

Effect of Annealed Oxides on the Formation of Inhibition Layer During Hot-Dip Galvanizing of 590Mpa Trip Steel

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The selective surface oxidation of a transformation-induced-plasticity (TRIP) steel containing 1.6 wt.% Mn and 1.5 wt.% Si during annealing at 800 °C was investigated for its influence on the formation of an inhibition layer during hot-dip galvanizing. The selective oxidation of the alloying elements and the oxide morphology were significantly influenced by the annealing atmosphere. The pure N₂ atmosphere with a dew point -40 °C promoted the selective oxidation of Mn as a crystalline Mn₂SiO₄ phase, whereas the N₂ + 10% H₂ atmosphere with the same dew point -40 °C promoted the selective oxidation of Si as an amorphous Si-rich oxide phase. During hot-dip galvanizing, the Mn₂SiO₄ phase was reduced more readily by Al in the Zn bath than the Si-rich oxide phase. Consequently, the pure N₂ atmosphere resulted in a higher formation rate of Fe₂Al₅ particles at the Zn/steel interface and better galvanizability than the N₂ + 10% H₂ atmosphere.

Keywords : TRIP steel, hot-dip galvanizing, oxide, annealing

1. Introduction

Transformation-induced-plasticity (TRIP) steels possess desirable properties such as high strength and excellent formability for automotive applications. To be successfully used in automotive applications, TRIP steels need corrosion protection, most effectively by means of a continuous hot-dip galvanizing process. However, it has long been known that the segregation and selective oxidation of alloying elements such as Si, Mn, and Al during annealing prior to hot-dip galvanizing deteriorate the galvanizability of TRIP steels, leading to bare spots on the coating surface.¹⁾⁻⁴⁾

Mn and Si are two most important alloying elements of TRIP steels. In order to produce the desirable multi-phase microstructure with a portion of retained austenite at room temperature, TRIP steel sheets need be annealed at a temperature in the ferrite-austenite two-phase region prior to hot dip galvanizing. Mn is added as an austenite stabilizer and Si is added to suppress the carbide formation during cooling from the inter-critical temperature.⁵⁾ The selective oxidation of Si and Mn on the steel surface is known to significantly depend not only on the compositions of Mn and Si,^{3),4),6)} but also on the annealing con-

ditions such as H₂/N₂ ratio and dew point.^{2),6)} For the TRIP steels containing similar levels of Mn and Si, SiO₂ and Mn₂SiO₄ are the main oxide phases formed on the steel surface during annealing,³⁾ both of them result in poor wettability with molten Zn.⁷⁾ In literatures, there seem to be general consensus that the N₂ + H₂ annealing atmosphere with a lower dew point is not necessarily beneficial to an improvement of galvanizability of TRIP steels. This is understood based on that the selective oxidation of Mn and Si changes from external to internal oxidation with increasing the dew point, i.e., increasing the oxygen partial pressure.^{2),8)} Nevertheless, it is still largely unclear how the selective oxidation of TRIP steels containing high levels of Mn and Si depends on the annealing conditions.

In order to achieve high-quality Zn coatings on TRIP steels, it is desirable to form a uniformly developed inhibition layer, known to be Fe₂Al₅, on the substrate surface at the early stage of hot-dip galvanizing.^{6),8),9)} The inhibition layer acts not only as a barrier to the fast reaction to form Fe-Zn intermetallic compounds but also as a promoter for Zn wettability and coating adhesion. Therefore, in order to improve the reactive wetting of TRIP steels during hot-dip galvanizing, it is important to understand how the inhibition layer formation during hot dipping is correlated with the surface oxide chemistry and structure developed prior to hot dipping.

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The aim of the present study is to understand the influence of annealing atmosphere on the selective oxidation of a TRIP steel containing 1.6 wt.% Mn and 1.5 wt.% Si, especially during isothermal annealing at an inter-critical temperature, and the effect of the annealed oxides on the inhibition layer formation during hot-dip galvanizing. For this purpose, the annealing and hot-dip galvanizing treatments were carried out in a hot-dip galvanizing simulator using two different annealing atmospheres, pure N₂ and N₂ + 10% H₂ with a dew point of -40 °C. The surface chemistry and structure before and after hot-dip galvanizing were examined in detail utilizing various characterization tools.

2. Experimental procedure

The 590 MPa grade TRIP steel used in the present study was provided in a form of cold-rolled sheets with a dimension of 120 mm x 200 mm x 1.5 mm by POSCO. Table 1 shows the detailed composition of the TRIP steel. In order to remove all influences of the prior sheet processing, the sheets were first mechanically polished to a mirror finish sequentially using SiC papers (up to grit 4000) and 1 µm diamond suspension, and then cleaned ultrasonically in ethanol.

All the annealing and hot-dip galvanizing treatments of the mirror-polished samples were carried out in a commercial galvanizing simulator which could accurately control both the sample temperature and the annealing atmosphere (H₂/N₂ ratio and dew point). Two different annealing atmospheres, pure N₂ and N₂ + 10 vol.% H₂, with a fixed dew point (DP) of -40 °C were used to examine the effect of the annealing atmosphere on the segregation and selective oxidation of the alloying elements Mn and Si. Since our particular interest was in the segregation and selective oxidation during the inter-critical annealing at 800 °C, the samples were heated rapidly at 10 °C/s up to 650 °C and then at 3 °C/s to 800 °C, as shown schematically in Fig. 1. After isothermal annealing at 800 °C for various times of up to 60 s, one set of samples were cooled at -20 °C/s to room temperature for the characterization of the annealed oxides and another set of samples were cooled to 460 °C for dipping in a Zn bath that was held at 460 °C. The Zn bath contained 0.2 wt.% Al and the dipping time

Table 1. Chemical composition of the 590 MPa TRIP steel used in the present study

Element	Fe	Mn	Si	Al	C	B
wt. %	Bal.	1.6	1.5	0.003	0.08	5 ppm

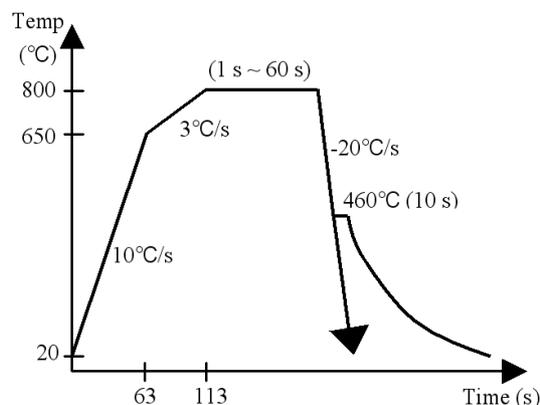


Fig. 1. Schematic representation of the temperature profile used for the annealing and hot-dip galvanizing treatments. Isothermal holdings at 800 °C were varied from 1 s to 60 s.

was fixed to 10 s. The hot-dipped samples were naturally cooled in the simulator. As calculated by using the FactSage database, the oxygen partial pressures (P_{O_2}) in the pure N₂ and N₂ + 10% H₂ atmospheres at 800 °C are 1.20×10^{-9} atm and 6.82×10^{-25} atm, respectively.

In order to characterize the selective oxidation and the inhibition layer formation depending on the annealing atmosphere, the experimented samples were analyzed using field emission scanning electron microscopy (FESEM) equipped with an energy-dispersive X-ray spectrometer (EDX), glow discharge optical emission spectroscopy (GDOES), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and glancing incidence X-ray diffraction (GIXRD). The GIXRD studies were carried out using Cu-K_α radiation with a X-ray incidence angle of 2° on the sample surface

3. Results and discussion

Fig. 2 shows representative FESEM secondary electron images of the surface microstructures after annealing at 800 °C for 1 and 60 s in the two different atmospheres. After 1 s of annealing (Fig. 2(a) and (c)), the sample surface was covered by an oxide film with some oxide particles scattered over the film, implying that the oxide film had been formed during the heating stage. The noticeable difference in the surface microstructure between 1 s and 60 s at 800 °C was that the particles formed on the oxide film became larger in size and more in number with increasing annealing time. Moreover, the morphology of the particulate oxides depends on the annealing atmosphere: an angular type in pure N₂ and a pancake-type in N₂ + 10% H₂. This implies that the chemistry and atomic structure of the oxides formed during annealing at the inter-critical temperature should be significantly affected by the

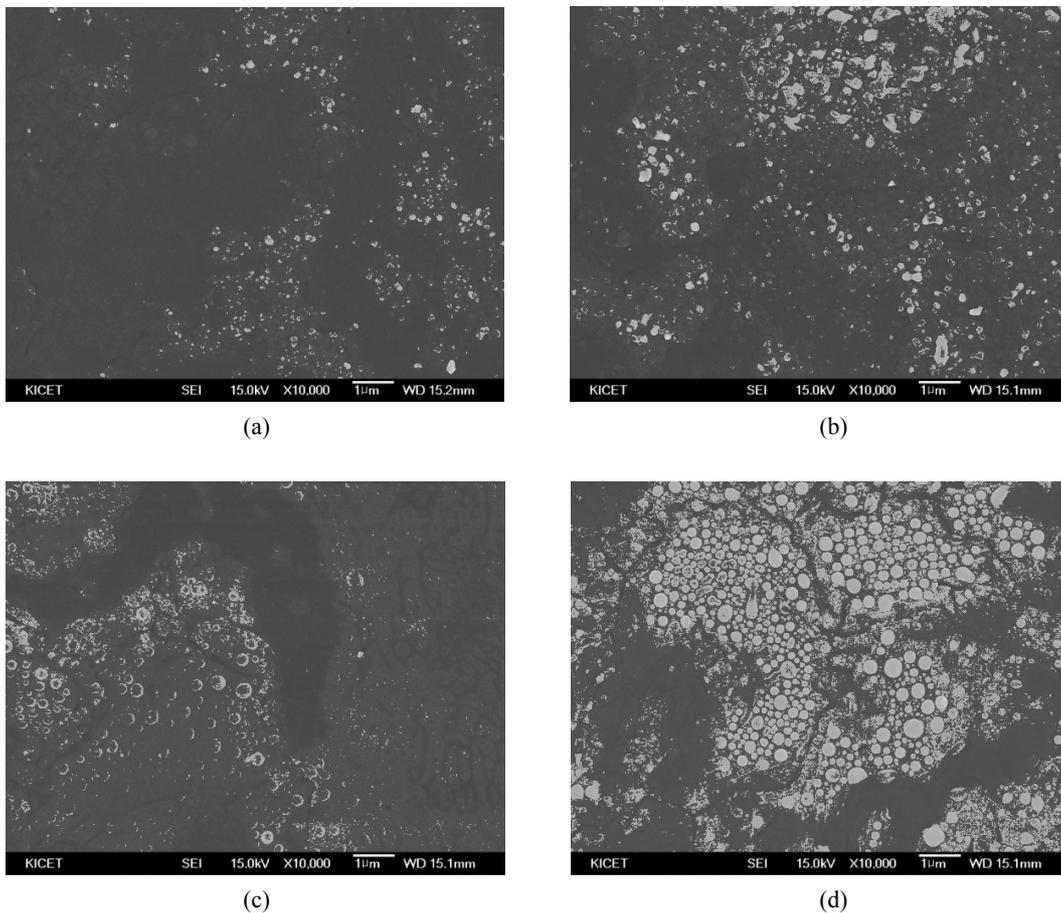


Fig. 2. FESEM secondary electron images showing the surface morphology of the scales after annealing at 800 °C for (a) 1 s and (b) 60 s in the pure N₂ atmosphere, and for (c) 1 s and (d) 60 s in the N₂ + 10% H₂ atmosphere.

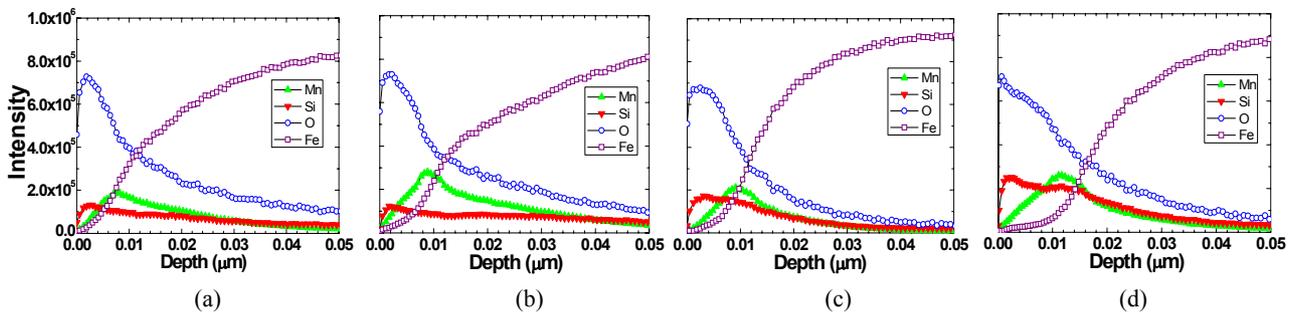


Fig. 3. GDOES depth profiles for elemental distributions in the scales of the corresponding samples shown in Fig. 2: (a) 1 s and (b) 60 s of annealing at 800 °C in the pure N₂ atmosphere, and (c) 1 s and (d) 60 s of annealing at 800 °C in the N₂ + 10% H₂ atmosphere.

annealing atmospheres.

In order to check the evolution of the surface oxide chemistry during soaking at 800 °C, the GDOES depth profiling was carried out for the samples soaked for various times. Fig. 3 shows the GDOES depth profiles obtained from the surface oxides corresponding to those shown in Fig. 2. After 1 s of soaking (Fig. 3(a) and (c)),

the two annealing atmospheres resulted in similar depth profiles of Si and Mn, suggesting a top surface layer of a Si-rich oxide and a sublayer of a Mn-rich oxide. This is in accordance with the previous report,¹⁰⁾ which used TRIP steels containing Mn and Si contents similar to those of the present study steel, that during the heating stage the selective oxidation of Mn and Si occurs by forming

first a particulate Mn-rich oxide at temperatures below ~ 650 °C and then a SiO₂ film at temperatures above 650 °C. From the depth of the crossover position of the Fe and O profiles, the thickness of the surface scale could be estimated to be approximately 10 nm. It is also known that the SiO₂ oxide formed above 650 °C tends to form a film covering all of the free steel surface and the Mn-rich oxide particles.¹⁰ Therefore, the surface oxide film shown in Fig. 2(a) and (c) is most likely to be SiO₂ formed during heating.

In contrast to that during heating, selective oxidation during soaking at 800 °C was strongly influenced by the annealing atmosphere. Compared with those after 1 s of soaking, the GDOES depth profiles after 60 s of soaking clearly showed that the surface scale became enriched by Mn in the pure N₂ atmosphere (Fig. 3(b)) whereas the surface scale was enriched by Si in the N₂ + 10% H₂ atmosphere (Fig. 3(d)). There was only a minor increase in the surface scale thickness during soaking for 60 s. This should be due to the particulate-type, not a layer-type, morphology of the oxides formed during soaking as shown in Fig. 2(b) and (d). Therefore, the present GDOES results suggest that the angular particles formed in the pure N₂ atmosphere are Mn-rich oxides (most likely Mn₂SiO₄) and the pancake-type particles formed in the N₂ + 10% H₂ atmosphere are Si-rich oxides (most likely SiO₂). It has been known that increasing the oxygen partial pressure in the atmosphere results in a change from external to internal oxidation of the alloying elements Si and Mn.^{2),8)} However, the present GDOES analyses did not reveal any indication of internal oxidation of Si and/or Mn in the pure N₂ atmosphere.

Figs. 4(a) and (b) show the evolution of Si 2p peaks in the XPS spectrum with soaking time at 800 °C in the pure N₂ and N₂ + 10% H₂ atmospheres, respectively. The binding energies of Si 2p electrons in Mn₂SiO₄ and SiO₂ are 102.1 eV and 104.2 eV, respectively.⁶⁾ All the XPS spectra showed a broad peak covering both of 102.1 eV and 104.2 eV, which is indicative of the coexistence of Mn₂SiO₄ and SiO₂ on the surface. It can be clearly seen that the relative intensities at the peak positions of Mn₂SiO₄ and SiO₂ changed with soaking time; the relative peak intensity of Mn₂SiO₄ became stronger with soaking time in the pure N₂ atmosphere (Fig. 4(a)), whereas that of SiO₂ became stronger in the N₂ + 10% H₂ atmosphere. These are consistent with the GDOES results shown in Fig. 3.

The oxide phases present in the surface scale were further examined using GIXRD which is suitable for phase identification in a thin film material. Figs. 5(a) and (b) show the evolution of the GIXRD patterns with soaking

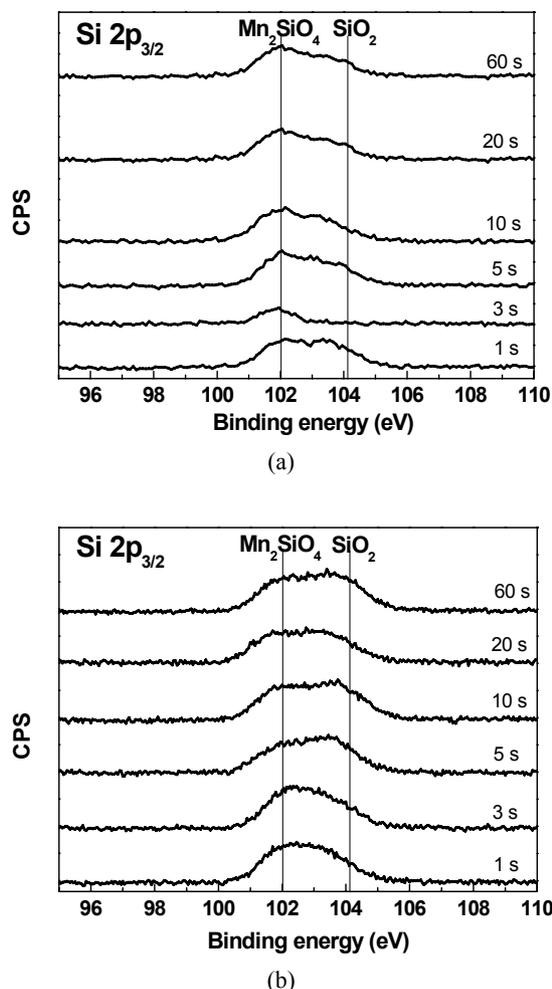


Fig. 4. Evolution of the XPS spectrum of Si 2p_{3/2} at the scale surface with annealing time at 800 °C in the (a) pure N₂ atmosphere and (b) N₂ + 10% H₂ atmosphere.

time in the pure N₂ and N₂ + 10% H₂ atmospheres, respectively. Only the Mn₂SiO₄ phase in the scale was identifiable by pattern indexing for both cases of the annealing atmospheres. From the absence of oxide peaks other than the Mn₂SiO₄ peaks, the Si-rich oxide formed during heating and soaking is thought to be amorphous, not crystalline, as reported previously.³⁾ Nevertheless, comparison of the intensity evolution of the Mn₂SiO₄ peaks in the two different atmospheres suggests that the amount of Mn₂SiO₄ phase formed during soaking for 60 s was greater in the pure N₂ than in the N₂ + 10% H₂ atmosphere, which is in agreement with the GDOES and XPS results shown in Figs. 3 and 4.

The present study on a 590 MPa TRIP steel confirmed that the morphology and chemistry of the surface oxide formed especially during the inter-critical annealing at 800 °C were significantly influenced by the annealing atmos-

phere. Upon heating to 800 °C in both of the pure N₂ and N₂ + 10% H₂ atmospheres, the steel surface was already covered with scale consisting of an amorphous SiO₂ film and Mn-rich oxide (i.e., Mn₂SiO₄) particles. The present

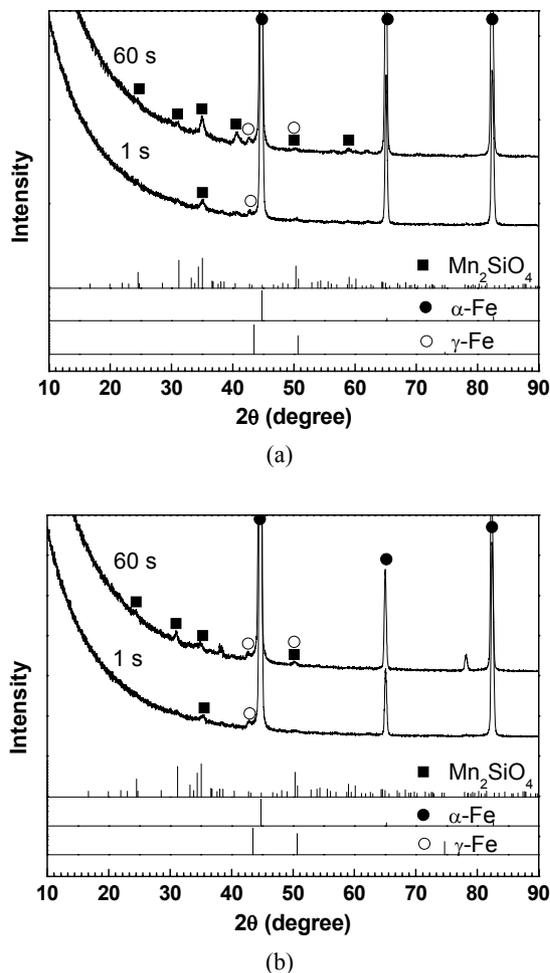


Fig. 5. GIXRD patterns of the annealed oxides after annealing for 1 s and 60 s at 800 °C in the (a) pure N₂ atmosphere and (b) N₂ + 10% H₂ atmosphere.

analyses results suggest that the selective oxidation and the evolution of surface morphology during isothermal annealing at 800 °C can be viewed in the following way. The N₂ + 10% H₂ atmosphere with a relatively low oxygen partial pressure ($P_{O_2} = 6.82 \times 10^{-25}$ atm) promotes the selective oxidation of Si over Mn, leading to the formation of pancake-type Si-rich oxide particles on the preexisting SiO₂ film, as shown in Fig. 2(d). On the other hand, the pure N₂ atmosphere promotes the selective oxidation of Mn over Si, leading to the growth of angular-type Mn₂SiO₄ particles, as shown in Fig. 2(b). It is noted that a similar change of the surface enrichment from Si to Mn with increasing the oxygen partial pressure has also been observed previously by increasing dew point of annealing ambient.^{4,6)}

The coating quality after hot-dip galvanizing was significantly deteriorated by increasing the annealing time at 800 °C in both atmospheres. Nevertheless, for a given annealing time, the samples annealed in the pure N₂ atmosphere exhibited consistently better galvanizability than those annealed in the N₂ + 10% H₂ atmosphere. In the pure N₂ atmosphere, annealing for 20 s or less resulted in good coating quality but prolonged annealing for 60 s caused a poor quality of Zn coating with many bare areas. When the N₂ + 10% H₂ atmosphere was used for the annealing, however, severe problems of wettability were encountered even after annealing for 20 s, leaving the sample surface mostly bare.

Fig. 6 shows FESEM backscattered electron images of the interfacial reaction products formed on the sample surface after hot-dip galvanizing of the samples soaked for 20 s and 60 s in the two different atmospheres. For Fig. 6(a) corresponding to the sample soaked for 20 s in the pure N₂ atmosphere, the Zn overlay was striped using a selective Zn etching solution to reveal the interfacial reaction products. Using EDX and GIXRD, the angular particles in dark contrast in Fig. 6(a) were identified as Fe₂Al₅.

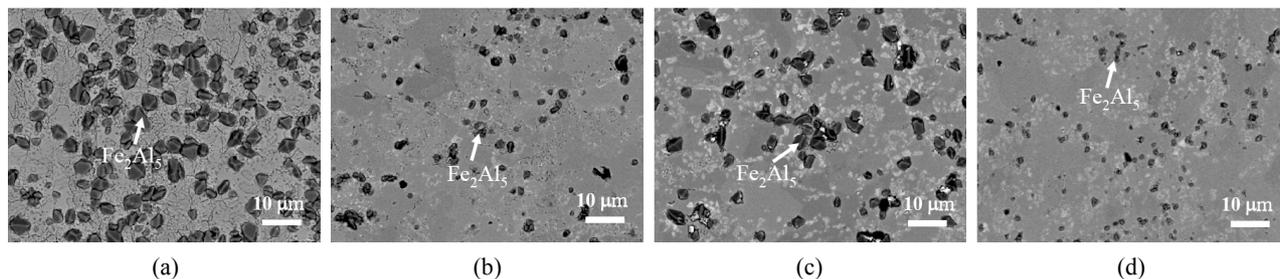


Fig. 6. FESEM backscattered electron images showing the interfacial reaction products formed on the sample surface after hot-dip galvanizing. Prior to hot dipping, the samples were annealed differently: (a) 20 s and (b) 60 s at 800 °C in the pure N₂ atmosphere, and (c) 20 s and (d) 60 s at 800 °C in the N₂ + 10% H₂ atmosphere. The micrograph in (a) was obtained after etching out the Zn overlay but those in (b)-(d) were taken from the bare areas without etching.

It is interesting that a good quality Zn coating could be obtained although the Fe_2Al_5 particles did not form a fully developed inhibition layer. In contrast to that in Fig. 6(a), the micrographs shown in Fig. 6(b)-(d) were taken from the bare areas without an etching treatment. Although there were no Zn coatings remained, the bare areas still exhibited the formation of Fe_2Al_5 particles. However, the size and number of the formed Fe_2Al_5 particles decreased with increasing the soaking time prior to hot-dipping, indicating that the selective oxidation during soaking hindered the reaction between Fe in the steel substrate and Al contained in the molten Zn bath. In Fig. 6(b)-(d), the regions in bright contrast around Fe_2Al_5 particles were revealed to be a Fe-Zn compound by EDX.

The presence of Fe_2Al_5 and a Fe-Zn compound even on the bare areas is a clear indication that the annealed oxides on the steel surface were reduced by the dissolved Al in the Zn bath during the hot dipping process. Moreover, as can be seen in Fig. 6(b) and (d), the particulate-type morphology of surface oxides formed by annealing for 60 s was completely disappeared after the hot dipping process. It is noted that the reduction of SiO_2 by Al in the Zn bath has been suggested previously.¹¹⁾ Reduction of the annealed oxides was further confirmed by AES depth profiling on the bare areas. Figs. 7(a) and (b) show the AES depth profiles for the samples that, prior to hot dipping, had been annealed at 800 °C for 60 s in the pure N_2 and $\text{N}_2 + 10\% \text{H}_2$ atmospheres, respectively. Regardless of the annealing atmospheres, the non-wetted bare areas were covered with a less than 2 nm thick oxide film, which is considerably thinner than ~10 nm before hot dipping (Fig. 2(b) and (d)). The thin oxide film remained after hot dipping was enriched by Si. This implies that the Mn-rich oxide was more rapidly reduced during the hot-dip galvanizing process than the Si-rich oxide. This can also explain why the samples annealed in the pure N_2 atmosphere exhibited more active interfacial reactions

for the Fe_2Al_5 particle formation and better galvanizability than those annealed in the $\text{N}_2 + 10\% \text{H}_2$ atmosphere.

4. Conclusions

The selective oxidation of a TRIP steel containing 1.6 wt.% Mn and 1.5 wt.% Si during annealing at 800 °C and its effect on the inhibition layer formation were examined using two different annealing atmospheres in a hot-dip galvanizing simulator. Pure N_2 and $\text{N}_2 + 10\% \text{H}_2$ with a fixed dew point of -40 °C were used for the two annealing atmospheres in comparison. From the experimental results, the following conclusions can be drawn:

1) At the heating stage to 800 °C, a selective oxidation of Mn and Si occurred to form a ~10 nm thick scale on the steel surface. The surface scale consisted of an amorphous SiO_2 film and Mn_2SiO_4 particles, regardless of the anneal atmospheres.

2) During isothermal soaking at 800 °C, the annealing atmosphere had a significant influence on the selective oxidation of Mn and Si. The pure N_2 atmosphere with a relatively high oxygen partial pressure promoted the selective oxidation of Mn, which resulted in the preferential growth of angular-type Mn_2SiO_4 particles at the expense of the amorphous SiO_2 film formed upon heating. On the other hand, the $\text{N}_2 + 10\% \text{H}_2$ atmosphere promoted the selective oxidation of Si, leading to the formation of pancake-type amorphous Si-rich oxide particles on the preexisting SiO_2 layer.

3) A significant reduction of the annealed oxide scale occurred during hot-dip galvanizing. The samples annealed in the pure N_2 atmosphere consistently exhibited more development of Fe_2Al_5 particles and better galvanizability than those annealed in the $\text{N}_2 + 10\% \text{H}_2$ atmosphere, which was attributed to a higher reduction rate of Mn_2SiO_4 than that of the Si-rich oxide by Al contained in Zn pot.

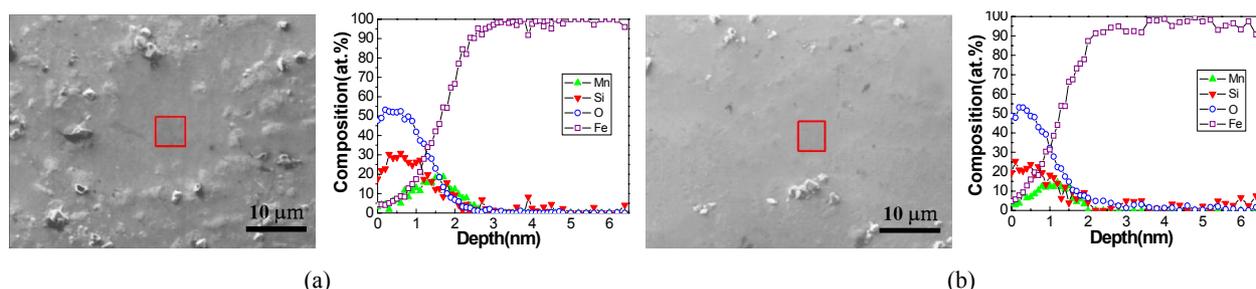


Fig. 7. AES analyses of the bare areas after hot-dip galvanizing of the samples annealed for 60 s at 800 °C in the (a) pure N_2 atmosphere and (b) $\text{N}_2 + 10\% \text{H}_2$ atmosphere. In each of (a) and (b), the AES depth profile was obtained from the position marked by square in the corresponding scanning Auger micrograph.

Acknowledgments

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