found that elongation at low temperatures is improved when B segregates along grain boundaries. The results of AES indicate that the grain boundary segregation of B markedly decreases the segregation of P and consequently the elongation is enhanced. Therefore, controlling of the cooling rate after recrystallization decreases the brittleness caused by P in IF steel. Segregation of B and P after heat treatment can be explained by a duplex equilibrium and non-equilibrium mechanism before and during cooling.

KEYWORDS: IF-steel; boron; grain boundary; phosphorous; heat treatment; segregation; site competition; alpha particle track etching; auger electron spectroscopy.

1. Introduction

To improve fuel economy is a primary goal in the automotive industry. One of the factors affecting fuel economy is the vehicle weight. To reduce the weight of the auto body, the development of high strength steel sheets and its application has been made. Phosphorus is a useful element in high strength sheet steels for automobiles because it improves the strength through solid solution hardening.\(^1\) On the other hand, P often causes intergranular fracture (IGF) to iron and steels. In order to utilize the beneficial effect of P, the P induced IGF must be suppressed. It has been well known that when trace boron is added to steels, their properties can be considerably improved and this beneficial effect of B is caused by the segregation of B at grain boundaries, refining precipitates and so on. The segregation of B along grain boundaries is classified into equilibrium and non-equilibrium ones and the segregation of B in steels cooled at intermediate rate is always superposition of equilibrium and non-equilibrium segregation. Many metallurgical aspects of IF steels have been investigated and it was found that B is useful to improve the ductility of grain boundaries because free B is considered to segregate along grain boundaries and strengthening them.\(^2\) It was reported that the addition of trace B to a high purity Fe–0.2%P alloy, upon quenching from 1073 K, almost prevents the IGF induced by the segregated P.\(^3\) This suppression of IGF by B is explained by two mechanisms. One is the increased grain boundary cohesion by the segregated B as its intrinsic effect, and the other is the decreased segregation of P by the segregated B. Takahashi et al.\(^4\) however, insist that the toughening mechanism through the latter mechanism in continuously annealed sheet steels is neglected. Liu et al.\(^3\) interpret the decreased segregation of P by the segregated B using site competition model between B and P, which depends on equilibrium segregation mechanism and do not consider segregation of B through non-equilibrium mechanism. They also didn’t consider the interaction term between P and B. Guttmann\(^5\) has proposed an analysis to equilibrium segregation in ternary systems in which the co-segregating species have a simple interaction term. As shown above, irrespective of the number of researches, the details of the IGF suppression mechanism by B addition have not yet been clear. Considering above background, this paper aims to give a broad characterization of the B and P behavior during heat treatment and the mechanism of toughening caused by B in interstitial free steels containing P using ATE, tensile testing, AES and SEM.

2. Experimental Work

Four steels were processed as follows: 1) Vacuum melt-
ing and 30 kg ingots were obtained; 2) Rough Hot-Rolled to 30 mm, preheating at 1 250°C for 1 h in a nitrogen atmosphere; 3) Removing Scale; 4) Finish Hot-Rolled to 5 mm, preheating at 1 200°C for 0.5 h in a nitrogen atmosphere; 5) Pickling and cold rolled to sheets of 2 mm thickness by Kawasaki Steel Corporation. The chemical compositions of these steels are shown in Table 1. The as received sheets were cut to 10×10×2 mm blanks for microscopy and ATE; other blanks 20×90×2 mm were cut for tensile test.

Specimens (1/2.6×16) were machined for AES. All blanks were recrystallized at 850°C for 1 h and cooled through FC (0.1°C/s), AC (10°C/s) and WQ (555°C/s). To investigate the effect of the cooling rate on the B segregation in more detail, blanks for ATE were recrystallized at 850°C for 1 h in a vertical furnace and cooled in air; quenched in water or ice brine with a weight of 100 gf. The cooling rate was changed [0.1°C/s (FC)–1 500°C/s (IBQ)] using specimens having various dimensions and was monitored with a high-speed recorder and a thermocouple welded on the surface of the specimen. The cooling rate was taken as the average cooling rate from 850 to 450°C and various cooling curves are shown in Fig. 1. The heat-treated sheets for tensile testing and AES were cold rolled to 40% reduction in order to simulate the second forming then machined. Tensile test was performed under the crosshead speed of 12 mm/min (0.01 s⁻¹) at 80°C and 196°C. Tensile test specimen of 20 mm gauge length and 7 mm gauge width was used and its dimensions shown in Fig. 2.

The AES measurements were carried out at the accelerating voltage of 3 kV with the modulation of 5 eV. Auger peak height ratios of the P peak at 120 eV and the B peak at 180 eV to the Fe peak at 703 eV were used to evaluate the degree of segregation. The simplest approximation to estimate the surface composition from Auger signal intensities was used:

\[ C_i = C_{i,\text{std}} \frac{f_i}{f_{i,\text{std}}} \] ..............................(1)

Where \( C \) is the concentration and \( f \) is the ratio of Auger peak size to its background intensity. The subscript \( i \) and std represent the element \( i \) in the sample and standard respectively.

Applying the atomic density correction to Eq. (1):

\[ C_i^n = \sum_j \frac{n_j C_j}{n_i} \] ..............................(2)

Where \( n_i \) is the atomic density of the standard sample of element \( i \). The Auger spectra of at least 10 different spots were taken on intergranular fracture region and the results were averaged. The procedure of ATE is as follows: a) A cellulose film is glued on to the polished surface of the specimen. b) Specimen is irradiated by neutrons; the following fission reaction between thermal neutron and \(^{10}\text{B} \) contained naturally by certain content with \(^{11}\text{B} \)

\[ ^{10}\text{B} + n \rightarrow ^{7}\text{Li} + ^{4}\text{He}(\alpha) \]

takes place in the surface layer of the specimen. c) The discharged alpha particles produce tracks in the cellulose film and these tracks density is proportional to the boron content of the specimen. d) The tracks are made visible by etching the cellulose film in aqueous NaOH. Irradiation of neutrons for ATE was performed in the reactor JRR-4 at the Japan Atomic Energy Research Institute. Thermal neutron flux is \( 1.6 \times 10^{10} \text{ n·cm}^{-2}\text{s}^{-1} \) and irradiation time is 12 h. Total flux of \( 6.9 \times 10^{14} \text{ n·cm}^{-2} \) was obtained. 

3. Results and Discussion

3.1. Segregation Behavior of B and P

The grain size of recrystallized ferrite shows no dependence on the cooling rate for the same steel. Figure 3 shows the ATE of Steels B and D (same B content) after different cooling rates. Two specimens were yielded to ATE experiment at a certain cooling rate for each steel and about five photographs were taken for each specimen.

After FC (0.1°C/s), the degree of boron segregation is weak for both steels but it is higher in Steel B than that of
Steel D. After AC (10°C/s), it can be seen that in Steel B (10 ppm P) the grain boundary segregation of B is more marked, nearly continuous as revealed by the closely spaced small etch pits. On the other hand in Steel D (0.105 % P), there is considerably less segregation, namely along the grain boundaries, the etch pit bands are much less distinct. Comparing different ATE micrographs for Steels B and D after different cooling rates, it can be seen that the degree of grain boundaries segregation shows maximum at about 10°C/s for Steel B while it shows maximum at about 555°C/s for Steel D. Such an appearance of a maximum degree of segregation is a unique characteristic of non-equilibrium segregation. For 1500°C/s cooling rate, Steels B and D show a similar degree of segregation as shown in Fig. 3. Results of ATE can be summarized as follows: low P steel shows higher B segregation than high P steel at all cooling rates. However increasing the cooling rate reduces the difference. The degree of grain boundaries segregation shows maximum at about 10°C/s in low P steel while it shows maximum at about 555°C/s in high P steel.

According to non-equilibrium mechanism of segregation of B, supersaturated vacancies combine with B to form B–V (vacancy) complex. During cooling, the complex move to grain boundaries and vacancies annihilate there, causing the decomposition of the complex. In a mean time the concentration of B segregated along grain boundaries increases much more than the equilibrium concentration and the free B will diffuse away from grain boundaries in a back diffusion process. Therefore the degree of segregation shows maximum at intermediate cooling rate. Tingdong defined the concept of the critical cooling rate, which leads to a maximum level of segregation and obtained a maximum degree of B segregation at 10°C/s. However the formulas developed failed to achieve an exact expression due to the variation of alloy composition. In addition, Karlsson et al. found that the strongest enrichment occurs at intermediate cooling rates (around 13°C/s) for 316L austenitic steels by means of secondary ion mass spectrum (SIMS) and atom probe (AP). Zhang et al. obtained a maximum degree of B segregation at 10°C/s for Fe–3%Si alloy. These cooling rates showing the maximum degree of B segregation consist to the result of the present
mole fractions of segregation levels of species according to: two species and depends on their mutual segregation levels $X^a_i$ and $X^a_j$ which are the grain boundary mole fractional segregation levels of species $i$ and $j$ respectively with bulk mole fractions $X^a_i$ and $X^a_j$, $X^s_i$ is the saturation value of $X^s_i$. $AG_i^s$ and $AG_i^c$ are the free energy of segregation of the two species and depends on their mutual segregation levels according to:

$$\Delta G_i^s = \Delta G_i^c + \alpha_i^c X^s_i$$

$$\Delta G_i^c = \Delta G_i^s + \alpha_i^s X^c_i$$

Where $\Delta G_i^s$ and $\Delta G_i^c$ are the free energies of segregation of the two species in their respective binary systems with iron and $\alpha_i^c$ is the relative interaction coefficient between the co-segregating species.

The free energy of segregation of B is higher than that of P.\(^{11,12}\) so in case of low P–high B, the B segregation along grain boundaries is dominant while in case of high P–high B, the concentration of B decreases. This means that there is a site competition between the two species. Comparing these results with the concentration obtained by AES measurements, it can be noted that there is a difference between the calculated results using Guttmann’s equations and the measured data using AES. Steel D shows a large deviation between the calculated and measured data, probably because Guttmann’s equation considers only the equilibrium segregation during holding at a certain temperature, and the non-equilibrium mechanism of B segregation during quenching and the effect of cooling rate on segregation of P are not considered. Even after considering the effect of non-equilibrium mechanism of B segregation during cooling and the effect of cooling rate on segregation of P, the difference between the calculated and measured degree of segregation for steel D remained very large. If the repulsive force between B and P were very large, this difference may be explained. But the repulsive force is thought to be small as discussed later. Unknown point remained to be clarified as a future work for this steel.

One may wonder how non-equilibrium mechanism of B segregation occurs at WQ samples. Considerable experimental and theoretical work has been carried out on the non-equilibrium segregation (and desegregation) of solute atoms as induced by vacancy currents in metals and alloys.\(^{14-17}\) The non-equilibrium segregation of B to grain boundaries during quenching has been analyzed by Williams \textit{et al}.\(^{13}\) as well as by Faulkner\(^{16}\) on the basis of a model originally proposed by Aust and Westbrook.\(^{17}\) The
former authors have suggested that non-equilibrium segregation will occur if the complexes move rapidly enough to keep the complex concentration reasonable. In keeping with this view, they assumed that the diffusivity of the B-vacancy complexes is 250 times higher at all temperatures than that of boron atoms and also much higher than that of the vacancies on their own.

The present investigation indicates that maximum degree of B segregation occurred at 555°C/s corresponding to WQ condition for Steel D (high P–high B) as shown in Fig. 3, which imply that this segregation is attributed to non-equilibrium segregation.

Segregation behavior of B should be explained in more detail considering followings: 1) equilibrium segregation of P before cooling; 2) equilibrium segregation of P during cooling; 3) equilibrium segregation of B before cooling; 4) non-equilibrium segregation of B during cooling; 5) back diffusion of B segregated by non-equilibrium segregation mechanism to the matrix. Considering all of them, segregation behavior of B and P can be shown schematically as Fig. 5 for high B–low P, low B–high P, and high B–high P respectively based on the ATE observation and AES measurements. As the non-equilibrium segregation is a dynamic phenomenon, it will be dispersed and homogenized by reverse diffusion once the supply of excess vacancies is exhausted.  In Fig. 5, it can be seen that the degree of B segregation shows maximum at AC condition for low P–high B steel due to non-equilibrium segregation of B. For high P–high B steel at AC condition, segregation of P approaching to the equilibrium occurs during cooling under the site competition with B segregation through non-equilibrium mechanism. As a result the degree of B segregation decreases comparing with low P–high B steel. If interaction between B and P is repulsive, this trend is promoted. But the repulsive interaction is reported to be small. At WQ condition there is no enough time for P to segregate to grain boundaries but B can move to grain boundaries as it depends on the B–V complexes which are very fast in reaching grain boundaries. For high P steels, when the B content is relatively low, the segregation of P is the dominant case and this segregation intensifies during AC due to the equilibrium segregation of P during cooling. Segregation behavior of B and P shown schematically in Fig. 5 consists qualitatively with the experimental results shown in Fig. 4. More detail discussion requires more quantitative experiments.

3.2. Tensile Properties

Figures 6 and 7 are comparing the variation of ultimate tensile strength (UTS) and elongation of all Steels with the cooling rate tested at −196°C and −80°C respectively. Steels C and D containing high P show higher UTS and smaller elongation comparing to Steels A and B with a lower content of P at both testing temperatures. Boron ad-
dition has a trend to increase both UTS and elongation. Neither solid nor precipitation strengthenings by B can be expected in steels containing 22 ppm B. Therefore the increase in UTS by boron addition is attributable to the effect of B on suppression of nucleation of micro-cracks.

For Steel A which neither B nor P was added, UTS is hardly affected by the cooling rate. For Steel C which contain 0.105 % P, the UTS increases slightly by increasing the cooling rate. UTS for Steel B shows a slight increase from FC (0.1°C/s) to AC (10°C/s) corresponding to maximum degree of B segregation obtained and then UTS decreases by increasing cooling rate to WQ (555°C/s). Steel D (0.105 % P, 22 ppm B) shows an increase in UTS by increasing cooling rate from FC to AC and further increase by reaching WQ condition due to the maximum degree of B segregation obtained for this Steel. Steel D shows the highest UTS due to the combined effect of P and B addition. Similar trend occurred at −80°C but with lower strength values due to the increase in testing temperature.

For the variation of elongation with cooling rate, it was observed that the elongation for Steels B and D is in good consistency with ATE and AES results. Steel B (0.001 P, 22 ppm B) shows higher elongation than steel D (0.105 P, 22 ppm B) at all cooling conditions. But the difference in elongation depends on the cooling rate is large at FC and AC conditions while it is small at WQ condition. Steel C shows the lowest elongation over all steels, whereas steel D shows nearly elongation value of Steel B after WQ at both tested temperatures. This indicates that the grain boundary segregation of B, which was observed in steel D at WQ has a great effect on the elongation. Figure 8 compares variation of grain boundary segregation of P and B and elongation with the cooling rate for Steels C and D. When steel D cooled through WQ, an increase in elongation together with a decrease in segregation of P are obtained. Segregation of P above 4 at % slightly affects elongation. Namely, increasing grain boundary strength by the intrinsic effect of B seems to be effective in suppressing IGF but decreasing the segregation of P works also as an indirect effect of B segregation.

![Figure 6. Variation of UTS and elongation with cooling rate at −196°C.](image)

![Figure 7. Variation of UTS and elongation with cooling rate at −80°C.](image)

![Figure 8. Variation of grain boundary segregation of P and B and elongation at −196°C with the cooling rate.](image)
3.3 Fracture Surface of AES Sample

Figure 9 shows the fracture surface of Steels B, C and D cooled through AC and WQ. They were impact-fractured at about -150°C in the AES chamber. The main fracture surface of AES samples is in agreement with the P and B segregation along grain boundaries; the fracture appearance changes from IGF (Steel C) to quasi-cleavage fracture (Steel D) as the P segregation decreases and that of B increases. It can be observed that there is a minor effect on the cooling rate for Steel B, which shows mainly quasi-cleavage. However as the cooling rate increases from AC to WQ for Steel B, the degree of quasi-cleavage fracture decreases and that of IGF increases, which agrees with the ATE obtained as B segregation decreases by increasing cooling rate from AC to WQ for this steel. On the contrary, increasing the cooling rate for Steel D from AC to WQ increase the degree of cleavage fracture as the B segregation shows maximum at WQ condition for this steel. In the previous section, relation between elongation and grain boundary segregation of B and P was discussed. The strain rate is different between the tensile test and the impact test in the AES chamber. Therefore it is not possible to think the fracture behavior in tensile test to be same in impact test. However, it is conceived that transition from ductile to brittle can be observed even in tensile test, although the transition temperature is lower than that in impact test. In addition, Steels C containing a high content of P fractured in a brittle manner in tensile tests and the elongation was increased by B addition. Therefore, it can be thought that even in tensile test B segregating along grain boundaries suppresses intergranular brittle fracture and increased elongation.

4. Conclusions

Boron behavior and its effects on intergranular fracture caused by P in IF steels (0.2%Mn–0.04%Ti) were investigated and the results can be summarized as follows.

(1) Low P steel shows higher B segregation than high P steel at all cooling rates, while increasing the cooling rate can lower the difference.

(2) The degree of grain boundary segregation of B depends on the cooling rate from 850°C and shows maximum at about 10°C/s for low P steel while it shows maximum at about 555°C/s for high P steel.

(3) Segregation of B and P after heat treatment can be explained by a duplex equilibrium and non-equilibrium mechanism before and during cooling however, more detail discussion requires more quantitative experiments.

(4) Grain boundary segregation of B markedly decreases the segregation of P and as a result elongation at low temperatures is improved when B segregates along grain boundaries, although grain boundary strengthening by the intrinsic effect of B cannot to be neglected.
(5) Optimizing the cooling rate after recrystallization decreases the brittleness caused by P in IF steel containing B.

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