Grain Boundary Segregation of Phosphorus and Boron in Extra-Low Carbon Steels

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Grain boundary segregation of P and B in extra-low carbon cold-rolled steel sheet containing from 0.01 and 0.15 mass% P and up to 38 mass ppm B after annealing at 1123 K was investigated by Auger electron spectroscopy (AES). AES measurements on the intergranular fracture surfaces of the specimen indicate that the Auger peak intensity ratio (PIR) of P increased and that of B decreased with increasing bulk concentration of P, and that PIR of P markedly decreased, while that of B increased with a B addition of up to 10 ppm. In the bulk concentration range of B of more than 10 ppm, however, these ratios hardly changed. The segregation behavior was nearly the same between specimens annealed for 20 s and 500 s, indicating that the segregation of P and B was in an equilibrium state. Calculations of the grain boundary coverages of P and B indicate that (1) the segregation free energy of B was about twice that of P, (2) the coverage of B was larger than that of P in the specimen with B concentration of more than 10 mass ppm, and (3) the total coverage of P and B was nearly constant in the specimen with B concentration of more than 10 mass ppm. It is concluded that the improvement in secondary workability of P-added steel sheet by also adding B is attributable to the segregation of less P and more B on the grain boundary, resulting in enhanced grain boundary cohesion.

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I. Introduction

An extra-low C interstitial atom-free (IF) cold-rolled steel sheet has been widely used by the automotive industry owing to its deep drawability⁽¹⁾⁽²⁾. High-tensile strength steel sheet has recently been developed and commercially used to reduce the weight of automotive bodies, the high strength being endowed by solid solution hardening elements such as Si, Mn and P. P is the most effective and economical element to increase the strength of steel, but it segregation at the grain boundary and induces brittle fracture during working processes⁽³⁾⁻⁽⁶⁾. In such a steel, the addition of a small amount of B is effective for preventing this brittle fracture⁽⁷⁾ and it is believed that the segregation of B suppresses the segregation of P at the grain boundary. The segregation behavior of P and B in some binary and ternary iron-based alloys has been investigated⁽⁸⁾⁻⁽¹⁰⁾, although the results have not yet been associated with the alloys commonly used, *e.g.*, extra-low carbon IF steel for automotive bodies. Furthermore, experimental evidence has not yet been reported to elucidate the effects of segregated elements on secondary working embrittlement, which is one of the most important practical properties of commercial steel sheet.

In this study, Auger electron spectroscopy (AES) was applied to quantitatively evaluate the segregation of P and B at the grain boundary in P- and B-added extra-low carbon IF steel to investigate the effects of the segregation

of P and B and of the annealing time on secondary working embrittlement.

II. Experimental Procedure

1. Specimen preparation

Ti- and Nb-added extra-low C IF steel ingots were melted in a vacuum induction furnace, the chemical composition being shown in Table 1. P at three concentration levels of 0.01, 0.08 and 0.15 mass%, and B with a concentration ranging from zero to 38 mass ppm added. The

Table 1 Chemical compositions of steels (mass%).

No.	C	P	B	N
R1	0.0019	0.010	0.0001	0.0020
R2	0.0023	0.010	0.0010	0.0040
R3	0.0016	0.010	0.0020	0.0025
S1	0.0018	0.0072	0.0001	0.0028
S2	0.0022	0.076	0.0009	0.0028
S3	0.0022	0.073	0.0020	0.0031
T1	0.0023	0.163	0.0001	0.0020
T2	0.0016	0.150	0.0003	0.0040
T3	0.0019	0.150	0.0011	0.0016
T4	0.0021	0.160	0.0019	0.0022
T5	0.0023	0.152	0.0038	0.0017

Base composition Si:0.01, Mn:0.15, S:0.01, Ti:0.04, Nb:0.005, Fe:Balance

concentrations of Ti and Nb of 0.04 mass% and 0.005 mass%, respectively, were chosen so that they would fix N and keep almost all B added to the steel in a solution state⁽¹¹⁾. A chemical analysis of the electrochemically extracted phosphides confirmed that more than 95% of added P was in a solution state⁽¹²⁾. The ingots were hot-rolled and cold-rolled to 0.7 mm thick sheets⁽⁷⁾ and then annealed at 1123 K for 20 or 500 s to simulate a conventional continuous annealing process. Specimens for AES of 3.5 mm × 17 mm in size were cut from the cup-shaped drawn test piece in order to induce intergranular fracture.

2. AES measurement

The segregation of elements at the grain boundary was measured with a PHI model 650 scanning Auger microscope. Each specimen was mounted on the fracture unit in the Auger microscope at a base pressure of 1.6×10^{-8} Pa. And after cooling to about 153 K, the specimens were fractured by impact. An AES analysis was conducted with a primary electron beam energy of 1.6×10^{-15} J (10 keV), beam current of 20 nA, and energy analyzer resolution of 0.6%. Since the beam diameter of 0.2 μ m was less than the grain diameter of 10–20 μ m, individual grain boundary facets could be measured. Auger spectra were measured on at least 15 different grain boundary facets in each specimen. The segregation of P and B was evaluated by the average of each Auger peak intensity ratio (PIR) that was obtained from the Auger peak intensity values for P-KLL and B-KLL normalized by that of Fe-LMM. The PIR scatter is indicated by vertical bars in the figure.

In order to quantitatively calculate the segregation, relative sensitivity factor (RSF) for P and B with respect to Fe were measured using standard specimens. For RSF of P, FXS-316 (P=0.077 mass%) and FXS-318 (P=0.321 mass%), which are the Japanese Standards for iron and steel (JSS), and FeP powder of 40 mesh with Ar⁺ ion sputtering were used. It has already been confirmed that these standard specimens were uniform in composition, that is, no local segregation was apparent. For RSF of B, pure Fe and B were used.

The ductile-brittle transition temperature (T_{cr}) of the specimens is defined as the lowest temperature at which no fracture was observed after a 5-kg test weight was dropped from a height of 0.8 m onto a cup-shaped specimen of 30 mm in diameter drawn in advance by a conical cup testing machine⁽⁷⁾.

III. Experimental Results

In order to quantify the segregation of P and B, the RSF value for P was measured using JSS standard specimens and FeP powder. Figure 1 shows the relationship between the bulk atomic concentration ratio of P to Fe and the Auger PIR value of P to Fe. The PIR value of P obtained from the FeP powder is less scattered than that from the standard Fe–P alloy, and remained substantially unchanged after Ar⁺ ion sputtering for several hours. This indicates that the specimen was uniform with

Fig. 1 Calibration curve for P in Fe using the scratched JSS standard sample (▲) and FeP powder with Ar⁺ ion sputtering (■).

Table 2 RSF and inelastic mean free pass, t , for P, B and Fe.

Element	RSF	t (nm)
P	2.10	0.30
B	0.69	0.38
Fe	1.00	0.93

respect to the constituent and that no effect of preferential sputtering had occurred. Therefore, the RSF value for P was determined by the PIR value obtained from FeP powder, while the RSF value for B was determined by the PIR values for pure iron and pure B specimens. RSF values for P and B are shown in Table 2.

Typical scanning electron micrographs of the fractured surface of specimens with 0.08 and 0.15 mass% P annealed at 1123 K for 20 s are shown in Fig. 2. The fracture mode of these specimens not doped with B (S1 and T1) is mostly intergranular and is rarely transgranular, while that with 10 mass ppm of B (S2 and T3) is predominantly transgranular. A small number of intergranular fracture facets are observed in the specimens with 10 mass ppm of B (S2 and T3) as indicated by the arrows. The fracture topography of the specimens annealed at the same temperature for 500 s was similar to that in the specimens annealed for 20 s. The intergranular fracture appearance of the specimens is summarized in Table 3. The specimens with 0.01 mass% P and more than 10 ppm of B (R2 and R3) annealed at 1123 K for 20 s did not present an intergranular fracture, but transgranular fracture was apparent, therefore, no Auger measurements were performed on these specimens. The grain size of the specimens not doped with B was smaller than that of the specimens with B, irrespective of the P concentration.

Auger survey spectra from the fracture surfaces of the specimens with 0.08 mass% P are shown in Fig. 3. The

Fig. 2 Scanning electron micrographs of the fracture surface of specimens with 0.08 mass% P, S1 (no B) and S2 (10 ppm B), and 0.15 mass% P annealed at 1123 K for 20 s, T1 (no B) and T3 (10 ppm B) annealed at 1123 K for 20 s.

Table 3 Intergranular fracture appearance and transition temperature of specimens.

Specimen No.	Intergranular fracture appearance/%		T_{α}/K
	Annealed for 500 s	Annealed for 20 s	
R1	50	50	193
R2	20	0	133
R3	20	0	113
S1	~100	~100	248
S2	10	10	163
S3	10	10	153
T1	~100	~100	283
T3	20	20	213
T4	20	20	208
T5	20	20	173

spectrum obtained from a transgranular cleavage facet in specimen S1 (no B) indicated only the Fe Auger peaks as shown in Fig. 3(a), whereas that from the grain boundary of the same specimen shows the Auger peak of P in addition to that of Fe as shown in Fig. 3(b), which proves that P had segregated at the grain boundary. In the spectrum of the grain boundary for specimen S2 (B = 10 mass ppm) peaks of P and B appeared in addition to that of Fe as shown in Fig. 3(c). The peak height of P from S2 was

smaller than that from S1, which indicates that the addition of B had significantly decreased P segregation.

The effect of the bulk concentration of B on the PIR value of P to Fe in the specimens with 0.15 (T1–T5), 0.08 (S1–S3) and 0.01 mass% P (R1) after annealing for 20 s is shown in Fig. 4(a). With increasing bulk B concentration up to 10 mass ppm, the PIR value of P to Fe markedly decrease, while in the B concentration range of more than 10 mass ppm, it remained almost constant with increasing bulk concentration of B. The scatter of the PIR values obtained from each grain boundary facet is attributable to the anisotropy of grain boundary segregation or the difference in segregation sites among grain boundaries⁽¹⁰⁾⁽¹³⁾. The effect of the bulk concentration of P on P segregation is also shown in the figure, indicating that the PIR value of P to Fe on the grain boundary in the specimens with the same bulk concentration of B increased with increasing bulk concentration of P. The PIR value of B to Fe has an inverse bulk composition dependency compared with that of P to Fe as shown in Fig. 4(b). With increasing bulk B concentration up to 10 mass ppm, the PIR value of B to Fe markedly increased, whereas it hardly changes in the B concentration range from 10 to 40 mass ppm. Since the intergranular fracture appearance of the specimens with 0.01 mass% P contain-

Fig. 3 Auger spectra taken from (a) the transgranular fracture surface and (b) the grain boundary in specimen S1 (P=0.08 mass%, B=10 mass ppm) and (c) the grain boundary in specimen S2 (P=0.08 mass%, B=10 mass ppm) after annealing at 1123 K for 20 s.

ing 10 and 20 mass ppm of B annealed for 20 s is 0% as shown in Table 3, the PIR values of P and B to Fe at the grain boundary could not be measured.

Figure 5 shows that the effect of the bulk concentration of B on the PIR values of P and B to Fe is the same as that shown in Fig. 4, but annealed for 500 s. The PIR values of P and B to Fe have nearly the same bulk composition dependency as those shown in Fig. 4; that is, the annealing time has no marked influence on the grain boundary segregation of P and B. Therefore, the segregation of P and B was in the equilibrium state after annealing for 20 s.

The ductile-brittle transition temperature (T_{cr}) of the specimens at three P concentration levels annealed for 20 s at 1123 K are shown in Table 3. Doping with 10 mass ppm B markedly lowered T_{cr} by 60–80 K for all P concentration levels, and with further increase in the bulk concentration of B, T_{cr} decreased gradually.

IV. Discussion

1. Quantification of the grain boundary segregation of P and B

In alloys containing two or more segregants, the segre-

Fig. 4 Relation between Auger peak intensity ratio for (a) P and (b) B to Fe at the grain boundary and bulk concentration of B in 0.15, 0.08 and 0.01 mass% P specimen annealed at 1123 K for 20 s.

gation of one segregant is effected by the other. It could be expected that the effect would be co-segregation, repulsive interaction or site-composition. In the latter two cases, repulsive interaction and site composition, which have not been distinguished experimentally⁽¹⁰⁾, one segregant excludes the other segregant at the grain boundaries. This is the case with Fe-P-C⁽³⁾, Fe-P-B⁽⁹⁾, Fe-P-S⁽¹⁴⁾ and Fe-C-S⁽¹⁵⁾ alloys. In the present case, the concentration of P decreased with the appearance of B at the grain boundary, as shown in Figs. 4 and 5. Since the diffusion coefficient of B ($4.47 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at 1123 K)⁽¹⁶⁾ is much larger than that of P ($5.25 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ at 1123 K)⁽¹⁷⁾ in the present annealing temperature region, it would be expected that B initially segregates and occupies a large part of the segregation sites at the grain boundary; there would be a mutual segregation change by competition for

Fig. 5 Relation between Auger peak intensity ratio for (a) P and (b) B to Fe at the grain boundary and bulk concentration of B in specimens with 0.15, 0.08 and 0.01 mass% P annealed at 1123 K for 500 s.

the available grain boundary sites or repulsive interaction between P and B. In order to quantify the grain boundary segregation of those elements, the grain boundary coverage (GBC) was calculated.

Briant⁽¹⁶⁾ has proposed a grain boundary structural model which is made up of a monoatomic segregation layer including segregation sites. This proposition assumes that the site density available to the segregant at the grain boundary depends on its geometry. This consideration seems to be supported by the scatter of the measured PIR values shown in Fig. 4. Therefore, it is reasonable to evaluate GBC of the segregation sites by segregant to identify the segregation behavior. In order to investigate GBC of P and B at the grain boundary, the grain boundary atomic concentrations of those elements should be calculated from the PIR values shown in Figs. 4 and 5. Since the segregants was measured by AES whose detec-

tion depth (about 6 nm) is larger than the thickness of the segregation layer, it is also necessary to calculate the atomic concentration at the grain boundary in consideration of the escape depth for an Auger electron.

Hirokawa *et al.*⁽¹⁹⁾ have derived the following relationships connecting N_i^{GB} , the atomic concentration of element i at the grain boundary, with PIR_i^{GB} :

$$PIR_i^{GB} = S_i^{Fe} (N_i^{GB} + (N_i - N_i^{GB}) \exp(-d/t_{ai})) / (N_{Fe}^{GB} + (N_{Fe} - N_{Fe}^{GB}) \exp(-d/t_{aFe})) \quad (1)$$

$$\sum N_i^{GB} = 1, \quad \sum N_i = 1 \quad (2)$$

where S_i^{Fe} is RSF of element i with respect to Fe, d is the thickness of the segregation layer, and t_{ai} and t_{aFe} are the inelastic mean free paths for elements i and Fe, respectively, depending on the analyzer geometry. N_i and N_{Fe} are the atomic fractions of elements i and Fe in the bulk material, respectively. The values of t_{ai} and t_{aFe} in equation 1 were calculated using Tanuma's equation for inelastic scattering mean free path of an Auger electron⁽²⁰⁾, which are also shown in Table 2. The value of d was tentatively defined as 0.5 nm, which was evaluated from the depth profile of P and B at the intergranular fracture surface.

Since the grain boundary segregation of P and B was already in the equilibrium state after annealing for 20 s as mentioned in Section III, it seems to be reasonable to calculate the GBC of P and B, n_P^{GB} and n_B^{GB} , respectively, at annealing temperature T by the following pair of equations⁽⁴⁾⁽⁵⁾:

$$n_P^{GB} = n_P (1 - n_P^{GB} - n_B^{GB}) \exp(\Delta E_P^{GB} / kT) \quad (3)$$

$$n_B^{GB} = n_B (1 - n_P^{GB} - n_B^{GB}) \exp(\Delta E_B^{GB} / kT) \quad (4)$$

Here, n_i and ΔE_i^{GB} are the bulk concentration and segregation free energy, respectively, for element i , which is P or B. The concentration of an element on the grain boundary, N_i^{GB} , which can be calculated by eqs. (1) and (2), is given by $n_0 \times n_i$, where n_0 is the fraction of the segregation sites available to P and B at the grain boundary. The value of $-(24 + 0.03 T) = -57.7$ kJ/mol at 1123 K was used for $\Delta E_P^{GB(9)}$. Using the results for grain boundary atomic concentration of P and B in the specimen with 0.15 mass% P and 10 ppm of B derived from eqs. (1) and (2), n_0 and ΔE_B^{GB} were evaluated to be 0.28 and -99.7 kJ/mol, respectively. It is believed that P segregates at the grain boundary in α -Fe in the form of a Fe_3P type of molecular unit⁽¹⁸⁾; therefore, the calculated value of $n_0 = 0.28$ is reasonable. Paju *et al.*⁽²¹⁾ have investigated an Fe-10Mn-P-B alloy by AES and reported $\Delta E_B^{GB} = -97$ kJ/mol, while Liu *et al.*⁽⁹⁾ have evaluated ΔE_B^{GB} at 1023 K for an Fe-0.2P-B alloy as -100 kJ/mol. The calculated ΔE_B^{GB} value in the present study agrees well with the previously reported values. The segregation free energy of B is approximately twice that of P, leading to the result that B should segregate more intensively than P. The calculated GBC changes with bulk concentration of B in the specimens with three P concentration levels as shown in Fig. 6. A comparison between (a) and (b) in the

Fig. 6 Relation between coverage of (a) P, (b) B and (c) P+B at the grain boundary and bulk concentration of B after annealing at 1123 K.

figure indicates that GBC of B is larger than that of P in the B concentration range of more than 10 mass ppm. Also, as shown in (c) in the figure, the total GBC of P and B at the grain boundary was about 80% in the bulk B concentration range of more than 10 mass ppm, irrespective of the bulk concentration of P. The invariance of the total GBC of P and B in this concentration range seems to indicate that site competition rather than repulsive interaction was predominant between P and B at the grain boundary. In the specimens without B and with 0.01 and 0.08 mass% P, it was less than 40%. These results indicate that B would be much more liable to segregate than

P, and it corresponds with the foregoing discussion, that is, ΔE_B^{GB} is about twice ΔE_P^{GB} .

Considering the relationship among bulk concentration and GBC of P and B described in eqs. (3) and (4), one could expect some increase in GBC of P, and at the same time, some decrease in GBC of B with increasing bulk concentration of P. Figure 6 reveals the increase in GBC of P from 8 to 26% and the decrease in GBC of B from 75 to 50% with increasing bulk concentration of P from 0.01 to 0.15 mass% at bulk B concentrations of 10 and 20 mass ppm. This experimental result confirms the expectation. This is also the case with the change in GBC of P and B with increasing bulk concentration of B from 0 to 10 mass ppm.

The same proposition as that just mentioned might also lead to an increase in B and decrease in P at the grain boundary in specimens with more than 10 ppm of B. In Fig. 6, however, the GBC of P and B shows no apparent change with increasing bulk concentration of B in the range of more than 10 mass ppm. The maximum solubility of B in the ferritic region of an Fe-B binary alloy system is only about 10 mass ppm⁽²²⁾. It has also been reported that coarse carbides or nitrides including Ti and B are formed in Ti-added low C steel with 1300 mass ppm of B⁽²³⁾. However, B could hardly be detected in the precipitates from the 0.15 mass% P-added specimens (T4 and T5) with 20 and 40 mass ppm bulk B concentration, respectively, by a chemical analysis⁽²⁴⁾. In the present experiment, furthermore, Ti of 0.04 mass% could stabilize almost all N with a concentration of less than 0.004 mass%. These results indicate that almost all B in the specimens with 20 and 40 mass ppm bulk concentration of B was in the solution state without precipitating. As already mentioned, the concentrations of P and B at the grain boundary depend on the bulk concentration of P. The fracture topographies shown in Table 3 indicate that the intergranular fracture appearance of specimen T3 with a bulk B concentration of 10 mass ppm is only 20%, while that in specimen T1 without B is 100%. This indicates that transgranular fracture was predominant in specimen T3 due to the grain boundary strengthened by segregated B. Furthermore, the scatter in PIR values of P and B to Fe seen in Figs. 4 and 5 occurred because of the difference in segregation sites. All of these results suggest that the apparent independence of GBC for P and B on the bulk concentration of B of more than 10 mass ppm comes from the scatter in the grain boundary strength in the specimen with a high bulk B concentration, in which the grain boundaries strengthened by the highly segregated B would not be easily exposed, only a comparatively weak grain boundary with low segregation of B being fractured and measurable. This is the reason why the GBC of segregated P and B did not apparently change with increasing bulk B concentration in the range of more than 10 mass ppm.

2. Improvement in the secondary workability by B addition

The results already mentioned here lead us to believe

Fig. 7 Relationship between the transition temperature and the difference in coverage of P and B.

that T_{cr} is markedly lowered by adding B to steel. The resistance to secondary working embrittlement is affected by the grain size, yield strength, and such segregated elements as P at the grain boundary⁽²⁵⁾⁽²⁶⁾. Lower yield strength and smaller grain size is more favorable for improving secondary workability, while the yield strength of steel has no dependence on the bulk concentration of B⁽⁹⁾. As can be seen from the SEM image in Fig. 2, the grain size of the specimens without B is rather smaller than that with B, although there was no difference in the grain size of the B-doped specimens with increasing bulk concentration of B. These experimental results indicate that the rise in T_{cr} is attributable to the grain boundary segregation of P. It is well known that, in many alloy steels, P segregates at the grain boundary and reduces the grain boundary cohesion⁽¹⁰⁾. On the other hand, segregants having lower group numbers in the Periodic Table have a lower embrittlement effect⁽²⁷⁾ and B raises grain boundary cohesion in steels⁽⁹⁾ and in Ni⁽²⁸⁾, owing its high negative electrical potential. Figure 7 shows the relationship between T_{cr} and the difference in GBC of P and B, or GBC of P-GBC of B. T_{cr} linearly increase with the increasing difference. This suggests that T_{cr} is lowered by a decrease in P segregation as well as increase in B segregation; that is, P weakens grain boundary cohesion while B strengthens it. T_{cr} is slowly lowered with increasing bulk B concentration in the range of more than 10 mass ppm B, as shown in Table 3, while GBC of P and B at the grain boundary showed little change with increasing bulk B concentration of more than 10 mass ppm. This result can be interpreted as, in a transgranular and intergranular fracture-coexisting surface, the grain boundaries with relatively high P concentration being measurable and, as a result, leading to an overestimation of the average concentration of P at the grain boundary. Therefore, even in the B concentration range of more

than 10 mass ppm, GBC of B actually increases with increasing bulk concentration of B.

V. Conclusions

The segregation of P and B at the grain boundary of extra-low carbon steel sheets containing from 0.01 to 0.15 mass% P and up to 38 mass ppm B was quantitatively examined by means of AES. The following results were obtained:

(1) The grain boundary segregation of P increased with increasing bulk concentration of P after annealing at 1123 K.

(2) The grain boundary segregation of P markedly decreased while that of B increased with the addition of B up to 10 ppm.

(3) No difference in the segregation behavior of P and B was recognized between the specimens annealed at 1123 K for 20 s and those for 500 s. There existed segregation equilibrium between P and B at the grain boundary after annealing at 1123 K for 20 s.

(4) The grain boundary coverage of B was much larger than that of P in the specimens with more than 10 ppm B. The total grain boundary coverage of P and B was constant with a bulk concentration of B of more than 10 mass ppm.

(5) The ductile-brittle transition temperature was linearly reduced with decreasing grain boundary coverage of P and increasing grain boundary coverage of B; this improvement in workability is attributable to the enhanced grain boundary cohesion due to the lower in segregation of P as well as the increase in B at the grain boundary.

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