

Effect of B on Surface Oxidation Behavior and Phosphatability of Cold-Rolled High-Strength Steel Sheets

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Abstract:

The effect of B on the surface oxidation behavior and phosphatability of cold-rolled steel sheets was investigated using 0.001 wt% B-added and B-free steels containing 0.6 wt% Si and 2.0 wt% Mn. The specimens were annealed at 800 °C in a 5 vol% H₂-N₂ atmosphere with a dew point of -50 °C. In the initial stage of annealing, fine granular Mn₂SiO₄ mainly formed and film-like SiO₂ partly formed on both steels. As annealing time increased, Mn₂SiO₄ simply increased in the B-free steel, whereas in the B-added steel, Mn₂SiO₄ coarsened and MnSiO₃, MnO, and B₂O₃ formed, with an expanded area of film-like SiO₂. B addition caused Si and Mn oxides to melt and combine, exposing the base steel and generating local inhomogeneity in oxygen potential, thereby changing oxidation behavior. Furthermore, the coarse Mn₂SiO₄ and expanded film-like SiO₂ on the B-added steel surface deteriorated its phosphatability.

1. Introduction

Application of high-strength steel sheets to automobile body components is contributing to reduction of CO₂ emissions through improved fuel efficiency, while also enhancing automobile collision safety¹⁾. In addition to high strength, excellent formability is also required in high-strength steel sheets since many automobile body components have complex shapes. To achieve the required balance of strength and formability, various alloying elements are added to the steel, and the steel microstructure is controlled by heat treatment. High-strength steel sheets often contain alloying elements such as Si, Mn, and B in addition to C, and it

is known that these elements influence not only mechanical properties but also surface properties²⁻⁸⁾. Recrystallization annealing for microstructure control is generally performed in an atmosphere of 3 to 20 vol% H₂-N₂, which is a reducing atmosphere for Fe. In this process, easily oxidizable elements such as Si, Mn, and B, which have lower equilibrium oxygen partial pressures than Fe, are selectively oxidized in the annealing furnace atmosphere and form oxides on the steel surface⁹⁻¹⁸⁾.

These surface oxides are known to deteriorate reactivity in zinc phosphate treatment²⁻⁴⁾, which is commonly used as a pretreatment for automotive painting¹⁹⁾. For instance, Nomura et al. reported that a high Si/Mn ratio in Si-Mn-containing steel sheets leads to the formation of a film-like silicon oxide, which subsequently reduces phosphatability³⁾. Masuoka et al. also reported that the formation of coarse Mn oxides results in a decrease in phosphatability, even in Mn-based steel sheets without Si⁴⁾. Therefore, understanding the surface oxidation behavior of Si and Mn is crucial for producing high-strength steel sheets with favorable phosphatability.

It has been reported that addition of B in combination with Si and Mn can influence the surface oxidation behavior of these elements^{4,9,10,13)}. Suzuki et al. reported that addition of B to Mn-containing steel sheets changes the morphology of Mn oxides⁹⁾, and B addition in Si-Mn-containing steel sheets promotes the spheroidization of Si-Mn complex oxides and enhances their surface enrichment¹⁰⁾. Both of these phenomena are considered to be caused by lowering of the oxide melting point due to the combination of Si and Mn oxides and B oxides. As an element that enhances hard-

[†] Originally published in *JFE GIHO* No. 57 (Feb. 2026), p. 21–27

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enability, B is effective for microstructural control in high-strength steel sheets and is often added to steel together with Si and Mn. However, few studies have examined the surface oxidation behavior of steels with combined Si-Mn-B addition, and no studies have investigated the effect of combined addition on phosphatability.

Therefore, in this study, the changes in surface oxidation behavior caused by B addition and their effects on phosphatability were investigated to clarify the effect of B on the surface properties of steels with combining addition of Si and Mn.

2. Experimental

The chemical compositions of the specimens used in this experiment are shown in **Table 1**. The test steel was cold-rolled to a thickness of 1.4 mm, and test pieces measuring 70 mm × 170 mm were cut out. The test pieces were subjected to anodic electro-degreasing in a 3 mass% NaOH aqueous solution at 70°C at a current density of 12 A·dm⁻² for 30 s, followed by immersion in a 5 mass% HCl aqueous solution for 5 s to clean the surface, and then used in the annealing experiment.

The annealing experiment was carried out in an infrared heating furnace with an atmosphere controlled to 5 vol% H₂-N₂ and a dew point of -50°C. The test pieces were first heated from room temperature to 800°C at a heating rate of 10°C·s⁻¹, followed by soaking for 1 s to 324 s, and then cooled to room temperature using N₂ gas.

The elemental concentration profiles in the depth direction were measured on the annealed steel surface using a glow discharge optical emission spectrometer (GD-OES). Glow discharge sputtering was performed at a gas pressure of 600 Pa and an output power of 35 W with a sputtering rate of 60 nm·s⁻¹ for Fe. Oxides were identified by high-sensitivity reflection adsorption spectroscopy in a Fourier transform infrared spectrometer (FT-IR) at an infrared ray incidence angle of 85°. Surface observation was also performed using a low-voltage scanning electron microscope (LV-SEM) at an acceleration voltage of 1 kV, and elemental analysis was performed using an energy dispersive X-ray spectrometer (EDX) attached to the LV-SEM at an acceleration voltage of 3 kV. 45° cross sections of the annealed steels subjected to soaking for 324 s were prepared with a focused ion beam (FIB) apparatus, and were

observed using the same LV-SEM at an accelerating voltage of 1 kV.

The annealed steels were subjected to zinc phosphate treatment using a commercially available titanium-based surface conditioner and a zinc phosphate treatment agent, which are commonly used in pretreatment for automotive painting. The test pieces were immersed in the surface conditioning solution at 25°C for 30 s, followed by immersion in the phosphating solution at 40°C for either 15 s or 120 s, and then rinsed with water and dried. After phosphating, crystal nucleation in the initial stage of the reaction was observed in the specimens immersed for 15 s, while crystal coverage at the end of the reaction was examined in the specimens immersed for the standard duration of 120 s. These observations were performed using a scanning electron microscope (SEM) at an accelerating voltage of 15 kV. Areas of the specimens where no crystal formation was observed after 15 s of immersion were examined using the LV-SEM at an acceleration voltage of 1 kV.

3. Results

3.1 Surface segregation behavior during annealing process

The depth profile of the elements in the specimens after annealing is shown in **Fig. 1**. In the B-added steel, peaks of Si, Mn, and B were observed on the surface, and the peak areas increased with soaking time. This indicates that Si, Mn, and B segregated to the steel surface during annealing, and their amounts increased with soaking time. Peaks of Si and Mn were also observed on the surface of the B-free steel, and the peak areas increased with soaking time, confirming that soaking promotes surface segregation of Si and Mn and an increase in the amounts of the segregated elements. At a soaking time of 1 s, the peak shapes of Si and Mn were similar in the B-added steel and the

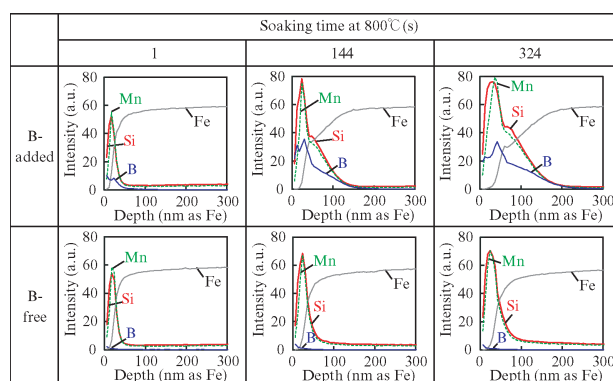


Fig. 1 GD-OES depth profiles of annealed steel surface

Table 1 Chemical composition of the specimen (mass%)

Steel	C	Si	Mn	P	S	B
B-added	0.17	0.59	2.01	0.014	0.0007	0.0010
B-free	0.17	0.59	2.01	0.015	0.0005	—

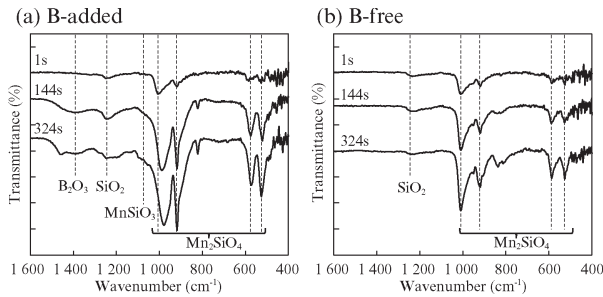


Fig. 2 FTIR spectra of annealed steel surface

B-free steel. However, at soaking times of 144 s or longer, the peaks of Si and Mn were higher and extended to a deeper region in the B-added steel, indicating that surface segregation of Si and Mn at 800°C was enhanced by B addition.

The FTIR spectra of the annealed specimens are shown in Fig. 2. In the B-added steel in Fig. 2 (a), strong peaks attributed to Mn_2SiO_4 at 520 to 1 000 cm^{-1} and a weak peak attributed to SiO_2 at 1 230 cm^{-1} were observed at all soaking times^{10,20}. In addition, at soaking times of 144 s or longer, a small shoulder peak²⁰ attributed to MnSiO_3 at 1 100 cm^{-1} and a broad peak²¹ attributed to B_2O_3 around 1 400 cm^{-1} were observed. The intensity of each peak increased with soaking time, suggesting that the amounts of the oxides increased during soaking at 800°C. In the B-free steel in Fig. 2 (b), peaks attributed to Mn_2SiO_4 and SiO_2 were observed, but peaks attributable to MnSiO_3 and B_2O_3 were not detected. The peak intensity attributed to Mn_2SiO_4 increased with soaking time, while intensity attributed to SiO_2 was almost constant regardless of soaking time. This indicates that the amount of Mn_2SiO_4 increased during soaking at 800°C in the B-free steel, while the amount of SiO_2 remained unchanged.

3.2 Distribution and composition of surface oxides

Figure 3 shows the surface SEM images and elemental maps of O, Mn, Si, and B in the same field of view of the annealed B-added steel at various soaking times. At a soaking time of 1 s, the SEM image shows fine granular or mesh-like regions with a grain size of about 100 nm, together with relatively flat regions. In the elemental maps, O, Mn, and Si are distributed in granular and mesh-like patterns, which correspond to the morphologies observed in the SEM image. This indicates that Si-Mn complex oxides formed in the granular or mesh-like regions. In the relatively flat areas, the low presence of Mn and detection of O and Si suggest formation of Si oxides. At 144 s, the SEM image shows a region containing coarse granular substances with a

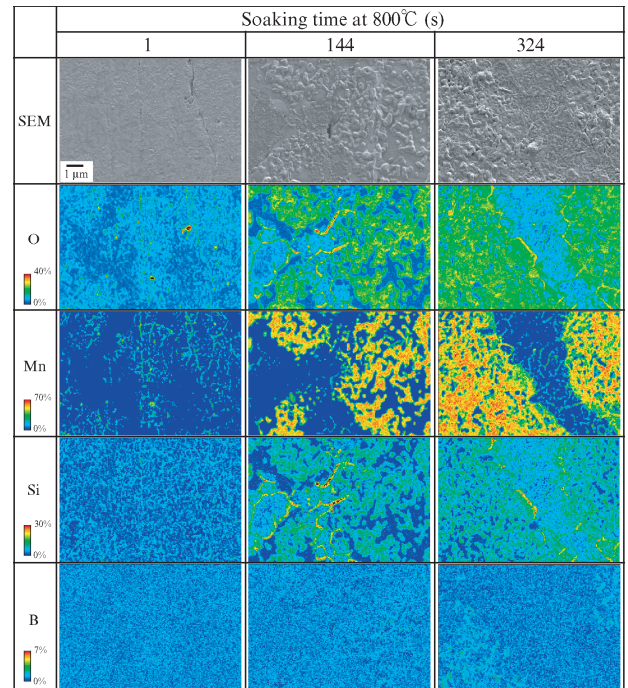


Fig. 3 SEM image and EDS elemental map of B-added steel

grain size of about 500 nm, as well as a region containing film-like layers with fine irregularities. The elemental maps indicate that the coarse granular substances are Si-Mn complex oxides, as they contain O, Mn, and Si, while the film-like layers were identified as Si oxides, since only O and Si were detected. Similarly, at 324 s, a region where coarse granular substances with a particle diameter of about 500 nm were present and a region covered with filmy layers with fine irregularities were confirmed from the SEM image. However, compared to the features observed at 144 s, the granular substances were more densely packed, with almost no gaps. From the elemental maps, the regions of densely-packed coarse granular substances included not only particles containing O, Mn, and Si, but also some particles containing O, Mn, and B. This suggests the formation of Mn-B complex oxides in addition to Si-Mn complex oxides. In the areas covered by the film-like layers, O and Si were detected, indicating that these layers are Si oxides.

Figure 4 shows the surface SEM images and elemental maps of O, Mn, Si, and B in the same field of the annealed B-free steel. As in the B-added steel in Fig. 3, at 1 s, the SEM image shows fine granular or mesh-like regions with a grain size of about 100 nm, which correspond to the mesh-like distribution of O, Mn, and Si in the elemental maps. The other regions were relatively flat. In these regions, the elemental maps indicated a low presence of Mn, but O and Si were detected. Therefore, at 1 s, Si-Mn complex oxides formed in the fine granular or mesh-like regions, while Si oxides

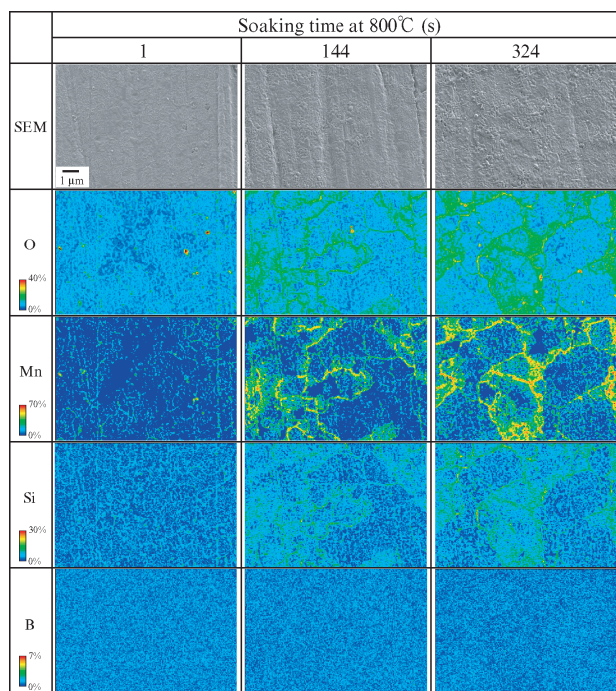


Fig. 4 SEM image and EDS elemental map of B-free steel

formed in the relatively flat areas. This is similar to the behavior of the B-added steel. On the other hand, at 144 s, the SEM image shows mesh-like structures composed of interconnected particles with diameters of about 100 nm to 200 nm, which covered almost the entire surface. The surface morphology was different from that of the B-added steel in Fig. 3. In the elemental maps, the mesh-like distribution of O, Mn, and Si indicates the formation of Si-Mn complex oxides. A similar surface condition was also observed even at a soaking time of 324 s.

Figure 5 shows 45° cross-sectional backscattered electron (BSE) images of a region which is densely packed with granular oxides and a region covered with

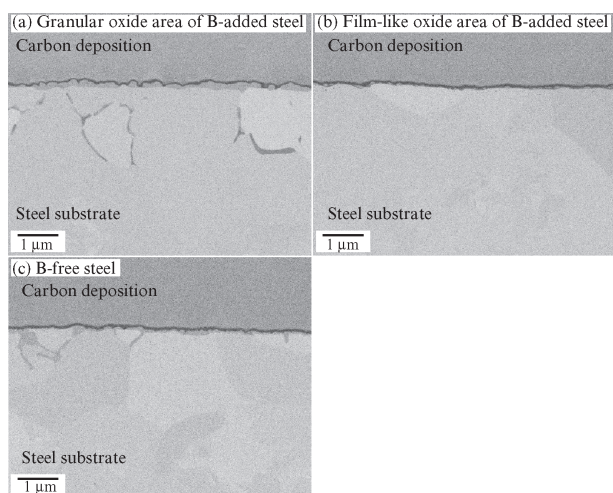


Fig. 5 45° cross-sectional BSE image of steel surface

a film-like oxide in the B-added steel, as well as a region with a network-like oxide formed in the B-free steel, in both cases after soaking for 324 s. In the BSE images, the contrast corresponds to the atomic number, and oxides containing lighter elements such as O show a darker contrast compared to the base steel. In the region of the B-added steel containing densely packed granular oxides in Fig. 5 (a), granular oxides were observed on the steel surface, and internal oxidation along the grain boundaries was confirmed at a depth of up to 2 μm from the surface. In the film-like oxide formation region of the B-added steel in Fig. 5 (b), only a thin film-like oxide was observed on the surface, and almost no internal oxide was present in the subsurface region. In the region with a network-like oxide formed in the B-free steel in Fig. 5 (c), granular oxides were present on the surface, and internal oxidation was observed in region having a depth of about 1 μm inward from the steel sheet surface.

3.3 Results of phosphatability evaluation

Figure 6 shows surface SEM images after the annealed steels were phosphated for an immersion time of 120 s. In the case of the B-added steel with a soaking time of 1 s during annealing, the entire steel sheet surface was covered with zinc phosphate crystals with a grain size of about 5 μm, indicating good phosphatability. However, at 144 s, a region covered with fine zinc phosphate crystals with a grain size of about 2 μm and a defective part where the crystals did not completely cover the surface were observed. At a soaking time of 324 s, the grain size of the crystal had coarsened to about 10 μm, and the area of the defective part had also increased. In the B-free steel, the entire surface was covered with crystals with a grain size of about 5 μm regardless of the soaking time during annealing, indicating satisfactory phosphatability.

Figure 7 shows the surface SEM images of the B-added steel when the immersion time during phosphating was shortened to 15 s. Zinc phosphate crystals with a grain size of about 2 μm formed sparsely over

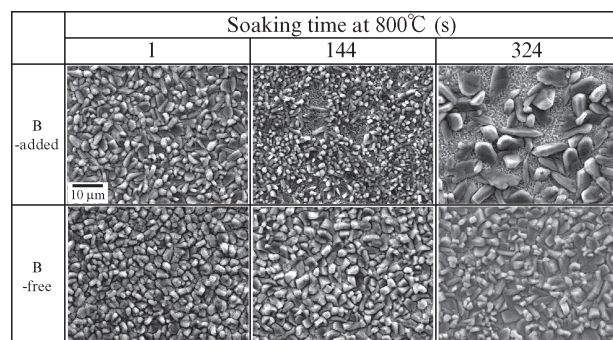


Fig. 6 SEM image of steel after phosphate treatment for 120 s

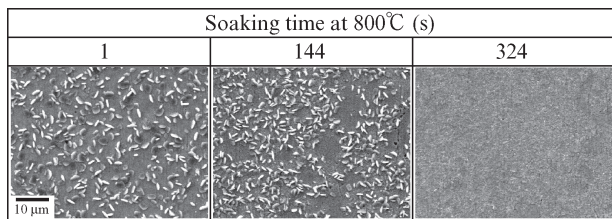


Fig. 7 SEM image of B-added steel after phosphate treatment for 15 s

the entire steel surface with a soaking time of 1 s during annealing. However, with a soaking time of 144 s, the steel displayed both regions where crystals having a grain size of about 2 μm had densely formed, and regions where crystal formation was slight. At 324 s, almost no crystals were formed.

4. Discussion

4.1 Effect of B on oxide formation behavior during annealing

From the SEM images and elemental analysis results shown in Figs. 3 and 4 and the FTIR spectra shown in Fig. 2, the formation of fine-grained or network-like Mn_2SiO_4 and film-like SiO_2 on the steel surface was observed independent of B addition at 800°C with a soaking time of 1 s. This means that B had little influence on oxide formation behavior in the initial stage of annealing. As the soaking time increased, only formation of Mn_2SiO_4 increased in the B-free steel. Although formation of Mn_2SiO_4 also increased in the B-added steel, formation of several kinds of oxides, such as MnSiO_3 , B_2O_3 , and Mn-B complex oxides, and the growth of film-like SiO_2 were also observed, indicating that the presence of B had a significant influence on the growth behavior of surface oxides. The following discusses the mechanism of the influence of B on the formation and growth of such oxides.

Regarding the effect of B addition on the morphology and distribution of oxides formed during annealing, it has been reported that Mn oxides that form on the surface of Mn-containing steel coarsen into a spherical shape due to B addition^{4,9)}. This is attributed to oxidation of B on the steel surface during annealing, forming B_2O_3 , which then combines with the Mn oxide to lower the melting point, resulting in melting and bonding of the oxides. It has also been reported that addition of B lowers the melting point of the oxides in Si-Mn-containing steel, leading to coarsening into a spherical shape, as in the case of Mn-containing steel¹⁰⁾. In the present study, it is therefore inferred that the SiO_2 and Mn_2SiO_4 which formed in the initial stage of annealing melted and bonded together, leading to

the subsequent growth of coarse granular Mn_2SiO_4 during soaking. However, in this experiment, not only coarsening of Mn_2SiO_4 particles, but also formation of MnSiO_3 and Mn-B complex oxides and an increase in film-like SiO_2 occurred. This behavior cannot be explained only by lowering of the melting point by B.

From the results of the cross-sectional analysis shown in Fig. 5, it can be observed that oxide formation extended into the subsurface region directly below the granular oxide of the B-added steel, whereas internal oxidation did not occur below the film-like oxide. It is known that internal oxidation is promoted when the oxygen potential in the annealing atmosphere is high^{12,14,15)}. In this experiment, a difference in the internal oxidation behavior was observed in the same steel sheet, suggesting that a difference in the local oxygen potential occurred. When the steel surface is covered with oxides, diffusion of oxygen is inhibited by the presence of those oxides, reducing the oxygen potential at the steel surface. In contrast, when no oxides exist and the steel surface is exposed to the atmosphere, the oxygen potential remains relatively high. In the regions where granular oxides formed on the B-added steel, the reduction of the melting point by B causes the oxides to melt and bond together, resulting in coarsening and localized exposure of the steel surface. As shown in Fig. 3, after soaking for 324 s, almost the entire surface of the B-added steel was covered with oxides. However, after soaking for 144 s, the steel surface was exposed around the coarse oxides, where the oxygen intensity was low, suggesting that internal oxidation was promoted by the high oxygen potential during exposure of the steel surface around the coarse oxides. On the other hand, since SiO_2 forms a dense protective oxide layer²²⁾, the oxygen potential on the steel surface directly under the film-like SiO_2 is low. As shown in Fig. 3, because the film-like SiO_2 formed even at a soaking time of 1 s, a low oxygen potential state was maintained from the initial stage of annealing, suppressing the progress of internal oxidation.

Figure 8 shows the relationship between the oxygen potential for the formation of the various oxides that can form on the steel surface in this experiment and temperature. The annealing condition in this experiment was a dew point of -50°C in a 5 vol% H_2 - N_2 atmosphere, corresponding to $\log(p\text{H}_2\text{O}/p\text{H}_2)$ of -2.9. Therefore, when the steel surface is exposed to the atmosphere, all of the oxidation reactions shown in Fig. 8 can proceed. In the initial stage of annealing, the most easily oxidized element, Si, is oxidized to form SiO_2 on the steel surface¹²⁾, followed by the formation of MnSiO_3 and Mn_2SiO_4 . Coverage of the steel surface by these oxides results in a decrease in the apparent oxygen potential.

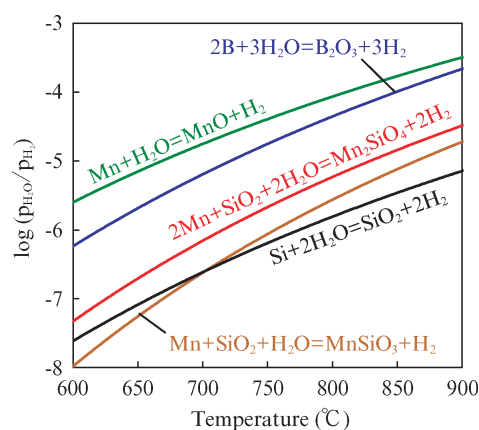


Fig. 8 Equilibrium $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ of various oxides on the B-added steel with annealing in $\text{H}_2\text{-H}_2\text{O}$ mixed gas atmosphere

From the FTIR spectrum in Fig. 2 (b) and the SEM-EDS analysis in Fig. 4, it can be seen that SiO_2 formed in the initial stage of annealing in the B-free steel, and then rapidly transformed into Mn_2SiO_4 as it grew. As the soaking time increased, the amount of Mn_2SiO_4 increased, and the surface was covered with net-like Mn_2SiO_4 , which lowered the apparent oxygen potential. Under this apparent oxygen potential, Mn_2SiO_4 formed preferentially instead of MnO , and the growth of Mn_2SiO_4 is considered to have continued. At this stage, since the diffusion rates of Si and Mn are higher along the grain boundary than within the grains, a network-like structure is formed due to the accumulation of a large amount of oxide along the grain boundaries. In the B-added steel, formation of SiO_2 and transformation into Mn_2SiO_4 also occur in the initial stage of annealing, as in the B-free steel, while the formation reaction of B_2O_3 also proceeds simultaneously. As mentioned above, B_2O_3 lowers the melting point of the surrounding Mn_2SiO_4 , leading to melting and bonding of the oxides, and this causes grain coarsening, which results in localized exposure of the base steel. In the regions where the base steel is exposed, the apparent oxygen potential becomes high, resulting in formation of MnO . Formation of MnO and Mn-B complex oxides consumes Mn, leading to the formation of MnSiO_3 , which has a lower Mn content than Mn_2SiO_4 , in the surrounding areas. In contrast, in the region covered with SiO_2 , the apparent oxygen potential is low, and Mn is consumed by the formation of MnO and Mn-B complex oxides in adjacent areas, creating a Si-rich state that promotes the growth of SiO_2 . In this way, in the B-added steel, the formation of heterogeneous oxides progresses due to the localized distribution of the oxygen potential on the steel surface during annealing.

4.2 Effect of surface oxides on phosphatability

To investigate the relationship between the oxides formed on the B-added steel and its phosphatability, the steel surface of the annealed B-added steel before and after phosphating for 15 s was observed in detail. **Figure 9** shows the SEM images. The image for a soaking time of 1 s highlights the network-like regions, while the images at 144 s and 324 s focus on areas of coarse oxide formation. At a soaking time of 1 s, after phosphating, recesses were observed as gaps in the network-like oxides, indicating that the exposed steel surface had dissolved. Similarly, at 144 s, the base steel had also dissolved around the granular oxides. The formation reaction of zinc phosphate crystals proceeds driven by the increase in the surface pH resulting from dissolution of the steel¹⁹⁾. At a soaking time of 1 s, the dissolution reaction occurs on the exposed steel surface at gaps in the network-like oxides distributed over the entire surface. As shown in Fig. 7, this results in the formation of sparsely-distributed crystals on the surface after phosphating for 15 s. The dissolution reaction at the exposed steel surface continues until the surface is covered with crystals. As shown in Fig. 6, after 120 s of phosphating, the entire surface is covered with crystals. At a soaking time of 144 s, the dissolution reaction also occurs at the exposed steel surface surrounding the granular Si-Mn complex oxides, leading to the formation of zinc phosphate crystals. In the regions where the granular Si-Mn complex oxides are coarsened due to B and the surface area of the exposed steel increases, zinc phosphate crystals form more densely than at a soaking time of 1 s, as shown in Fig. 7. However, in the regions covered with the film-like Si oxides, crystal formation does not occur because the substrate steel surface is almost entirely unexposed. In this region, dissolution of the steel does not occur even with an extended phosphating time, and as a result, the defect areas remain uncovered by crystals after 120 s of treatment, as shown in Fig. 6. At a soaking time of 324 s, Fig. 9 shows that the density of granular oxides is high

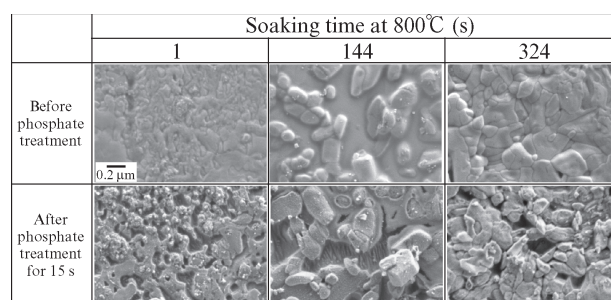


Fig. 9 Magnified SEM image of B-added steel after phosphate treatment for 15 s

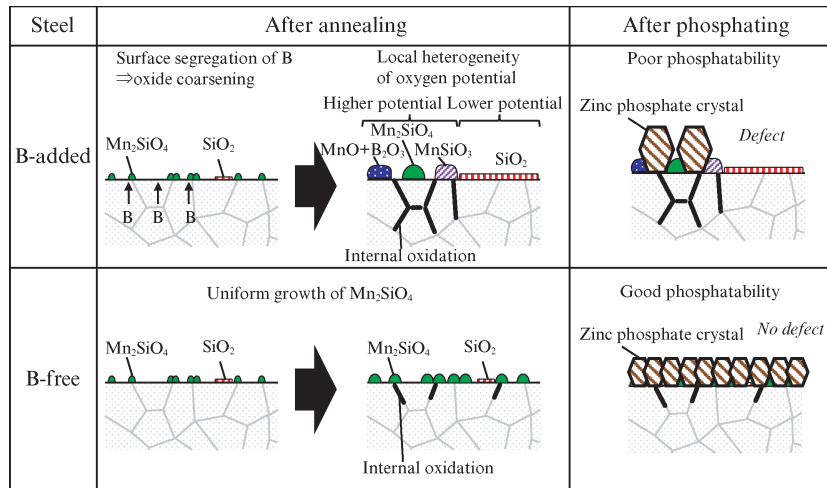


Fig. 10 Schematic image of effect of B on formation of surface oxides during annealing and on phosphatability

and the substrate steel is not significantly exposed before phosphating. Therefore, dissolution of the base steel does not occur, and as shown in Fig. 7, almost no crystals form after 15 s of treatment. However, in the image taken 15 s after the phosphating in Fig. 9, gaps have formed in the areas of densely-packed granular oxides, indicating that slight dissolution of the granular oxides occurred during phosphating. In other words, as the duration of phosphating increases, dissolution of the granular oxides gradually exposes the base steel, allowing the crystal formation reactions to occur. However, due to the high density of the granular oxides and the limited dissolution of the base steel, only coarse, sparsely-distributed crystals formed even after 120 s of phosphating, as shown in Fig. 6. In contrast, in the B-free steel in Fig. 4, formation of zinc phosphate crystals occurs easily because the mesh-like Si-Mn oxides form regardless of the soaking time, and the base steel is exposed in the gaps.

Based on the above, **Fig. 10** shows a schematic illustration of the effect of B addition on the oxide formation behavior and inhibition mechanism of the zinc phosphate reaction. It has been reported that addition of B lowers the melting point of oxides, leading to melting and coarsening of the oxides during annealing. However, this study demonstrated that exposure of the base steel due to oxide coarsening causes local heterogeneity of the oxygen potential on the steel surface, resulting in the separation of regions of film-like SiO_2 formation and the regions of granular oxide formation (i.e., formation of complex oxides of Mn_2SiO_4 , $MnSiO_3$, MnO , and B_2O_3). The difference in the local distribution of the oxygen potential is also reflected in the internal oxidation behavior. Internal oxidation is promoted in regions where the oxides have coarsened and the base steel is exposed, but is not observed in

regions covered with the film-like SiO_2 . In the B-free steel, coarsening of the oxides does not occur, and relatively uniform growth of granular Mn_2SiO_4 and uniform internal oxidation are observed. Zinc phosphate crystals do not form in the film-like SiO_2 formation region of the B-added steel. Moreover, even in the granular oxide formation region, the base steel dissolution reaction in the initial stage of zinc phosphate treatment is inhibited when the oxide density is high and the exposed area of the base steel is small, resulting in the formation of sparsely-distributed coarse zinc phosphate crystals.

5. Conclusions

To clarify the effect of B on the surface properties of steel with combined addition of Si and Mn, the effect of B addition on the surface oxidation behavior and phosphatability of B-added steel sheets was investigated and compared with that of B-free steels. The following conclusions were obtained.

- (1) Formation of fine granular and network-like Mn_2SiO_4 and film-like SiO_2 was observed in the initial stage of annealing, independent of B addition. During soaking at 800°C, Mn_2SiO_4 increased with soaking time in the B-free steel. In contrast, the B-added steel exhibited not only an increase in Mn_2SiO_4 , but also formation of $MnSiO_3$, B_2O_3 , and Mn-B complex oxides and an increase of SiO_2 .
- (2) In the regions of granular Mn_2SiO_4 formation in the B-added steel, melting and coarsening of Mn_2SiO_4 occurred due to combination with B_2O_3 , resulting in local exposure of the base steel and an accompanying increase in the apparent oxygen potential, whereas the apparent oxygen potential was low in the film-like SiO_2 formation region. This

resulted in local inhomogeneity of the oxygen potential, leading to a change in the types of oxides formed during annealing compared to the B-free steel. This local inhomogeneity of the oxygen potential was also reflected in the internal oxidation behavior.

- (3) In the film-like SiO_2 formation region of the B-added steel, zinc phosphate crystals did not form because dissolution of the steel did not occur during zinc phosphate treatment. In addition, the zinc phosphate treatment reaction was inhibited in regions where dense formation of coarse granular Mn_2SiO_4 , MnSiO_3 , B_2O_3 , and Mn-B complex oxides occurred, even where film-like SiO_2 did not form.

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This paper is a reprint, with translation and partial modification, of “Effect of B on Surface Oxidation Behavior and Phosphatability of Si-Mn-added Cold-Rolled Steel Sheets” (published in *Tetsu-to-Hagané*. 2025, vol. 111, no. 6. p. 275–287), which was also written by the lead author of this paper. © Iron and Steel Institute of Japan.