

# Influence of Substrate Molybdenum on Galvannealing Kinetics of an Advanced High Strength Steel

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Advanced high strength steels (AHSS) are used for car body applications in the automotive industry to improve passenger safety, improve fuel efficiency and to lower harmful carbon emissions. Galvannealed AHSS are used to provide corrosion protection. AHSS are alloyed with several elements such as Mn, Si, Al, P, Mo, *etc.* to achieve better mechanical properties. However, the knowledge of the effects of Mo on galvannealing behavior is limited. This investigation was conducted to study the influence of molybdenum in steel on galvannealing kinetics. Five dual-phase steels with Mo varying from 0 wt% to 0.4 wt% were used for this study. The results showed a delay in the galvannealing kinetics with an increase in the steel molybdenum content. No obvious improvement in the coating appearance was observed with increasing molybdenum.

KEY WORDS: galvannealing kinetics; dual phase steels; molybdenum; surface segregation; AHSS.

## 1. Introduction

Galvannealed (GA) steels are widely applied in the automotive industry due to its improved paintability and welding performance combined with good corrosion protection.<sup>1)</sup> GA steels are produced in a continuous galvannealing line by annealing a steel sheet in a ~ 5% H<sub>2</sub>/ 95% N<sub>2</sub> reducing atmosphere, dipping in an iron saturated molten zinc bath containing trace aluminum and subsequent heating of the hot-dip steel in a gas-fired or an induction furnace located above the zinc bath. The aluminum in the zinc bath reacts preferentially with the substrate iron and forms a Fe–Al intermetallic layer. This Fe–Al intermetallic layer retards the formation of brittle Fe–Zn intermetallic compounds. A small amount of zinc is also reported in this inhibition layer and tends to be present as Fe<sub>2</sub>Al<sub>5</sub>Zn<sub>x</sub>.<sup>2,3)</sup> Galvannealing of the steel results in the breakdown of the Fe–Al inhibition layer via an outburst mechanism and results in the formation of  $\zeta$ -phase and  $\delta$ -phase Fe–Zn intermetallic compounds at the steel/zinc interface. As the galvannealing proceeds, these two phases continue to grow until all liquid  $\eta$ -phase is consumed. Further galvannealing results in the decrease of  $\zeta$ -phase, increase of  $\delta$ -phase and formation of  $\Gamma$ -phase. As the galvannealing reaction progresses, the iron content of the coating also increases. Hence, the change in the coating microstructure and coating iron content can provide a good measure of the galvannealing kinetics.

The kinetics of the above galvannealing reactions is dependent on several factors such as bath aluminum, galvannealing time, galvannealing temperature, steel chemistry, *etc.*<sup>2,4)</sup> Inagaki *et al.*<sup>2)</sup> observed a thick Fe<sub>2</sub>Al<sub>5</sub>Zn<sub>x</sub> layer in

the coatings produced with a 0.15 wt% bath aluminum as compared with the coatings produced with a 0.13 wt% bath aluminum. This intermetallic layer acts as a barrier for Fe–Zn diffusion and inhibits the formation of  $\zeta$ -phase and  $\delta$ -phase. Hence, increase in bath aluminum slows down the galvannealing reaction. Increase in the galvanneal temperature and/or galvanneal time enhances the GA kinetics and leads to an increase in the coating iron content. The effect of steel alloying elements on GA kinetics is briefly discussed here. Automobile manufacturers are applying increasing quantities of various advanced high strength steels (AHSS) automobiles in order to improve fuel efficiency by lowering vehicle weight and to improve passenger safety. AHSS contain a variety of alloying elements such as Ti, P, Mn, Si, Mo, Nb, *etc.* to obtain the required mechanical properties. It has been shown by multiple researchers that these alloying elements affect the steel/zinc interaction. Inagaki *et al.*,<sup>2)</sup> Nishimoto *et al.*,<sup>4)</sup> Lin *et al.*<sup>5)</sup> showed that phosphorus and carbon can segregate to the surface and grain boundaries and inhibit the outburst reaction and slows down the formation of Fe–Zn intermetallic compounds. Rangarajan *et al.*<sup>6)</sup> found carbon and phosphorus segregation in extra low carbon steels and rephosphorized steels, respectively. Jordan *et al.*<sup>7)</sup> attributed the slow galvannealing kinetics in P containing steels to slow zinc diffusion along the grain boundaries due to P segregation at the grain boundaries. Bhattacharya and Cheng<sup>8)</sup> investigated the steel surface at temperatures the steel would enter the zinc bath and attributed surface segregation of niobium to influence galvannealing behavior in interstitial-free (IF) steels. In recent studies, Blumenau *et al.*,<sup>9)</sup> Yasui *et al.*,<sup>10,11)</sup> and Kim *et al.*<sup>12)</sup> reported delayed galvannealing in steels with 1.2 wt% Si and 1.5 wt% Mn. The slowdown was attributed to the formation of manganese and/or silicon oxides at the sur-

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face and hindering the iron diffusion from the steel into the Fe–Al and Fe–Zn intermetallic phases. Kim *et al.* suggested that solute Si also contributed to delayed galvannealing. Bode *et al.*<sup>13)</sup> did limited tests using steels with different combinations of alloying elements such as Mn, Al, Cr, Si, Mo, B, and Nb. They investigated the surface enrichment after annealing process and the effect on wettability (galvanized steel). Mn, Al, Si and Cr enriched to the surface. Mo did not segregate to the surface. Galvannealing studies were not conducted. Kyono *et al.*<sup>14)</sup> evaluated annealed steel surface of silicon-containing and molybdenum-containing steels. Similar to Bode *et al.*, Si surface segregation was observed in the silicon-containing steel. However, Mo surface segregation was not observed in the molybdenum-containing steel. Their results also showed that addition of 0.15 wt% Mo did not retard the galvannealing reaction and did not deteriorate zinc wettability. However, for galvannealing effects, Kyono *et al.* studied the molybdenum-containing steel versus a phosphorus-containing steel and a mild steel. The influence of different Mo contents in modern advanced high strength steel chemistries was not investigated. There is limited understanding of the influence of molybdenum on the galvannealing reactions.

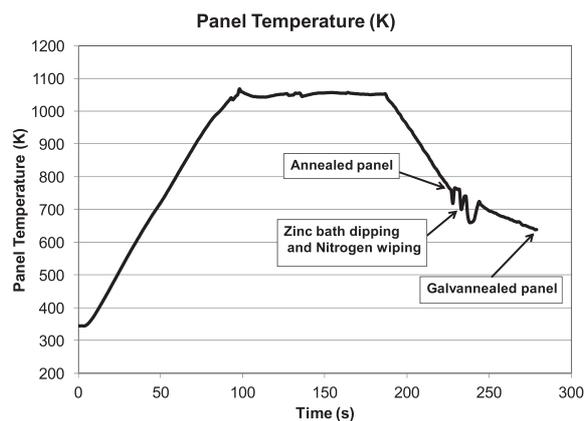
The present study was conducted to gain better understanding of the influence of substrate molybdenum on the galvannealing kinetics. Mo improves the hardenability of the automotive steels and is added in limited quantity from 0 to 0.3 wt% due to its high cost. The key aspect of this study is that the analysis was conducted on steel samples quenched from the temperature at which the steel enters the zinc pot and not on samples at room temperature. Rangarajan *et al.*<sup>6)</sup> have shown that the surface segregation of the active alloying elements is dependent on temperature and hence, it is critical to study the surface segregation occurring at real steel processing temperatures. To the best of the authors' knowledge, no studies are available in the literature investigating the influence of controlled change in the steel molybdenum content on galvannealing kinetics, through examination of the steel surface state as it enters the galvanizing pot.

## 2. Experimental Method

Five experimental dual phase (DP) steel chemistries were cast as 64 mm thick × 200 mm wide × 250 mm long slabs at ArcelorMittal Global R&D East Chicago laboratory. In these steels, Mo was varied as 0, 0.1, 0.2, 0.3 and 0.4 wt% while all other elements such as C, Mn, Si, Al, *etc.* were kept the same. These steels are referred to as M0, M1, M2, M3 and M4, respectively, and their chemistries are given in **Table 1**. The five slabs were heated to 1 143 K (870°C) and hot rolled twice to a final thickness of 3.4 mm, surface ground to remove scale and then cold rolled about 50% to produce 1.2 mm thick sheets. 100 mm × 300 mm sheets were

cut, alkaline cleaned and galvannealed in a hot dip simulator. The details of the simulator were reported previously.<sup>15)</sup> The long side of the panel is cut along the rolling direction and dipped in the same orientation. A K-type thermocouple was welded to the steel panel. Annealing was done in a ~ 5% H<sub>2</sub>/95% N<sub>2</sub>, at a dewpoint of 243 K (–30°C) to 238 K (–35°C) and less than 20 ppm oxygen atmosphere. The steel panels were heated to 1 053 K (780°C) at 8 K/s (8°C/s), soaked for 90 s at 1 053 K (780°C) and cooled to 738 K (465°C) at 8 K/s (°C/s) using nitrogen. The panels at this stage were (a) rapidly cooled to room temperature to preserve the surface chemistry for analysis or (b) dipped in iron-saturated liquid zinc metal for 3 seconds. The zinc bath was secured from a continuous galvanizing line. The zinc bath temperature was 731 K (458°C) and the effective aluminum was ~ 0.130 wt% – 0.134 wt%. The zinc bath chemistry was analyzed using an inductively coupled plasma (ICP) method and the effective aluminum was calculated using Tech Cominco's DEAL<sup>®</sup> software. The dipped panels were removed from the zinc bath and wiped with nitrogen to produce a target coating weight of 45 g/m<sup>2</sup> – 55 g/m<sup>2</sup> and galvannealed in an induction furnace. All the panels were galvannealed to the same aim temperature of 733 K (460°C) with +/- 4 K/s (4°C/s) in the simulator. A typical thermal profile of the annealed and galvannealed panel is shown in **Fig. 1**.

Five sets of M0 through M4 steels (total twenty five panels) were galvannealed in a random order and on different days to test for repeatability. Of the total panel size of 100 mm wide × 300 mm long, a 80 mm × 150 mm located in the top portion of the test panel results in uniform heating and coating. 65 mm discs were punched from this uniform coated area. The coating is stripped with 1:1 inhibited hydrochloric acid and was analyzed for coating chemistry using an ICP. The coating weight was measured using weigh-strip-weigh method. Coating cross-sections were



**Fig. 1.** Thermal profile of the annealing and galvannealing (GA) experiments. Panels were collected (a) just before entering the zinc pot to study the surface properties and (b) after the galvannealing process.

**Table 1.** Chemistry of the five experimental DP steels (wt%) with varying Mo levels.

C	Mn	Si	Al	P	Ti	Nb	Mo (5 levels)					
<0.10	<2.5	<0.5	0.040	0.004	0.002	0.015	0	0.10	0.19	0.30	0.38	
								M0	M1	M2	M3	M4

etched with Kilpatrick's reagent and steel cross-sections were etched with 2% nital to reveal the coating and steel microstructures, respectively. These were then observed using a JEOL® 5800 20 kV scanning electron microscope. Surface chemistry of the annealed panels was determined by using glow discharge optical emission spectroscopy (GDOES). Sputtering rate of ~ 100 nm/s (or 6  $\mu\text{m}/\text{minute}$ ) depth was used for the analysis. Three locations per annealed panel were analyzed.

### 3. Results and Discussion

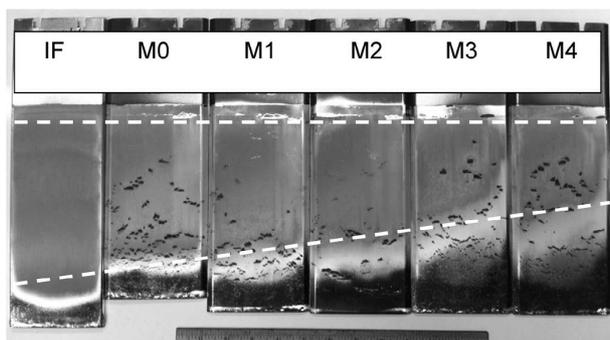
The galvannealing kinetics of the five dual phase steels was evaluated using the galvanneal coating appearance, coating iron content and coating microstructure. The steel surface chemistry and steel microstructure were also studied to understand their influence on coating development.

#### 3.1. Galvannealed Coatings

##### 3.1.1. Visual Observations

A photograph of a panel of all five steel chemistries galvannealed to the same temperature is shown in **Fig. 2**. The dark spots observed on the galvannealed DP steels are uncoated areas. Visual examination of all five replicates of the coated steels showed no significant difference in coat-ability of different steel chemistries. Addition of molybdenum to the steel did not show any obvious improvement in the coat-ability of the DP steels. It is to be noted that these steels are alloyed with about 2 wt% manganese and 0.3 wt% silicon. Under the above annealing conditions, these two elements produce manganese oxides and silicon oxides or combination of both which have been reported to cause poor wetting.<sup>13)</sup> An IF steel produced in a random order along with DP steels is shown in the same figure. An obvious difference between the IF steel and DP steels was observed. IF steel coated better than the DP steels and did not exhibit uncoated areas, which indicates that the poor coat-ability is due to the effect of the steel chemistry and not other galvannealing process conditions. In the current study, lab simulations were not done using high dew points<sup>16)</sup> or preoxidation/reduction<sup>17)</sup> to improve the coat-ability of the steel. The aim was to evaluate change in galvannealing with increasing Mo in the steel.

As the galvannealing reaction proceeds, iron diffuses from the steel into the coating and planar surface appearance



**Fig. 2.** Photographs of five different steels (M0 through M4) after galvannealing at the same temperature. An interstitial-free steel (on the left) is included for reference.

changes from a reflective zinc surface to a dull (grey) galvannealed surface. On a continuous galvanizing line (CGL), the coated surface appearance provides a quick indication to the operator if the coating is galvannealed (dull grey) or underalloyed (shiny). For a given steel chemistry and a given GA temperature, the galvannealed coating remains relatively the same. The area of uniform galvanneal coating on the simulated panel can be used as an indication of the galvannealing kinetics. The smaller the galvannealed area, the slower is the galvannealing kinetics. The area of uniform galvannealed coating (grey area) can be visually observed in **Fig. 2**. IF steel was easier to galvanneal and exhibited more uniform GA area than the DP steels. Presence of alloying elements such as Mn<sup>18)</sup> and Si<sup>11)</sup> are known to form oxides and delay the galvannealing reaction by retarding the iron diffusion from the steel to the coating. However, in the present study where Mn and Si were kept the same and for the same aim GA temperature, the area of uniform GA coating decreased with an increase in the steel molybdenum content as indicated by the narrowing dashed lines in the figure. This suggests slower galvannealing kinetics with increase in the steel Mo content.

##### 3.1.2. Coating Chemistry

Iron in the zinc coating is supplied from the steel substrate during galvannealing. Hence, coating iron content was used to evaluate galvannealing kinetics. Higher amount of coating iron content indicates faster galvannealing. Coating iron content was evaluated for all twenty five test panels. The coating weight and chemistry of the tested panels is given in **Table 2**. The aim of the coating weights was 45 gm/m<sup>2</sup> to 55 gm/m<sup>2</sup>. Due to the experimental variation in the coating weight, coating iron was normalized to 50 gm/m<sup>2</sup>. A plot of the normalized coating iron wt% versus the substrate molybdenum content is shown in **Fig. 3**. A plot of the average coating iron content of all five sets versus the substrate molybdenum is given in **Fig. 4**. A general trend showing a decrease in iron content with an increase in the steel molybdenum from 0 wt% to 0.4 wt% was observed. This observation is consistent with the visual observations of the coated panels (see **Fig. 2**), where the area of uniform GA coating decreased with an increase in the steel molybdenum content.

##### 3.1.3. Coating Microstructure

In galvanneal coatings, the liquid zinc reacts with iron to form various intermetallic compounds. Zeta, delta and gamma phases contain about 5.1–6.1 wt%, 7.0–11.5 wt% and 16.0–27.8 wt% iron, respectively.<sup>19)</sup> Zeta phase is a soft

**Table 2.** Coating weight and chemistries of the tested panels.

Series# /ID	Coating weight (gm/m <sup>2</sup> )					Coating iron content (wt%)				
	M0	M1	M2	M3	M4	M0	M1	M2	M3	M4
1	53.1	61.3	45.8	57.7	48.5	12.6	10.5	10.7	11.3	11.9
2	61.0	45.5	48.2	46.1	48.5	13.2	9.7	13.0	13.8	12.7
3	49.7	49.7	54.0	49.1	49.1	13.2	12.8	12.9	11.8	12.2
4	47.0	49.4	65.9	47.0	48.8	12.2	10.3	10.4	11.7	8.9
5	55.2	55.5	53.1	61.0	51.0	12.4	11.5	11.2	8.4	10.4

phase and forms at the coating surface. Gamma phase is an iron rich brittle phase that grows at the steel/coating interface. Delta phase forms above the gamma phase. As the galvanneal reaction progresses, gamma and delta phases grow and the zeta phase is consumed. For a coating with similar thickness, presence of zeta phase indicates slower galvannealing kinetics than the coating without the zeta phase.

All twenty five galvannealed panels were prepared for cross-section examination. These were etched with Kilpatrick's reagent and observed using the SEM, see Fig. 5. The coatings typically consisted of gamma and delta phases for M0, M1 and M2 steels. M3 and M4 steels exhibited small amounts of Zeta phase in addition to the gamma and delta phases. The presence of zeta phase indicates slower galvannealing rates for M3 and M4 steels than M0, M1 and M2

steels. This result is consistent with the coating chemistry (decrease in the iron content) and the visual observations with increase in the Mo content presented above.

The above analysis, visual surface appearance, coating iron content, and microstructure, clearly indicated that there was a delay in galvannealing with an increase in the molybdenum content for the above DP steels.

### 3.2. Steel Substrate

#### 3.2.1. Surface Chemistry

One panel of all five DP steels was heat treated to simulate annealing and cooling paths up to the hot dipping process. These panels were then rapidly cooled to room temperature with nitrogen to preserve the surface condition as much as possible to study the steel surface chemistry just before entering the zinc bath. These panels were then analyzed for

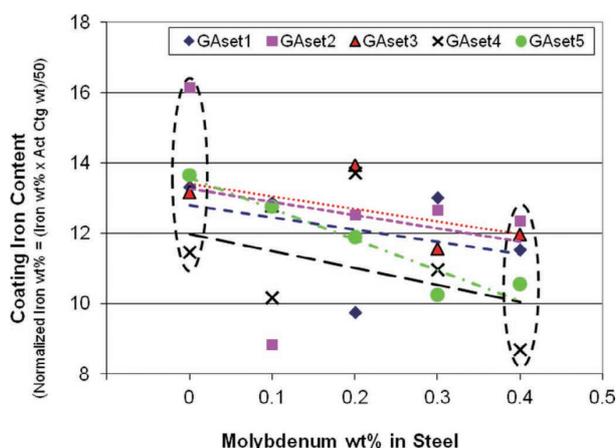


Fig. 3. Variation in coating iron content vs. molybdenum wt% in steel for five test panels per each chemistry.

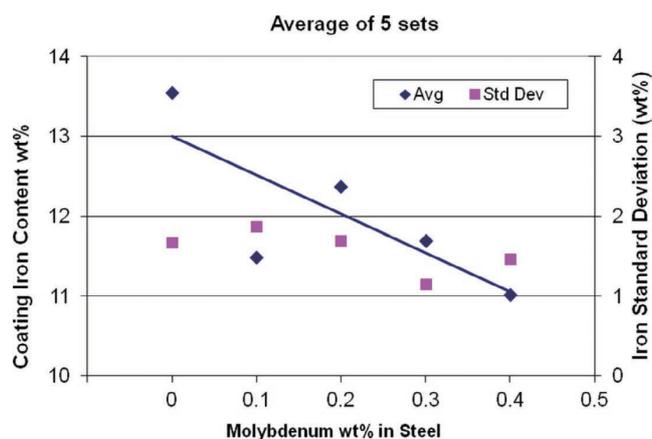


Fig. 4. Average and standard deviation of coating iron contents for five test panels per each chemistry.

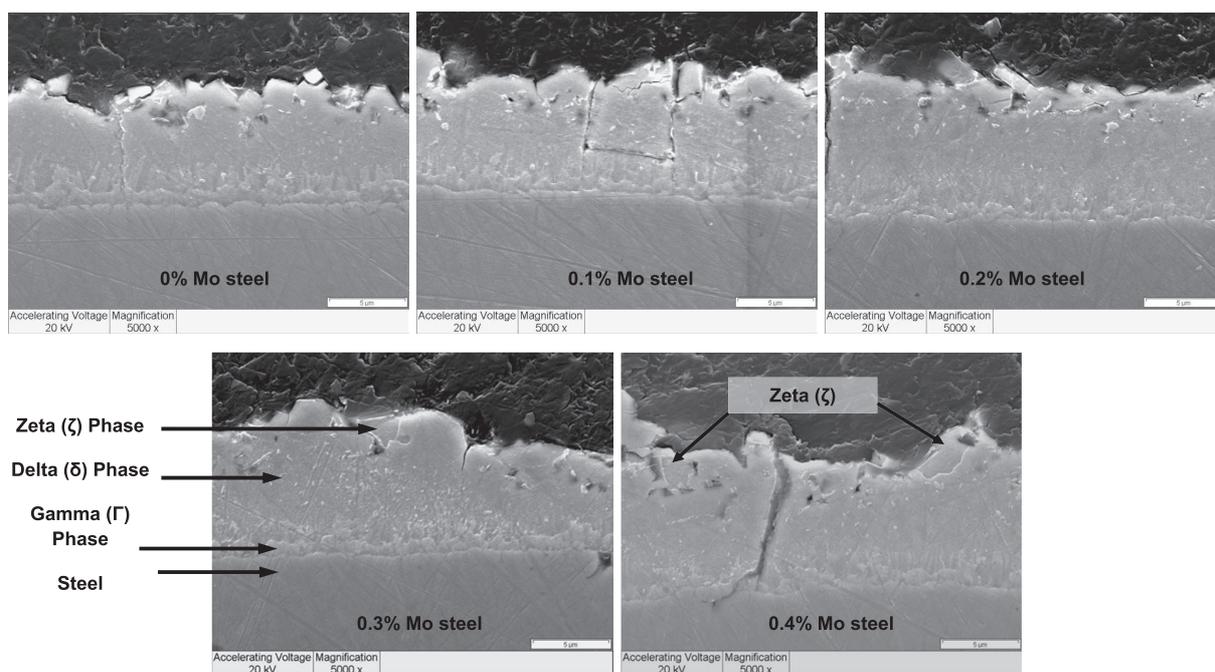


Fig. 5. Galvannealed coating microstructure development with increase in molybdenum wt% in steel. Chemically etched cross-sections exhibit gamma phase as a thin layer at the steel/coating interface. Delta phase exists over the gamma phase. Zeta phase, when present, occurs at the coating surface and exhibits a smooth delineation. All the coatings primarily contained delta and gamma phase. In addition, 0.3 wt% and 0.4 wt% molybdenum steels exhibited some amount of zeta phase (indicated by arrows).

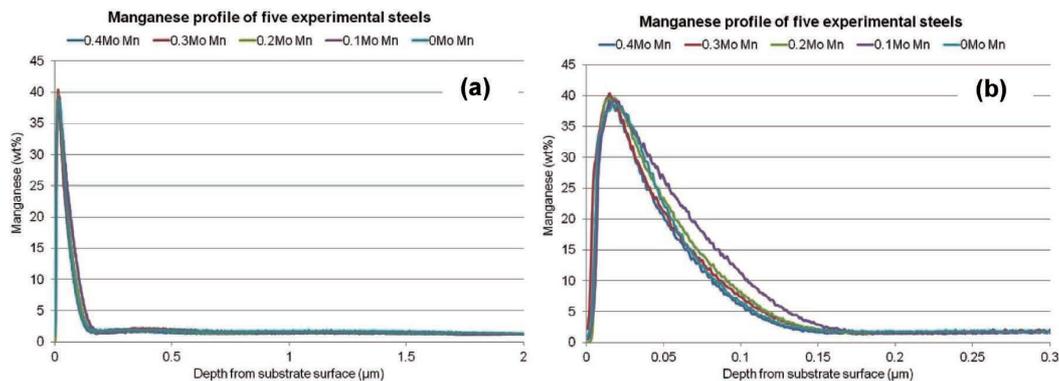


Fig. 6. Manganese depth profiles showing similar surface segregation for all five steels (a) is showing top 2  $\mu\text{m}$  of the steel and (b) is showing top 300 nm of the steel.

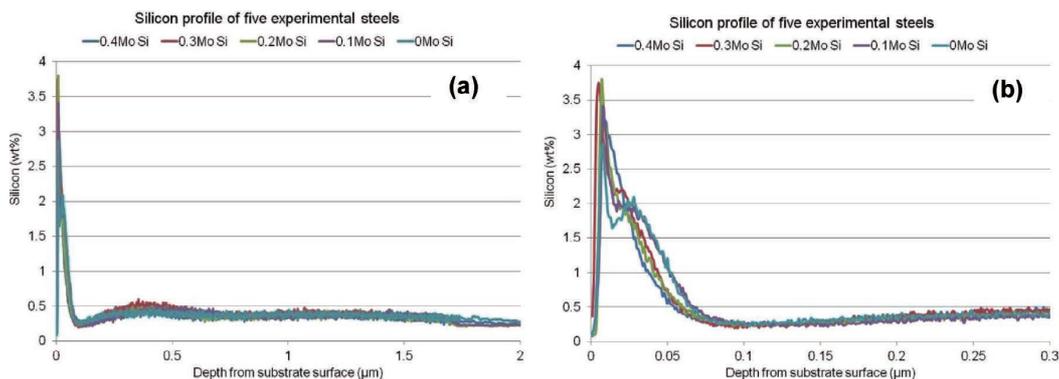


Fig. 7. Silicon depth profiles showing surface segregation for all five steels (a) is showing top 2  $\mu\text{m}$  of the steel and (b) is showing top 300 nm of the steel.

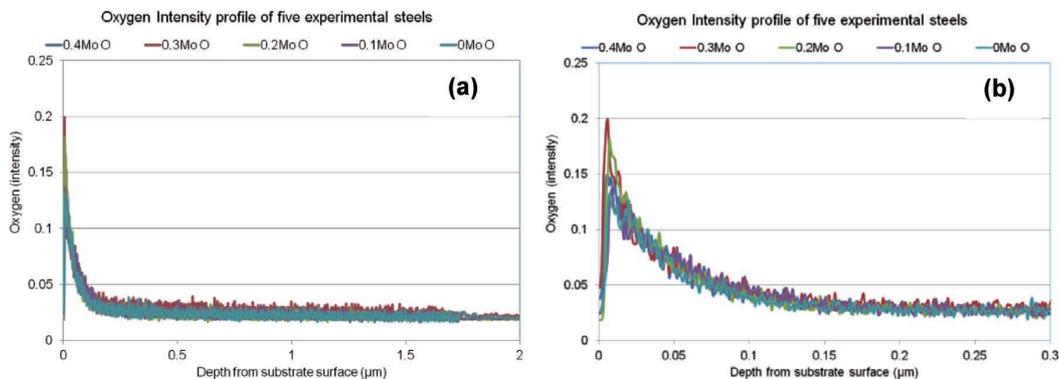


Fig. 8. Oxygen intensity profiles of all five steels showing surface segregation (a) is showing top 2  $\mu\text{m}$  of the steel surface and (b) is showing top 300 nm of the steel surface.

steel chemistry near the surface using GDOES in order to establish any possible explanation for differences in the galvannealing behavior.

Depth profiles of manganese for all five steels are given in Fig. 6. These profiles show that manganese segregates to the surface and there was no significant difference between the manganese profiles of different steels. Figure 7 shows silicon depth profiles for different steels. In all steels, silicon segregates to the surface and there was no significant difference between the different steels. Similar oxygen segregation to the surface can also be observed in all five steels as shown in Fig. 8.

Figure 9 shows the molybdenum elemental profile of all five steels. Unlike Mn or Si, no Mo segregation or depletion was observed at the steel surface. This shows that molybde-

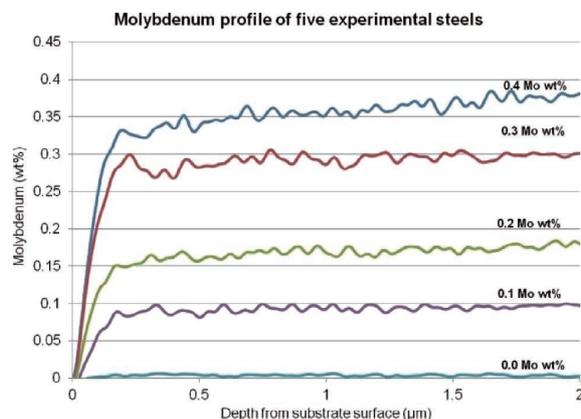


Fig. 9. Molybdenum depth profiles of top 2  $\mu\text{m}$  of the steel surface for all five steels showing no surface segregation.

num is not a surface segregant and has no obvious influence on the near surface chemistry. Hence, it can be suggested that Mo did not directly interfere with steel/zinc reactions.

The above results are consistent with the literature.<sup>13,14</sup> Bode *et al.*<sup>13</sup> tabulated free enthalpy of formation data from literature for oxidation of individual elements for a given annealing condition. The data given in **Table 3** shows that the enthalpies of formation of MnO and SiO<sub>2</sub> are much lower than that of MoO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>. Similar to Fe, Mo is less likely than Mn and Si to form oxide at the given annealing conditions. Bode *et al.* annealed several steels with different chemistries containing Mn, Si, Al, Cr and Mo at 1 073 K (800°C) for 60 seconds in 5% H<sub>2</sub>/ 95% N<sub>2</sub> by volume at 243 K (−30°C)

**Table 3.** Enthalpies showing the annealing atmosphere is reducing to Fe and Mo and oxidizing to Mn and Si.<sup>13</sup>

Element	Free formation enthalpy at −1 073 K (800°C) (kJ/ mol O <sub>2</sub> )	Reduction atmosphere 5–8% H <sub>2</sub> / N <sub>2</sub> DP = 243 K (−30°C) Anneal temperature = 1 073 K (800°C)
Al	−890 (Al <sub>2</sub> O <sub>3</sub> )	No
B	−775 (BO <sub>3</sub> )	No
Ti	−725 (TiO <sub>2</sub> )	No
V	−716 (V <sub>2</sub> O <sub>3</sub> )	No
<b>Si</b>	−680 (SiO <sub>2</sub> )	<b>No</b>
Nb	−619 (NbO <sub>2</sub> )	No
<b>Mn</b>	−615 (MnO)	<b>No</b>
Cr	−561 (Cr <sub>2</sub> O <sub>3</sub> )	No
P	−394 (P <sub>2</sub> O <sub>5</sub> )	Yes
<b>Mo</b>	−393 (MoO <sub>2</sub> )	<b>Yes</b>
<b>Fe</b>	−375 (Fe <sub>3</sub> O <sub>4</sub> )	<b>Yes</b>

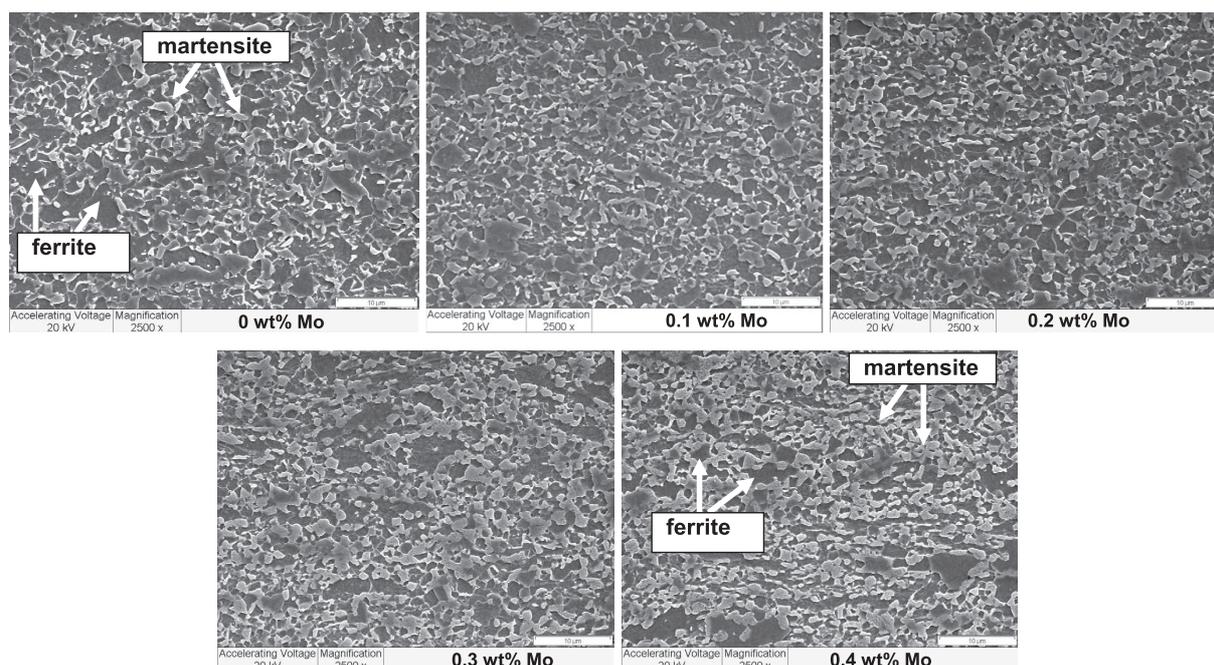
dew point. Molybdenum content was varied between 0.01 wt% to 0.25 wt%. They reported that Mo does not become enriched on the surface. However, Bode *et al.* did not investigate galvannealing kinetics. Kyono *et al.*<sup>14</sup> also did not detect any Mo surface segregation in annealed 0.15 wt% Mo Steel. They reported that there was no significant influence on galvannealing at 0.15 wt% Mo. In addition, the above two studies showed that addition of Mo does not deteriorate zinc wettability.

The above surface chemical analysis did not identify any obvious differences between the steels with and without Mo. Elevated amount of oxygen in the steel was attributed to the formation of manganese - silicon oxides. No correlation was observed between the surface chemistry and the galvannealing kinetics of the above steels.

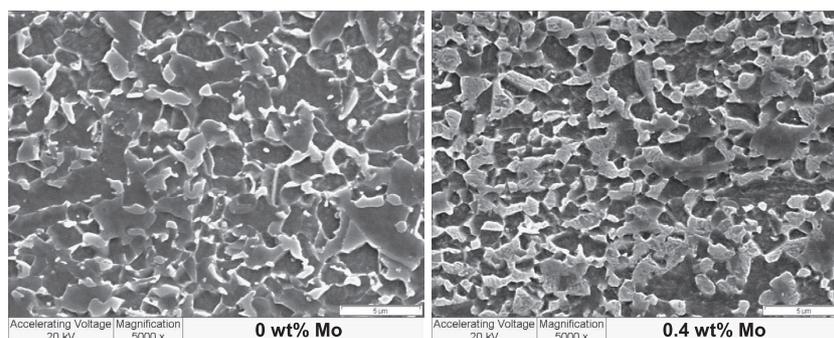
### 3.2.2. Steel Chemistry and Steel Microstructure

Since no obvious relation was observed between the steel surface chemistries and galvannealing kinetics, it was suspected that the steel microstructure may be the main source for the differences in the galvannealing behavior. Nitta *et al.*<sup>20</sup> studied diffusion behavior of iron and molybdenum using radioactive tracers in alloys made of high purity iron and molybdenum in the temperature range of 823 K (550°C) to 1 173 K (900°C). At ~1 123 K (850°C), an increase in Mo from 0.4 wt% to 1.0 wt% resulted in a small increase in iron diffusion coefficients from  $1.02 \times 10^{-15}$  m<sup>2</sup>/s to  $1.12 \times 10^{-15}$  m<sup>2</sup>/s, respectively, while Mo diffusion coefficients decreased slightly from  $1.29 \times 10^{-15}$  m<sup>2</sup>/s to  $1.27 \times 10^{-15}$  m<sup>2</sup>/s. Hence, it can be inferred that for the steels studied in the present work with Mo up to 0.4 wt%, Mo addition is less likely to influence the iron diffusivity. This led the authors to investigate the influence of steel microstructure on galvannealing.

The steel microstructures of all five steels are given in **Fig. 10**. The amount of ferrite decreased and the amount of



**Fig. 10.** Galvannealed steel microstructure development with increasing molybdenum content. Ferrite phase (dark) decreased and martensite phase (light grey islands) increased with increase in steel Mo.

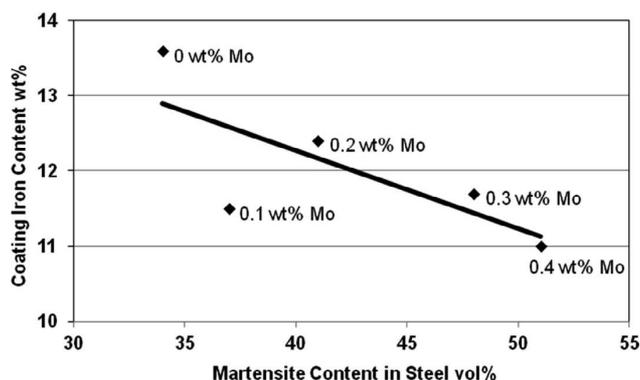


**Fig. 11.** M0 (0 wt% molybdenum) steel contained more ferrite (dark phase) and less martensite (light grey islands) as compared with M4 (0.4 wt% molybdenum) steel.

martensite increased with an increase in the steel molybdenum content. Phase analysis, done using a point count method with Image Pro Plus<sup>®</sup> software, showed about 34 vol% and 51 vol% of martensite for M0 and M4 steels, respectively. **Figure 11** shows a higher amount of ferrite and less martensite in the M0 steel as compared with M4 steel. The amount of martensite in the final product indicates the amount of austenite present after cooling from the intercritical annealing soak temperature, and as it passes through the zinc bath and the galvanneal furnace. Different amounts of martensite in the final product indicate different amounts of austenite at the time of galvannealing in M0 through M4 steels. **Figure 12** clearly shows the effect of steel martensite content on the coating iron content, which indicates the galvannealing rate. With increase in the steel molybdenum content, the amount of martensite in the steel increased and resulted in slower galvannealing kinetics.

Diffusion data<sup>21,22)</sup> shows that iron self-diffusion in FCC iron is an order or two orders of magnitude slower than in BCC iron. Due to the lack of iron self diffusion data for the present experimental DP steels, self-diffusion in iron was used as an approximation for self diffusion in the FCC austenite phase and the BCC ferrite phase. The differences in self-diffusion in austenite vs. ferrite phase can provide an explanation to the observed slow galvannealing kinetics with increasing molybdenum in the present study of DP steels. At the time of galvannealing, M4 steel contained less ferrite and more austenite than M0 steel. Hence, it is suggested, that due to the higher amount of austenite (FCC phase), iron diffusion was relatively slower in M4 steel than in M0 steel. It is well known that iron dissolution in the liquid zinc is the rate determining factor for galvannealing.<sup>23,24)</sup> During the initial moments of the strip immersion into the liquid zinc, the iron is not in equilibrium with zinc. Iron dissolution occurs to produce intermetallic compounds in equilibrium with iron and liquid zinc. Slower iron self diffusion in austenite phase than ferrite phase leads to slower iron dissolution and hence, slower galvannealing rate in M4 steel than M0 steel.

In summary, the authors would like to propose a possible mechanism that the substrate microstructure can have an influence on the galvannealing kinetics. Increase in the steel austenite content can reduce the iron self-diffusion and its dissolution into the liquid zinc and hence, slow down the galvannealing kinetics. Additional experiments using steels with different combinations of ferrite/austenite



**Fig. 12.** Coating iron content decreased as the martensite phase content in the steel increased.

phases will be investigated to confirm or refute the above hypothesis.

#### 4. Conclusions

In our experience, silicon and manganese segregate to the surface and form respective oxides which contribute to poor wetting and delayed galvannealing in AHSS. The present study was conducted to evaluate the influence of Molybdenum addition on galvannealing kinetics of an AHSS. Analysis of steel surface just before entering the zinc bath showed that molybdenum does not segregate to the surface, unlike silicon and manganese, and hence, has no “segregation” effect on the galvannealing reaction. On the other hand, the presence of molybdenum does alter the steel microstructure by suppressing the austenite to ferrite transformation during cooling from intercritical annealing. Mo containing steels contained more austenite during the period of galvannealing reaction. Iron dissolution in liquid zinc is considered as the rate determining factor for galvannealing. As the iron self diffusion is slower in austenite phase than in ferrite phase, increasing volume of austenite in the steel will lead to slower iron dissolution in zinc. The steels with higher austenite content (Mo containing steels) exhibited slower galvannealing rate than the steels with lower austenite content. Addition of Mo to the steel can lead to delayed galvannealing kinetics.

No obvious coatability improvement was observed with the addition of Molybdenum in the studied steels. The poor wettability of the DP steels studied here can be attributed to

the presence of high levels of Mn and Si in the steel.

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