

ROLE OF NIOBIUM ON THE SEGREGATION BEHAVIOR OF PHOSPHORUS AND MANGANESE IN COLD-ROLLED AND ANNEALED HIGH STRENGTH IF STEELS

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Abstract

Phosphorus and manganese are commonly used to increase the strength of interstitial free (IF) steels for automotive use. However, both phosphorus and manganese will segregate to the grain boundary (GB) of the steel during the annealing process and lead to the problem of secondary work embrittlement (SWE). Surface segregation of manganese also takes place in the annealing process and deteriorates surface property of the steel. In this study, high strength IF steels containing different levels of manganese, phosphorus, boron and niobium were used to investigate the role of niobium on the segregation behavior of manganese and phosphorus in the steel. Atom probe field ion microscopy (APFIM), glow discharge optical emission spectrometry (GD-OES), SEM and XRD were used to achieve this goal. Experimental results showed that manganese competed with phosphorus for the sites in GB of the high manganese IF steels. Site competition between boron and manganese also occurred in the boron-added high strength IF steels containing high level of manganese and phosphorus. The improvement of the SWE resistance of the steel is believed to be partially attributed to the decrease of GB manganese as well. Niobium also segregated to the GB and surface of the steel during the annealing process. Segregation of niobium decreased the GB concentration of phosphorus and the enrichment of manganese on the surface of the steel. The SWE resistance and surface property of the steel could be improved with the addition of niobium accordingly.

Introduction

High strength IF steels added with solid solution strengthening elements such as phosphorus, silicon and manganese are widely used in automotive parts for weight reduction and crashworthiness enhancement. Among these strengthening elements, phosphorus is the most effective element for increasing the strength without compromising the formability of the steel [1-4]. However, the addition of phosphorus in IF steels also leads the problem of SWE due to the segregation of phosphorus at grain boundaries (GBs) of these steels [3-12]. Addition of a small amount of boron helps to improve this problem by the mechanism of site competition between phosphorus and boron atoms at GBs [3, 9, 13-16] and by a direct increase of cohesion/strength of GB as well [3, 14-17]. Segregation of manganese at GB also increases the tendency of brittle fracture to the steel [6, 8, 9]. Besides that, enrichment and selective oxidation of manganese on the steel surface also deteriorates the surface property of the steel [18-22]. Suppression of both

GB and surface segregation of manganese in the high manganese containing IF steel is, therefore, a basic goal for steel makers to reach.

Although the segregation behavior of phosphorus and manganese had been well studied in the literature, discussions on the effect of niobium addition on this issue were not many [7, 11, 23, 24]. The role of niobium on the segregation behavior of phosphorus and manganese in high strength IF steels remains incomplete and needs to be further clarified. Also, most of the GB segregation studies were performed by using Auger electron spectroscopy (AES) in literature. Though it can make quantitative analyses on elements segregated to GBs, the sensitivity of AES is still limited. Analysis of GB segregation of boron-containing steels using AES can also be a problem because the intergranular fracture does not occur easily in these steels. In this case, use of APFIM for the analysis will be more suitable due to not only the field evaporation method it used, but also the unique atomic identification ability it had with the atom probe [25].

In this study, APFIM was applied to investigate the role of niobium on GB segregation behavior of phosphorus and manganese in high strength IF steels. The effect of boron addition on GB segregation behavior of these two elements was also studied. The result is correlated to the SWE properties of the steel. In addition, GD-OES, SEM and XRD were used to examine the surface segregation behavior of alloying elements in the steel. Emphasis was placed on the phenomenon of surface enrichment/oxidation of manganese and the effect of niobium additions on it. The results are discussed and compared with those published in literature.

Experimental Procedures

Materials

Six steel chemistries, identified as steels DQ, High Mn, MnP, MnPB, NbP and NbMnP, respectively, were used in the present study. All these steels were either Ti-stabilized or Ti+Nb-stabilized IF steels with different level of phosphorus and manganese. Steel DQ, with a low level of phosphorus and manganese, was used as the base material for the study. With an increase of the level of phosphorus and manganese and the addition of boron, steels High Mn, MnP and MnPB were produced to examine the effect of phosphorus, manganese and boron and the interactions among these alloying elements. Niobium was added to the NbP and NbMnP steels to further study the effect of niobium on the segregation behavior of phosphorus and manganese in the steel. All steels used in the study were produced by laboratory vacuum melting and casting. Detail compositions of these steels in weight percent (wt.%) are listed in Table I.

Table I. Chemical compositions of the steels used in this study (in wt.%).

Steel	C	Mn	P	S	Nb	Ti	Al	N	B
DQ	0.0018	0.15	0.014	0.0064	-	0.042	0.044	0.0016	-
High Mn	0.0018	0.98	0.014	0.0064	-	0.041	0.043	0.0016	-
MnP	0.0026	1.00	0.072	0.0069	-	0.041	0.050	0.0023	-
MnPB	0.0026	0.99	0.071	0.0069	-	0.040	0.045	0.0023	0.0008
NbP	0.0016	0.14	0.072	0.0067	0.030	0.040	0.041	0.0022	-
NbMnP	0.0016	0.95	0.072	0.0067	0.030	0.030	0.041	0.0022	-

Thermal Mechanical Treatments

Thermal mechanical treatment, including hot rolling, cold rolling and annealing, was carried out in laboratory by the process schematically shown in Figure 1. To simulate the process of hot

rolling, ingots from each steel composition were reheated at 1250°C for 2 hours and followed by roughing, finishing and coiling process simulations. Thickness of the steel ingots was reduced from 43 mm to 5.4 mm after rolling. The finishing temperature (FT) and coiling temperature (CT) of the hot rolling were controlled to be 900°C and 700°C, respectively. The hot-rolled plates were then machined to a thickness of 4.2 mm to clean up the surface scale formed on both sides of the plates. After machining, the hot-rolled plates were cold rolled to a final thickness of 0.8 mm with the reduction ratio of 81%. The cold-rolled sheets were annealed at 830°C for 60 seconds using infrared furnace under a protective atmosphere of 7% H₂ + N₂ gas mixture with a dew point of -60°C.

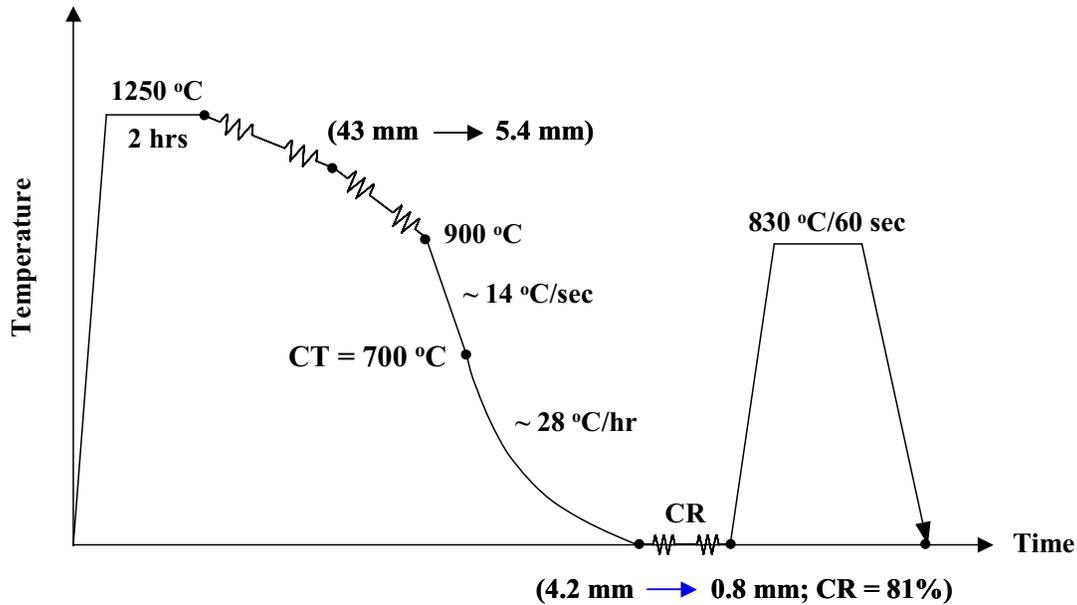


Figure 1. Schematic diagram showing the thermal mechanical process used in this study.

Secondary work embrittlement test

The resistance to the SWE of the annealed steel sheets was evaluated by means of drop weight test. To determine the SWE transition temperature (SWET), the annealed specimens were punched into 66 mm diameter blanks and drawn into 33 mm diameter cups with a drawing ratio of 2.0. Each cup was first laid upside down onto a 60° cone in a tank and held at a predetermined temperature between 0 °C to -80°C for ten minutes. A 10 kg weight was then dropped from a height of 0.5 m onto the cup after the low temperature holding. Three cups were used in each temperature condition of the test. SWET was determined as the highest temperature at which brittle fracture occurred in two of the three cups in test.

Microstructure and segregation behavior examination

Microstructure of the fracture surface of the cup used in the drop weight test was examined by SEM. APFIM was applied to the as-annealed steel samples for the GB segregation behavior investigation. Needle samples prepared by electropolishing were used in the APFIM study. Mass spectrums collected by APFIM from both matrix and GB of the steel were analyzed and compared. Only the GB segregation behavior of phosphorus, manganese, boron and niobium will be discussed in details in this study. To compare the data consistently, the specific intensity of the alloying elements was used in the APFIM study. The specific intensity of the particular alloying element of interest is defined as:

$$\text{Specific Intensity} = I_x/I_{Fe} \quad (1)$$

where I_x is the number of ions of the particular alloy element (such as P, Mn, B and Nb) and I_{Fe} is the number of ions of the major Fe peak ($^{56}Fe^{+2}$ ions) collected by APFIM from matrix or GB of the specimen, respectively. Only the DQ, High Mn, NbP and NbMnP steel samples will be examined to clarify the role of niobium on the GB segregation behavior of phosphorus and manganese and the relative interactions among these elements in the high strength IF steels.

Surface segregation study was carried out by the use of SEM, XRD and GD-OES. To distinguish the role of niobium on this issue, the as-annealed MnP and NbMnP steel samples were used. Both surface morphology and concentration depth profiles of manganese and niobium of these two steels were examined and compared.

Results and Discussion

SWE properties

Table II shows the SWET obtained from the drop weight tests for the steels used in this study. It can be seen from the table that DQ steel, as the base material with low level of phosphorus and manganese, has the lowest SWET of $-80^{\circ}C$. The SWET is increased by the addition of manganese and phosphorus directly. Additions of manganese to a level of 1.0 wt.% in the High Mn steel reduce the SWE resistance of the steel and increase the SWET to a higher value of $-40^{\circ}C$. Further additions of phosphorus deteriorate the embrittling resistance even more, as can be seen from the SWET of $-20^{\circ}C$ found in the MnP steel. The addition of boron leads to a remarkable reduction in the SWET of the steels. With the addition of 8 ppm boron, the SWE resistance of the MnPB steel is greatly improved. The SWET of the MnPB steel is reduced to $-80^{\circ}C$, which shows almost the same anti-SWE property as the DQ steel. The improvement of the SWE resistance can also be seen in steels added with niobium. With the addition of 0.03 wt.% niobium, the NbMnP steel shows a better SWE resistance than the MnP steel. The SWET of the NbMnP steel is $-30^{\circ}C$. The improvement is noticeable as compared with the SWET of $-20^{\circ}C$ found in the MnP steel.

Figure 2 shows typical fracture surfaces on the cup wall of the as-annealed specimens after the drop weight test. As can be seen in the figure, cleavage fracture is the predominant fracture mode that occurred in the DQ steel. Increase of the bulk concentration of manganese in the steel (as in the case of High Mn steel) decreases the fraction of cleavage fracture and leads to the intergranular fracture in the steel. A further increase of the bulk concentration of phosphorus in the steel changes the fracture mode totally into intergranular fracture, as can be seen in the MnP steel. Increase of SWET of the steel is evident as the fraction of intergranular fracture increased in the steel. These results suggest that the increase of SWET correlates directly with the increase of GB fracture in the steel. Additions of boron, on the other hand, have the effect to reduce the intergranular fracture and therefore the SWET of the steel can be reduced as seen in the MnPB steel. The mode of fracture in both of the niobium-added NbP and NbMnP steels is primarily intergranular fracture along ferrite GBs of the steel. However, characters of the cleavage fracture can still be seen in some areas of the fracture surface of these two steels. The decrease of SWET in NbMnP steel is believed to be attributed from the cleavage fracture included fracture mode that occurs in the steel. Since the fracture mode of the steel depends on its GB composition directly, further study on GB segregation of phosphorus, manganese, boron and niobium in these steels is necessary.

Table II. SWE transition temperature of the steels in study.

Steel	DQ High	Mn MnP		MnPB NbP		NbMnP
SWET	-80 °C	-40 °C	-20 °C	-80 °C	-60 °C	-30 o

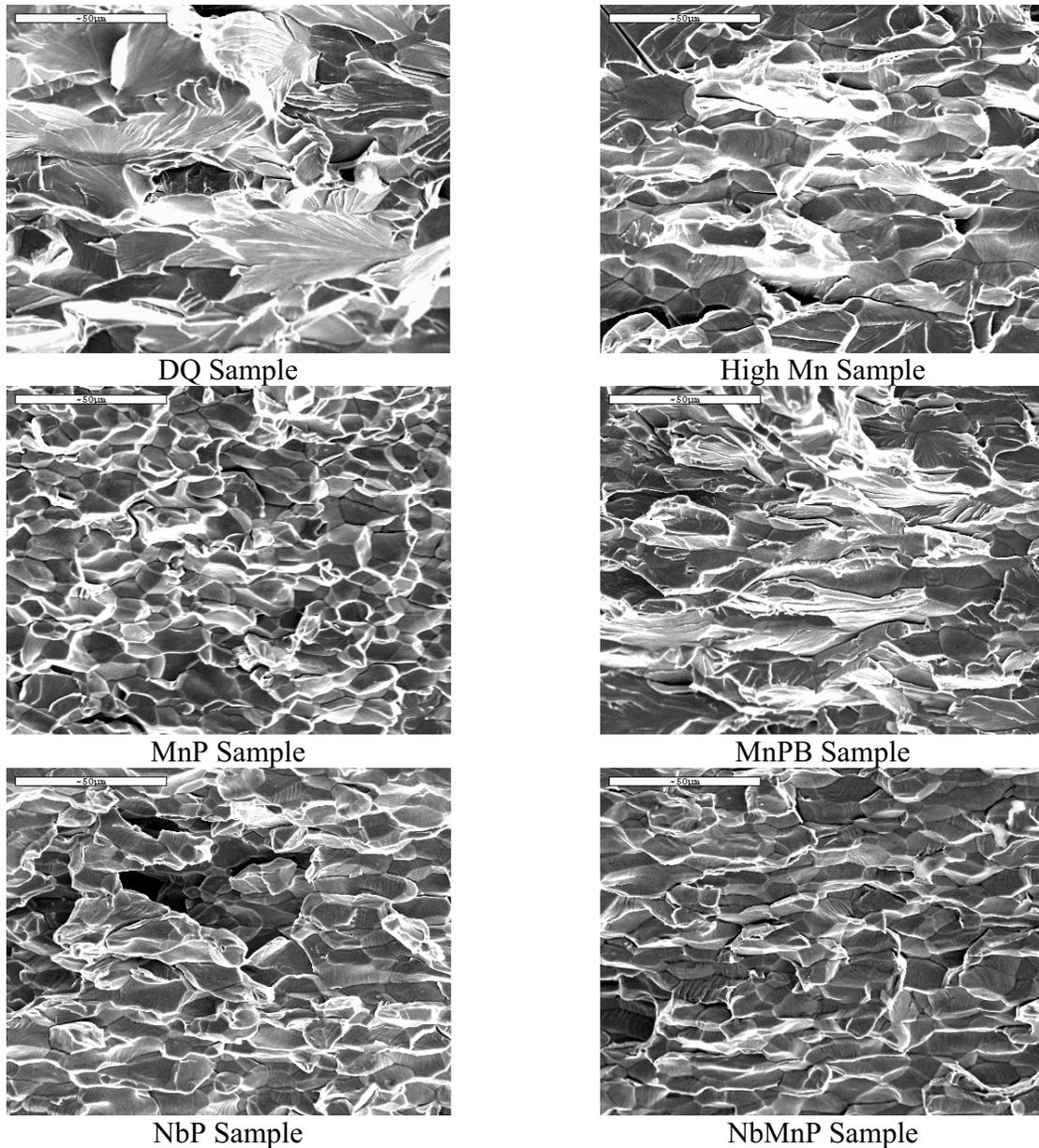


Figure 2. Fracture surfaces on the cup wall of the as-annealed steel samples after the drop weight test.

Grain Boundary Segregation

Figures 3 shows typical APFIM mass spectrums collected from both matrix and GB of the as-annealed DQ steel sample. As can be seen in the figure, GB segregation of phosphorus is evident even in the DQ steel base metal with a bulk concentration of phosphorus as low as 0.014 wt.%. In addition to the GB segregation of phosphorus, segregation of boron and carbon at the boundary are also found in the steel. Boron is the trace element in the DQ steel. Segregation of boron at GB of the steel indicates that it is a strong GB segregation element as reported in

literature [13-17, 25]. Although all the carbon atoms should be theoretically stabilized as precipitates in the DQ steel, experimental results show this is not absolutely true in the real case. K. Seto et al. [25] found a similar result about carbon atoms segregated at GBs of the boron-added IF steels in their study using the three-dimensional atom probe. The result reveals that carbon is also a strong GB segregator and some carbon atoms may remain in solution and segregate to the GB in the IF steel after annealing, even though the steel had been fully-stabilized by the carbon stabilization elements such as titanium and niobium. The ability to detect the extremely small amount of carbon on the GB of these IF steels also shows the enormous advantage of using the APFIM rather than the AES for the study of GB composition analysis. Besides the segregation of phosphorus, boron and carbon at GB of the steel, some solute aluminum and titanium segregated at GBs in the DQ steel. However, the concentration of these elements at the boundary is limited and the effect of these two elements on the SWE property of the steel is also not so significant as phosphorus and manganese. To avoid the complexity of the analysis, the present study will focus on the segregation behavior of phosphorus, manganese, boron and niobium and their interactions only.

Figure 4(a) and (b) show the APFIM mass spectrums collected from GB of both MnPB and NbP steel samples, respectively. Besides the phosphorus found at the boundary, segregation of manganese and boron at GBs of the MnPB steel is also evident as seen in Figure 4(a). The level of boron at GB of the MnPB steel is also found to be much more pronounced as compared it with that found at GB of the DQ steel from the analysis made by APFIM. Segregation of niobium at GBs of the niobium-added steels can be clearly seen in the GB mass spectrum collected from the NbP steel shown in Figure 4(b). The present of niobium at GB of the steel shows the tendency to suppress the segregation of phosphorus to the GB of the steel. To further clarify the effect of niobium on the segregation behavior of phosphorus and the interaction between niobium and other alloying elements, the specific intensity of the phosphorus, manganese, boron and niobium mass spectrums were examined and compared.

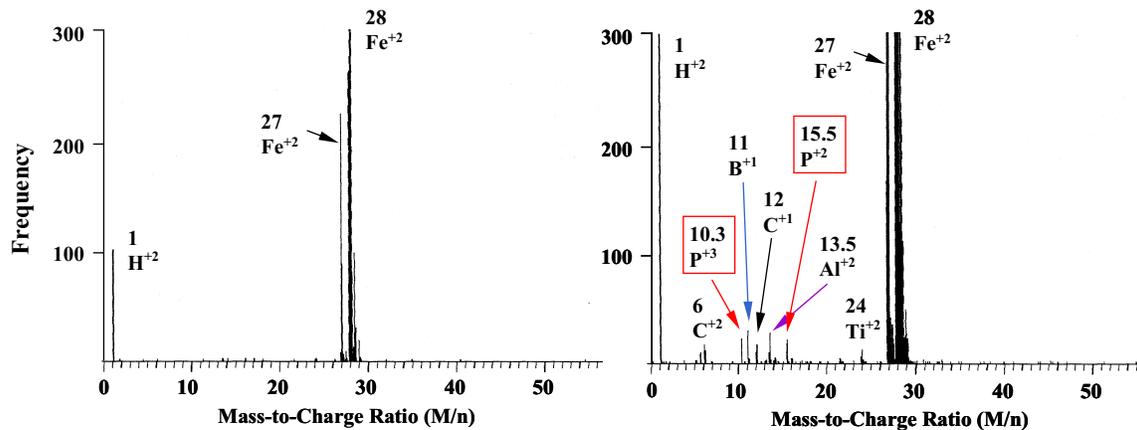


Figure 3. APFIM mass spectra collected from both (a) matrix and (b) GB of the DQ steel sample.

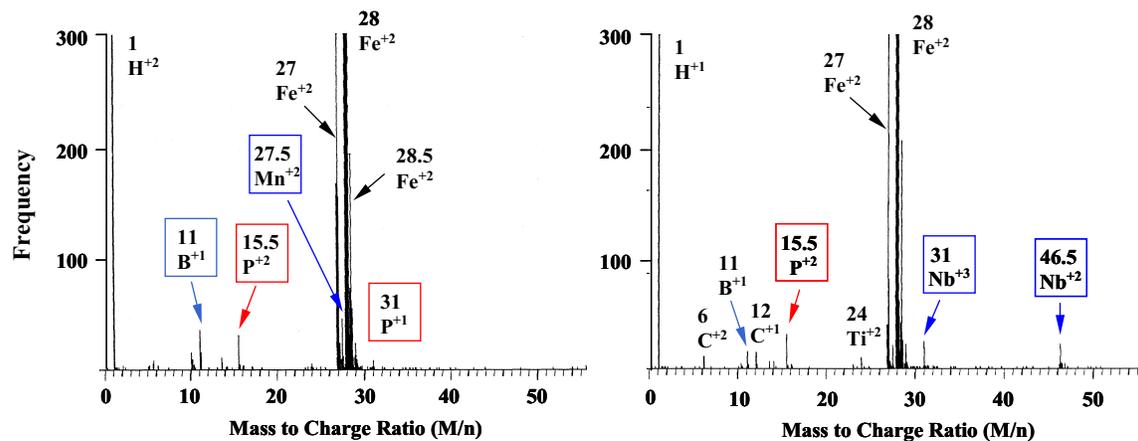


Figure 4. APFIM mass spectra collected from GB of both (a) MnPB and (b) NbP steel samples.

Figure 5 shows the specific intensity of phosphorus, manganese, boron and niobium received from both matrix and GB of the annealed DQ, High Mn, MnPB and NbP steel samples. It can be seen clearly from the figure that segregation of boron at GBs is evident in all these steels. Boron is also the trace element in the High Mn and NbP steels. Segregation of boron at GBs of these steels shows once again that boron is prone to segregate to the boundary of the steel with the annealing treatment. The increase of the specific intensity of manganese at GB of the High Mn steel reveals that the amount of manganese segregated to the GB increases with the increase of bulk concentration of manganese in the steel. It had been reported by D. Y. Lee et al. [6] and Y-Q Weng et al. [8] that segregation of manganese at GBs will reduce the GB cohesive energy and cause GB embrittlement. D. Y. Lee et al. [6] and T. Mega et al. [12] also found that phosphorus and manganese segregate to GB independently in their studies. However, the specific intensity of phosphorus at GB of the High Mn steel seems to be reduced by the increase of GB manganese intensity in this study. The result suggests that site competition between phosphorus and manganese may also occur in the high manganese IF steels with relatively low level of phosphorus in it. Increase of manganese concentration at the boundary is, therefore, responsible for the increase of intergranular fracture and the SWET found in the High Mn steel in study.

The specific intensity of GB boron found in the boron-added MnPB steel is much more pronounced as compared with that observed in the other steels. The result shows that GB segregation of boron is also enhanced by the increase of boron content in the bulk. Although the decrease of GB segregation of phosphorus cannot be sure from the result shown in Figure 4, suppression of manganese segregation at GBs is clearly seen with the addition of boron in the MnPB steel. Suppression of phosphorus segregation at GBs by boron had been well addressed in the literature [9, 12-16]. However, site competition between manganese and boron at GB of the steel is rarely seen. The present study shows that boron competes with manganese for the sites in GBs of the high manganese containing IF steels as well. It had been well known that segregation of boron at the boundary helps to increase GB strength and reduces the tendency of brittle fracture in the steel [3, 14-17]. The result of present study shows that part of the improvement of the SWE in the boron-added high manganese and high phosphorus IF steel may also come from the decrease of manganese segregation at the boundary. The decrease of SWET of the MnPB steel is attributed to the increase of GB strength due to the segregation of boron at the GB and the decrease of GB segregation of phosphorus and manganese, accordingly. To clarify the contribution from each species more precisely, further study of the GB intensity of phosphorus and manganese in the MnP steel will be necessary.

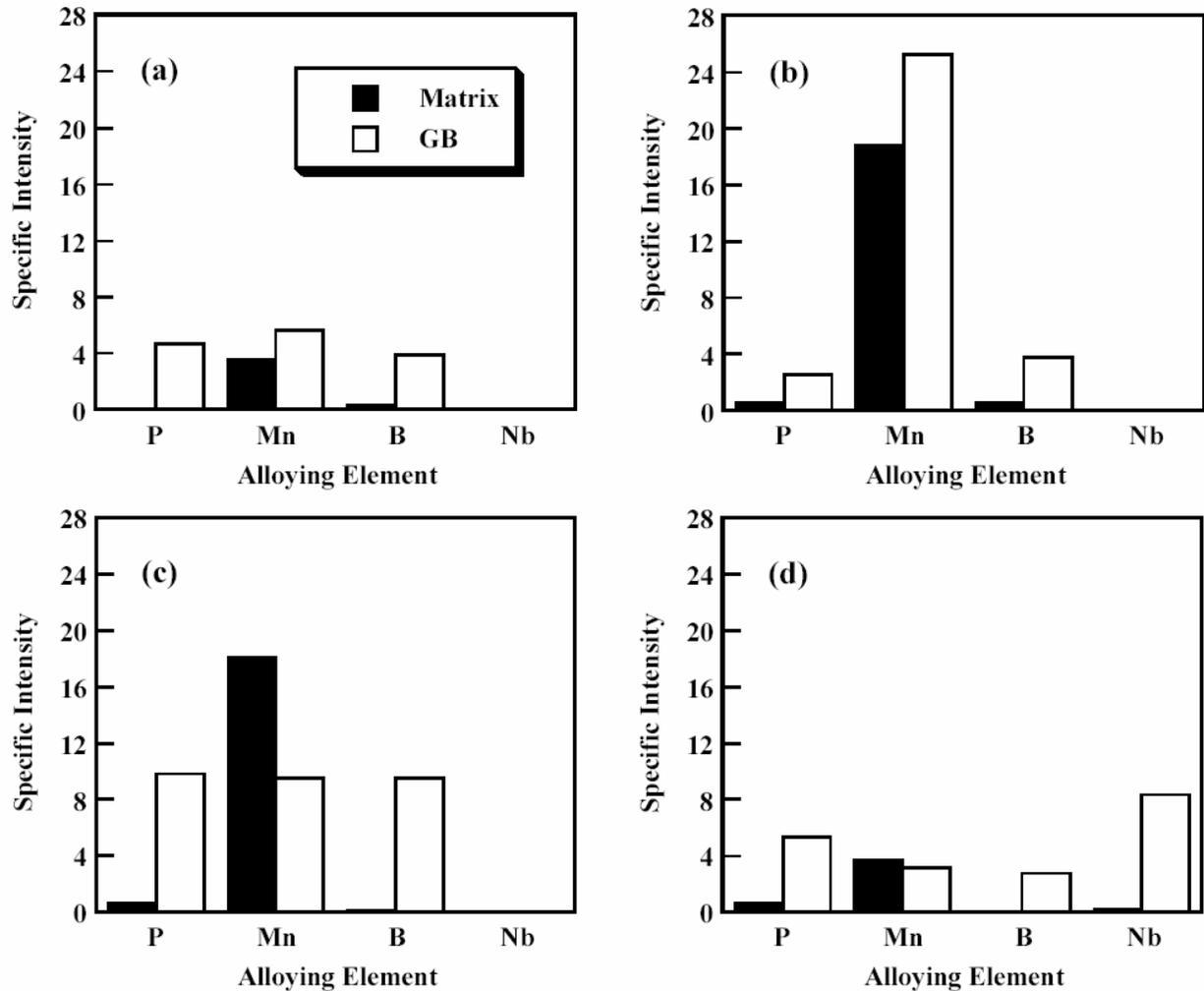


Figure 5. Specific intensity of alloying elements received by APFIM from both matrix and GB of (a) DQ, (b) High Mn, (c) MnPB and (d) NbP steel samples after annealing.

Decrease of the specific intensity of phosphorus in the NbP steel is evident as we compare it with the GB phosphorus intensity of the MnPB steel shown in Figure 4. Experimental results show clearly that niobium segregates to the boundary after annealing and the concentration of GB phosphorus can be markedly reduced due to the segregation of niobium at the boundary. H. J. Grabke et al. [7] considered the decrease of phosphorus segregated at the boundary is due to the formation of NbP precipitates or clusters that occurred during the heat treatment. Other researches [11, 23, 24] suggested that the decrease of GB phosphorus is attributed to the segregation of niobium at the boundary. The fact that the degree of GB phosphorus intensity decrease is approximately equal to the intensity of the segregated niobium at GB of the NbP steel implies that the mechanism proposed by the later researchers is more likely to be true. Besides, the site competition behavior that occurs between boron and manganese in the MnPB steel, the same phenomenon is also found in the NbP steel between niobium and phosphorus. The size of niobium atoms is larger than that of iron atoms. Segregation of niobium to the boundary will help to reduce the Gibbs free energy of the material. This may be the reason for the GB segregation behavior of niobium found in these steels after annealing. It had been reported by J. S. Rege et al. [11] that presence of niobium on the ferrite GBs will help to increase the GB cohesion and improve the SWE property of the steel. The slight improvement of the SWE resistance of the NbP and NbMnP steels found in this study shall be attributed to the increase of

GB strength and the decrease of GB phosphorus, due to the segregation of solute niobium at the boundary, accordingly.

Surface segregation

Besides the site competition effect on the GB segregation behavior of phosphorus, niobium also alters the surface segregation behavior of manganese in the high manganese IF steels as well. Figure 6 shows the as-annealed surface microstructure of both MnP and NbMnP steels. As can be seen in the figure, formation of small oxide particles is evident on the surface of both steels. EDS analysis (Figure 7) and the study made by XRD (Figure 8) show that these surface oxides are basically the MnO particles. Though the MnO particles formed on both two steels, the amount of oxide particles found on the surface of these two steels is not the same. It can be seen clearly that the number of the surface MnO particles formed in the niobium-added NbMnP steel is much less than that formed in the MnP steel. The result indicates that the addition of niobium in the manganese-containing IF steel has the effect on suppressing the formation of manganese oxides on the surface of the steel during the annealing process. GD-OES analysis shows that the surface segregation/enrichment behavior is also not the same in both steels. Figure 9 shows the GD-OES depth profiles of manganese and niobium obtained from both MnP and NbMnP steels. It is evident that segregation/enrichment of manganese occurs at the surface and sub-surface of both two steels. However, the level of the manganese segregation/enrichment is slightly different. NbMnP steel, containing niobium, shows a little bit less surface segregation/enrichment of manganese as compared with that of the MnP steel without the addition of niobium.

Besides the segregation of manganese at the surface of the NbMnP steel, segregation of niobium is also found at the surface of the steel. The same phenomenon of niobium enrichment on the surface of the steel had been reported by I. Hertveldt et al. [18] in their study carried out with the high strength TiNb IF steels after annealing. The present result indicates that segregation of niobium at the surface of the niobium-containing steels should be the reason for the less enrichment of manganese and less MnO particles formed on the surface of the steel. The result implies that site competition between niobium and manganese atoms may also occur on the free surface of the NbMnP steel. It is well known that the formation of MnO oxide particles on the surface will degrade the surface property of the steel and bring the problem of bare spots on the coating surface of the steel after galvanizing [18-22]. Improvement of Zn wettability on the surface of the steel can, therefore, be expected in the manganese containing high strength IF steels with the addition of niobium.

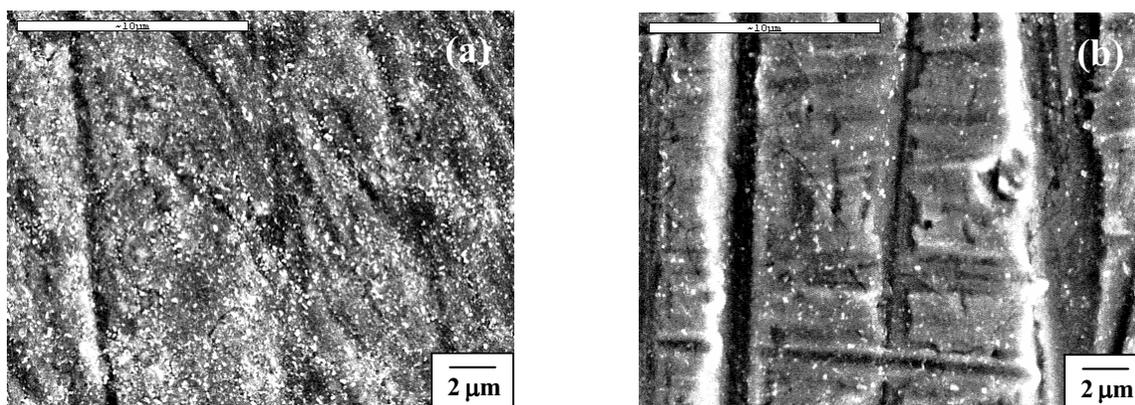


Figure 6. Surface microstructure of the as-annealed (a) MnP and (b) NbMnP steel samples.

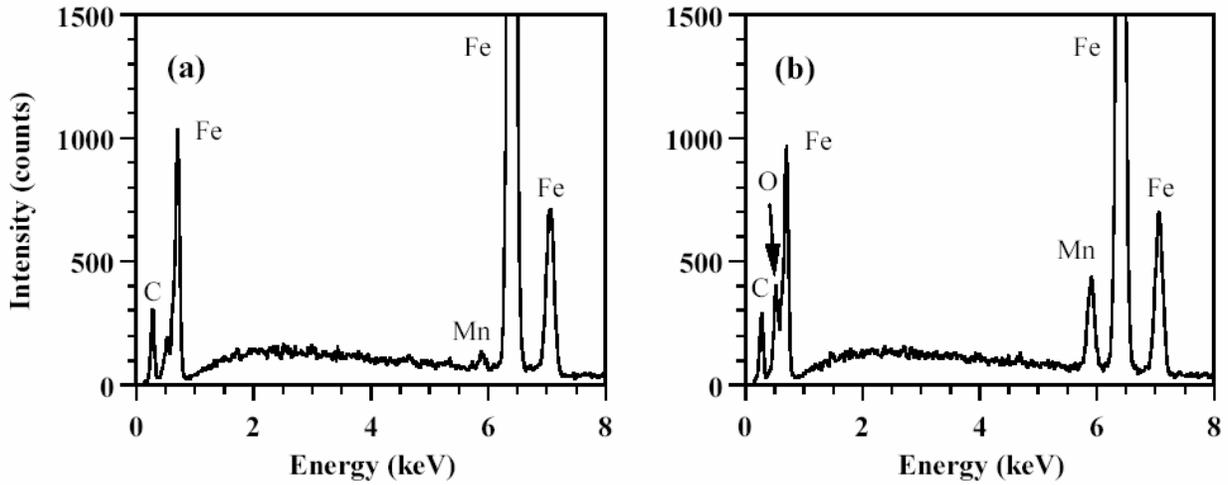


Figure 7. Results of EDS analysis from both (a) matrix and (b) oxide particles formed on the surface of MnP and NbMnP steel samples after annealing.

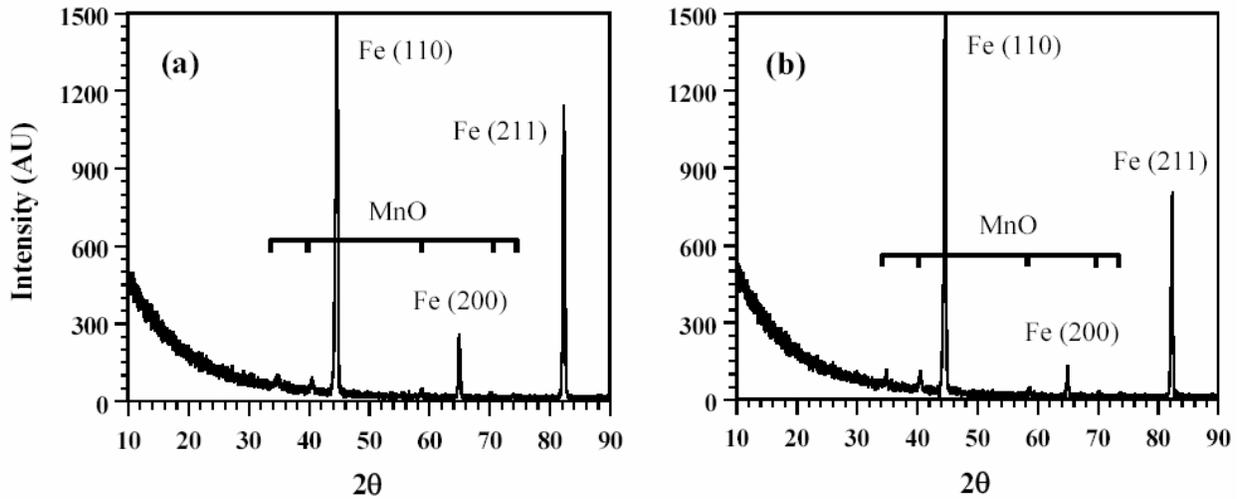


Figure 8. Results of XRD analysis on the surface of both (a) MnP and (b) NbMnP steel samples after annealing.

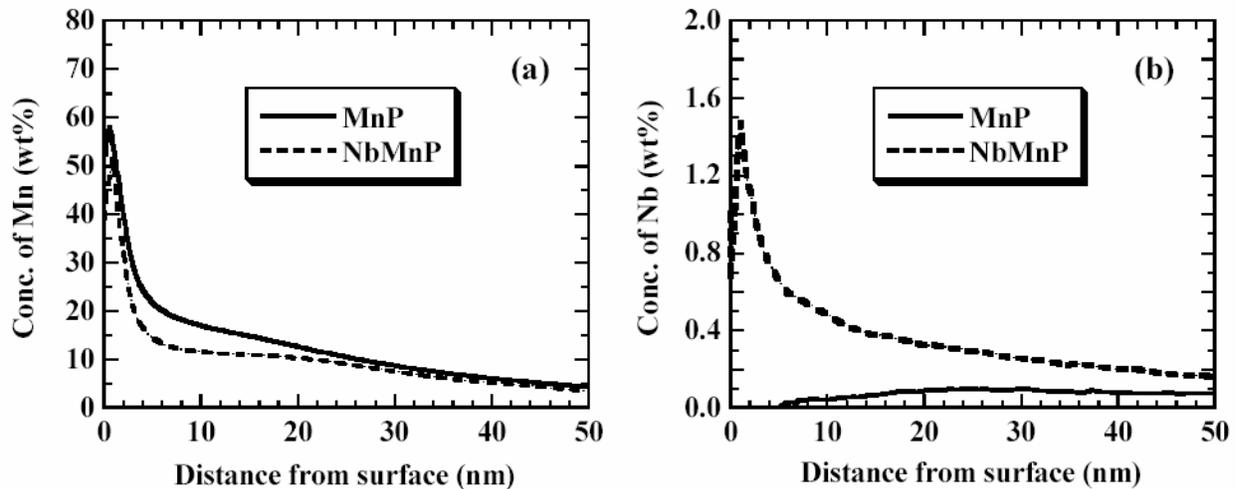


Figure 9. GD-OES depth profiles showing (a) Mn and (b) Nb distribution in the as-annealed MnP and NbMnP steel samples.

Conclusion

1. Phosphorus and manganese are prone to segregate to GBs of the high strength IF steels after annealing. The segregation of phosphorus and manganese at the boundary increases with the increase of bulk concentration of these two alloying elements. The SWE resistance of the steel is reduced as the GB concentration of phosphorus and manganese increases.
2. Site competition between manganese and phosphorus was observed in the study. Segregation of manganese at the boundary can lead to the decrease the GB phosphorus in the high strength IF steels contained with high level of manganese and low level of phosphorus. High levels of manganese at the boundary are also deleterious to the SWE property of the steel.
3. Boron is a strong GB segregation element. It was found that site competition between boron and manganese also occurred in the manganese and high phosphorus IF steels added with boron. The improvement of the SWE resistance of the steel is attributed to the decrease of GB manganese and the increase of GB strength due to the segregation of boron at the boundary.
4. Niobium segregates to GB and the surface of the steel by the annealing treatment as well. Segregation of niobium decreases the GB concentration of phosphorus and the level of surface enrichment/segregation of manganese in the high strength IF steels with high level of phosphorus and manganese. The SWE resistance and the surface property of the steel can be improved with the addition of niobium accordingly.

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