Examination and Analysis of 2 Pct Mg-55 Pct Al-1.6 Pct Si-Zn Coating on Steel

YISHENG R. CHEN

The current study was conducted to examine the microstructure of the 2 pct Mg-55 pct Al-1.6 pct Si-Zn (wt pct) coating on steel in detail and analyse the formation mechanisms of various reaction products in the coating. The coating microstructure was comprised of an α-Al dendrite framework, and an interdendritic network, occupied by a number of solidification products, which were fine Al-Zn mixtures, Mg₃Si, Si, MgZn₂, and lamellar MgZn₂/Zn mixtures. It was found that the Al-Zn mixtures observed in the interdendritic region were the decomposition products of the high Zn α-Al components of various eutectic reactions taking place during solidification. A method was developed to differentiate the Si and Mg₃Si phases optically with colour contrasts. It was found that, when Si and Mg₃Si formed, they occupied the entire interdendritic spaces at the locations where they formed. Judging from the Al-Mg-Si liquidus projection, the Mg₃Si phase should form first during solidification, followed by the simultaneous formation of Mg₃Si and Si. On the other hand, the MgZn₂ phase formed into two different morphologies, with a large blocky shape and fine precipitates embedded in the lamellar Zn/MgZn₂ mixtures, both surrounded by Al-Zn mixtures. It was observed that all eutectic reactions involved the formation of an α-Al component, which formed in a divorced manner via either growing on existing dendrite arms, or sometimes as isolated islands embedded in blocky MgZn₂.

https://doi.org/10.1007/s11661-020-05983-y
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I. INTRODUCTION

AFTER the commercial production of the 55 pct Al-1.6 pct Si-Zn (wt pct, weight percent, which will be used throughout this paper, unless otherwise indicated) coated products (trademark Galvalume® or Zincalume® and various other brand names, such as COLORBOND®[** for prepainted Zincalume® steel) in 1972,[1] a new generation of Zincalume® and COLORBOND® products was launched in 2013 by Bluescope, Australia.[2,3] These new products are manufactured based on the original Al-Si-Zn composition, but with 2 pct Mg added, having a nominal composition of 2 pct Mg-55 pct Al-1.6 pct Si-Zn, designated as “AM” according to the Australian Standard AS1397-2011.[4]

* Galvalume is a trademark of BIEC International Inc.
** Zincalume® and COLORBOND® are trademarks of BlueScope Limited, Australia

There was a relatively short history of the development of the AM coating. In 1993, Nolan conducted a study,[5] evaluating the effects of separate additions of magnesium at a range of 0.1 to 2.5 pct, and other elements (calcium at 0.1 to 0.5 pct, gallium at 0.05 to 1.0 pct and copper at 0.05 to 1.0 pct) to the traditional Zincalume® coating on the microstructure development, mechanical properties, and corrosion resistance of the coating. The main contribution of this work was the discovery of the much-improved corrosion property of the Mg-added coatings.

The 2 pct Mg addition was finally selected after 20 years of further research and development[3,4] One of the main reasons for the performance improvement was identified to be the formation of Mg-containing phases, namely Mg₃Si and MgZn₂, in the interdendritic region of the coating microstructure.[2,3,6] The optimized composition at 2 pct Mg was later confirmed by the studies of Fujii and Shimoda[7] and Shimoda et al.[8] After a comparison of the Mg addition levels of 0.5, 1.5, and 2.5 pct, Li et al.[9] also found that the 1.5 pct Mg-55 pct Al-1.6 pct Si-Zn coating had the best corrosion resistance in a neutral salt spray environment. Another study carried out by Liu et al.[10] assessed the microstructures and corrosion resistance of several Mg-added 50 pct Al-1.5 pct Si-Zn coatings. The results of this latter study indicated that out of the four levels of Mg additions examined (0, 1.25, 3, and 4 pct), the 3 pct Mg-added coating had the best performance.
Despite the various studies conducted, little information is available to reveal the coating microstructure in detail. It appears that a consistent understanding of the solidification sequence and microstructural development in the coating, and even a consistent interpretation of the coating microstructure, has not been achieved.

Figure 1 is the only micrograph published thus far to reveal the cross-sectional microstructure of the 2 pct Mg-55 pct Al-1.6 pct Si-Zn coating. The microstructure shown in Figure 1 was similar to that of the 55 pct Al-1.6 pct-Zn coating but more phases and constituents were present. In addition, the morphologies of the Si and Mg2Si were found to be similar, but “morphologically indistinguishable and could only be differentiated by a chemical microanalysis technique” using an electron probe microanalyser (EPMA).

To interpret the microstructure observed, assisted by the cooling rate measurement from an ingot sample of about 30 cm³ cooled naturally in the air, a solidification sequence was proposed by Williams et al. as given in Table I. It was proposed that the solidification process started with the formation of primary α-Al, followed by the L → fcc-Al (at about 560 °C) → Diamond-Si or/and Mg2Si → MgZn2 → hcp Zn or/and Mg2Zn11, with the first two stages proposed being similar to those shown in Table I and the two subsequent stages being different. According to Figure 2, Stage 3 of the L → α-Al + Zn eutectic reaction proposed by Williams et al. (Table I) could not have been taking place at 379 °C. Also, as the compositions of Zn and Si in the remaining liquid phase were changing with the formation of the fcc-Al (α-Al)
and precipitation of Si, Mg$_2$Si and MgZn$_2$ phases, the actual solidification sequence would be expected to deviate significantly from that shown in Figure 2. In fact, one cannot use an isopleth to explain the solidification sequence of a multi-component alloy since the solidification path is not restricted to a certain plane,\cite{16,17} and a more rigorous reassessment is clearly required.

In view of the limited fundamental studies conducted and the inconsistent interpretations proposed in the previous studies, the current study was conducted to (a) examine the coating microstructure in more detail to determine various phases present in the 2 pct Mg-55 pct Al-1.6 pct-Zn coating, (b) use a thermodynamic computation package to simulate the solidification path of the coating, and (c) based on the microstructural observation and thermodynamic calculation results, further explore the solidification sequence so that the microstructure developed can be adequately interpreted. The results of the detailed coating structure examination and analysis are presented in this paper. The results of the thermodynamic simulation are presented in another paper.\cite{18}

### II. EXPERIMENTAL PROCEDURE

Several commercial low carbon, low silicon steel samples coated with the 2 pct Mg-55 pct Al-1.6 pct-Zn coating, manufactured according to the Australian Standard AS1397-2011 by BlueScope Limited, were obtained from a local steel supplier, K&K Steel, Hastings, Victoria, Australia. The process to produce these coated samples has been described by Williams et al.\cite{4} comprising a steel heating step in a direct-fired furnace using natural gas, followed by annealing in a 5

| Sequence | Reaction | Temperature, °C |
|----------|----------|-----------------|
| (1)      | L → α-Al | 559             |
| (2)      | L → Al + Si + Mg$_2$Si eutectic | 463             |
| (3)      | L → Al + Zn eutectic | 379             |
| (4)      | L → α-Al + Zn + MgZn$_2$ eutectic | 341             |
| (5)      | completion | 330             |
to 10 pct H₂-N₂ atmosphere with a dew point below – 20 °C, and then submerging the steel strip in a molten 2 pct Mg-55 pct Al-1.6Si-Zn alloy bath, maintained at a temperature sufficiently high to allow the molten metal to be coated onto the strip with a uniform thickness. After a layer of molten metal was coated onto the strip, excessive coating metal was removed by a pair of air-wiping nozzles and cooled rapidly in the upleg cooling section by a bank of air jets, followed by water quenching to a temperature under 50 °C.

For microscopic observation, the coated steel samples were mounted vertically or tilted at an angle of about 15° to 30° with the surface. By calculation, if the sample was tilted at an angle of 30° with the surface, the coating thickness was enlarged twice for examination. An even greater cross-sectional thickness could be obtained if the angle was smaller than 30°.

In order to reveal the interdendritic areas, nital (a small percentage of nitric acid in alcohol) was used to etch the sample. To differentiate the pure zinc and the MgZn₂ phases, it was found necessary to etch the sample lightly, usually with 2 pct nital for about 5 seconds or shorter. When the etching duration was too long, e.g., > 10 seconds, parts of the pure zinc and MgZn₂ phases could be dissolved. A scanning electron microscope (SEM) was used to examine the coating microstructure. It was found that using the back-scattered electron images, an SEM was effective in differentiating the pure zinc and MgZn₂ phases, it was found necessary to etch the sample and microstructures, and compositions of various phases could be more closely determined.

III. RESULTS

A. Surface Spangles

The uniform and fine spangle appearance is an aesthetic appeal of the traditional Zincalume® coating. By adding 2 pct Mg, it appeared that the spangle appeal was not as clear as that on the Mg-free Zincalume® coatings. Generally, a large number of regular six-sector spangles were present in a 55 pct Al-1.6 pct Si-Zn coating. However, such a regular spangle appearance could not be observed on a 2 pct Mg-55Al-1.6 pct Si-Zn coating. When observed under an optical microscope, some six-sector spangles were still visible, as seen in Figure 3, but a large proportion of the surface area appeared more similar to the unusual mini-spangle or non-spangle surfaces shown on the traditional Zincalume® coating, without the regular spangle appearance. This observation was consistent with that of Li and Hreso.

B. Cross-Sectional Microstructure

A back-scattered electron SEM image of the 2 pct Mg-55 pct Al-1.6 pct Si-Zn coating layer is shown in Figure 4. The microstructure is similar to that shown in Figure 1 comprising three important features, with (a) primary α-Al dendrites forming the framework of the coating, (b) an intermetallic alloy layer at the coating-steel interface to form a bond between the coating and the steel and (c) interdendritic regions where many different phases are present. As will be shown later, the dark grey phase in the interdendritic region is either the Mg₂Si or Si phase, and the lighter grey region is where all the zinc-rich phases are present. Figure 4(b) shows more clearly the various phases and constituents present in the zinc-rich region. As can be seen, it comprises three main features: (i) Al-Zn mixtures, (ii) blocky MgZn₂ phase surrounded by Al-Zn mixtures, and (iii) Zn/MgZn₂ lamellar structure also surrounded by Al-Zn mixtures. The identification of these different phases and constituents is presented as follows.

C. Al-Zn Mixtures in the Interdendritic Region and α-Al Dendrites

Extensive analyses were conducted to determine the compositions of the Al-Zn mixtures and the Al dendrite arms, with two examples shown in Figure 5. Spots 4 to 12 in Figure 5(a) and Spots 7 to 8 in Figure 5(b) were selected to analyse the Al-Zn mixtures. Spots 9 to 12 in Figure 5(b) were selected to analyse the α-Al dendrite arms. As the Al and Zn phases in the Al-Zn mixture areas were very fine, it was not possible to determine the actual compositions of the individual Al and Zn phases...
using SEM-EDS (energy dispersive spectroscopy), and therefore, the compositions obtained were close to the average compositions of the Al-Zn mixtures. The EDS results obtained are given in Tables II and III. Note that Spots 1 to 3 in Figure 5(a) were selected for analysing the intermetallic alloy layer. Discussion of the intermetallic alloy formation was outside the scope of the current study, and therefore, the data obtained were not presented in Table II. Also, Spots 1 to 6 in Figure 5(b) were not located in the Al-Zn mixtures, and therefore were not listed in Table III. It was revealed that both the Al-Zn mixtures and \( \alpha \)-Al dendrites comprised Al and Zn only with negligible levels of Mg and Si detected. From the data shown, the Al/Zn ratio (atomic ratio) in the \( \alpha \)-Al dendrite arms was consistent at about 87:13, whereas the Al/Zn ratio in the Al-Zn mixture areas varied from about 47:53 to 68:32. More extensive analyses of a larger number of the Al-Zn mixture areas in more samples revealed that the Al:Zn ratio varied between 30:70 to 66.5:33.5, as summarized in Figure 6, with the majority of the data falling in the range of atomic ratios of Al:Zn = 45:55 to 65:35.

D. Si and Mg\(_2\)Si Phases

Using the new etching method developed, Si and Mg\(_2\)Si could be differentiated clearly, as seen in an image taken from an ingot cross-sectional sample, as shown in Figure 7(a). The two phases share the same ‘Chinese script’ morphology, but the colours were distinctively different, with the Mg\(_2\)Si phase showing a blue colour and the Si phase dark grey.

The same colour contrasts were observed in the cross-sections of the steel coating samples, with the Mg\(_2\)Si phase appearing blue or purple, as seen in Figure 7(b) and Figures 8(a) through (b). The volume fraction of the Si phase was much smaller than that of the Mg\(_2\)Si. After an extensive search of the microstructure of a tapered cross-sectional coating sample, an area where the Si phase was present was located, as shown in Figure 8(a). An enlarged optical image and a SEM image were taken for this area, marked by the blue and red windows, respectively, as shown in Figures 8(b) and 8(c). EDS analyses of the spots shown in Figure 8(c) are given in Table IV. It is seen that the Mg concentrations from Spots 1 to 8 and 12 were very low at (0.4 to 1.59 at. pct), and those from Spots 9 to 11 were significantly greater (32 to 45 at. pct). Judging from the ratios between the Mg and Si concentrations detected, it can

| Spot | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Zn, At. Pct | 39.5 | 41.3 | 32.0 | 52.0 | 36.1 | 43.7 | 45.2 | 46.2 | 53.2 |
| Al, At. Pct  | 60.5 | 58.7 | 68.0 | 48.0 | 63.9 | 56.3 | 54.8 | 53.8 | 46.8 |
| Phases      | Al + Zn | Al + Zn | Al + Zn | Al + Zn | Al + Zn | Al + Zn | Al + Zn | Al + Zn | Al + Zn |

Fig. 4—Typical cross-sectional coating microstructure revealed by SEM: (a) overview and (b) zinc-rich interdendritic region.

Fig. 5—Images showing spot locations for EDS analyses for the Al-Zn mixtures and \( \alpha \)-Al dendrites: (a) Area I and (b) Area II. The composition results are given in Tables II and III, respectively.

Table II. EDS Results of the Al-Zn Mixtures in Fig. 5(a)
be confirmed that the blue phase and dark grey phases shown in Figures 8(a) through (b) were the Mg$_2$Si and Si phases, respectively. As the sample was tilted at a shallow angle, with the coating thickness underneath being 1 to 2 $\mu$m thick only, the high iron concentrations detected was attributed to the noise signals generated by the steel substrate underneath, rather than from iron in solution in the Si and Mg$_2$Si phases.

The results shown in Table IV also revealed that when EDS was used to analyse these phases, significant levels of Al and Zn were present. From further analyses, pure Si and “pure” Mg$_2$Si (containing no Al and Zn) were often detected in similar areas but with much larger sizes. Therefore, the Al and Zn detected were believed to be not an indication that they were in solution in these phases, but rather, an indication that they came from the adjacent Al and Zn rich phases.

E. Large MgZn$_2$ Particles and Zn/MgZn$_2$ Lamellar Mixtures

Figures 9(a), (b), and 10(a) showed several examples of how the various Zn-rich phases in the interdendritic regions in the steel coating samples were analysed. As Al was found to have a significant solubility in both the MgZn$_2$ and Mg$_2$Zn$_{11}$ phases, the (Mg + Al):Zn ratios obtained were used for determining whether the phase containing primarily Mg and Zn was MgZn$_2$ or
Mg$_2$Zn$_{11}$. In Figure 9(a), windows 1 to 2 are located in the large, blocky grey phase, and the compositions, as shown, are on average 22.4 at. pct Mg-9.7 at. pct Al-Zn with an (Mg + Al):Zn atomic ratio of approximately 1:2, suggesting that it is an MgZn$_2$ phase. This is confirmed from the results of Spots 1 to 3 in Figure 9(b) and the result from Spot 5 in Figure 10(a). More extensive analysis was conducted for the large, blocky Mg-containing phase, and an average composition of 22.5 at. pct Mg-11.4 at. pct Al-Zn was obtained from a set of 26 data points, ranging from 20.3 at. pct Mg-13.4 at. pct Al-Zn to 25.3 at. pct Mg-7.0 at. pct Al-Zn. It was therefore concluded that the large, blocky grey phase was most likely the MgZn$_2$ phase dissolved with about 10 at. pct Al.

From Figures 4(b), 5, 9, and 10(a), several two-phase regions containing a bright phase with some fine grey lines embedded were also seen. Analyses of the bright phase showed a very high zinc content, generally above...
Analyses of the fine grey phase in the lamellar structure were challenging, because thermodynamically, two possible phases, \( \text{Mg}_2\text{Zn}_{11} \) and \( \text{MgZn}_2 \), could be present, and we would like to determine which phase it was. After numerous attempts, some good results were obtained with an example shown in Figure 10(a). In Figure 10(a), Spots 1 to 3 were used to analyse the fine grey phase, Spot 4 for the bright phase, Spot 5 for the blocky phase, Spot 6 for the dark grey phase, and Spot 7 for the Al-Zn mixture. The results from Spots 4, 5, 6, and 7 confirmed the results obtained previously for the Zn phase, \( \text{MgZn}_2 \), \( \text{Mg}_2\text{Si} \), and the Al-Zn mixtures. The results for Spots 1 to 3 showed a much lower Mg content of about 13 at. pct as compared to about 20 at. pct detected from the blocky \( \text{MgZn}_2 \) phase. By adding the Al content of about 13 at. pct as compared to about 20 at. pct, the actual \( \frac{(\text{Mg} + \text{Al})}{\text{Zn}} \) ratio of approximately 0.25 was obtained. This number is significantly greater than the value of 0.18 \( \frac{2}{11} \) for the \( \text{Mg}_2\text{Zn}_{11} \) phase. Considering the inevitable influence from the neighbouring Zn phase, if this grey phase had been \( \text{Mg}_2\text{Zn}_{11} \), then the actual \( \frac{(\text{Mg} + \text{Al})}{\text{Zn}} \) value would have been even smaller than 0.18. Therefore, this Mg-containing phase was more likely to be \( \text{MgZn}_2 \), rather than \( \text{Mg}_2\text{Zn}_{11} \).

A similar area observed in an ingot sample was also used to confirm the above conclusion, as shown in Figure 10(b). In Figure 10(b), Spots 11, 12, and 13 were used to analyse the bright phase, whereas Spots 1 to 6 and 14 were used to determine the grey phase.

From Spots 11 to 12, a zinc concentration of 88 to 94 at. pct Zn-Al was obtained, confirming that it was the Zn phase. There was a small Mg level in Spot 13, but the Mg signal was believed to come from the adjacent Mg-containing phase. The Mg concentrations from Spots 1 to 6 and 14 were within the range of nearly 10 to 20 at. pct, greater than those obtained from Spots 1 to 3 in Figure 10(a). As Spots 1, 2, 4, and 5 were located near the Al-Zn mixture, much higher levels of Al were obtained. In contrast, the Al contents at Spots 3 and 6 were significantly lower at 2.8 at. pct with an Mg level of nearly 20 at. pct. The \( \frac{(\text{Mg} + \text{Al})}{\text{Zn}} \) ratios from these two spots were approximately 2.8 (0.25) and 2.3:7.7 (0.3), significantly greater than 0.18 (2/11). A lower Mg content (11.9 at. pct) was obtained from Spot 14, but this could be because the spot for analysis was too close to the adjacent Zn phase, and even with the lower Mg level, its \( \frac{(\text{Mg} + \text{Al})}{\text{Zn}} \) ratio (0.19) was still greater than 0.18. The results obtained thus further suggested that the grey phase was more likely \( \text{MgZn}_2 \), rather than \( \text{Mg}_2\text{Zn}_{11} \).

The results from Spots 7 to 10 further confirmed that the Al-Zn mixtures had an average concentration of around 50 to 56 at. pct Al-Zn.

The microstructures shown in Figures 4(b), 5(a), 9, and 10(a) also revealed that the Al-Zn mixtures could sometimes be present as isolated islands embedded in the blocky \( \text{MgZn}_2 \) phase.

**IV. DISCUSSION**

**A. Formation of the Si and Mg\(_2\)Si Phases**

As shown in Figures 4, 7, and 8, the Si and Mg\(_2\)Si phases had similar morphologies, and they appeared to form as discrete phases in the interdendritic regions, occupying the entire interdendritic regions at the locations where they formed. Between the Si or Mg\(_2\)Si phase and the \( \alpha \)-Al dendrite arms, Zn-rich phases or Al-Zn mixtures are not present. In theory, Si and/or Mg\(_2\)Si should form via a L \( \rightarrow \) (Si and/or Mg\(_2\)Si) + \( \alpha \)-Al eutectic reaction.\(^{[18]} \) Thus, with their formation, the \( \alpha \)-Al phase would also form as a component of the eutectic reaction. The discrete nature of the Si and Mg\(_2\)Si phases indicated that the L \( \rightarrow \) (Si and/or Mg\(_2\)Si) + \( \alpha \)-Al eutectic reaction must have been a divorced reaction, with the \( \alpha \)-Al phase formed separately at other locations, most likely via the growth of the existing dendrites.

From the microstructures shown in Figures 7(b) and 8, the population of the Mg\(_2\)Si precipitates was much greater than that of Si. As both Al and Zn were essentially not present in the Mg\(_2\)Si and Si phases, the sequence of Mg\(_2\)Si and Si formation was assessed using the Al-Mg-Si projection shown in Figure 11.\(^{[22,23]} \) At concentrations of 2 wt pct Mg and 1.6 wt pct Si, the atomic ratio of Mg-Si is 2.9:2.0, as indicated by the arrow shown in Figure 11. It can be seen that, upon cooling, Mg\(_2\)Si would precipitate out first, and then with the formation of the Mg\(_2\)Si phase, the Si:Mg ratio would increase, and the molten phase composition (assuming Zn was not present) would follow the red arrow towards the ternary eutectic point at \( E_1 \) where the Si phase would start to form as well. This could explain why, with the presence of 2 wt pct Mg, Si had a much smaller volume fraction of the Si and Mg\(_2\)Si phases.
fraction and was hard to find in the coating (Figure 7(b) and 8).

B. Formation of the Fine Al-Zn Mixtures in the Interdendritic Regions

One important aspect to understand how the microstructure in the interdendritic area was developed is the understanding of how the Al-Zn mixtures formed. From the microstructural observation and EDS analysis results obtained, two important features of the Al-Zn mixtures were observed. First, the two phases (Al and Zn) in the Al-Zn mixture were very fine, uniform, and dispersed. This suggests that they were more likely formed as the decomposition products from a solid phase rather than from a liquid phase because if they had been the eutectic products from a liquid, they would have developed into a layered structure or a divorced structure. However, this was not the case.

Second, the mixtures comprised Al and Zn only, having a composition range of atomic ratios of Al:Zn = 70:30 to 35:65. As the mixtures contain Al and Zn only, their nature can be analysed by examining the binary Al-Zn phase diagram, as shown in Figure 12.[24] From Figure 12, it can be seen that if they had been the products of the binary Al-Zn eutectic, then one would have expected that the mixture composition would have been close to Al:Zn = 10:90 (atomic ratio), or Al-95 wt pct Zn, but this, again, was not the case.

To assist in the understanding of how the Al-Zn mixtures formed, two bars are drawn in the Al-Zn phase diagrams for the composition range of Al:Zn = 70:30 to 35:65. As the mixtures contain Al and Zn only, their nature can be analysed by examining the binary Al-Zn phase diagram, as shown in Figure 12.[24] From Figure 12, it can be seen that if they had been the products of the binary Al-Zn eutectic, then one would have expected that the mixture composition would have been close to Al:Zn = 10:90 (atomic ratio), or Al-95 wt pct Zn, but this, again, was not the case.

In the study conducted by López et al. [14] a binary Al-Zn alloy comprising 95 wt pct Zn-Al (~ 90 at pct Zn-Al) was produced by melting corresponding amounts of high purity Zn and Al, and then cooled in a vacuum to room temperature (cooling rate not specified). Several slices of the alloy were then heated in a vacuum again back to different temperatures between 250 and 375 °C, with seven temperature points above the eutectoid temperature of 277 °C, between 283 and 375 °C, and held at these temperatures for 14, 28, and 84 days (annealing treatments), followed by water quenching. After the annealing treatments, the microstructures of the slices were examined.

It was found that the alloy comprised two regions, with one region being the (Zn) phase forming the matrix of the alloy microstructure, and the second region being (Zn) + (Al) mixtures. The (Zn) + (Al) mixtures had a stripy morphology in the as-cast state but appeared more spherical in the annealed states. An example of the alloy in the annealed state is reproduced in Figure 13.

The sample shown in Figure 13 was annealed at 375 °C for 28 days to convert the as-cast structure to a uniform two-phase structure, comprising a mixture of α'-Al, containing about 65 at. pct Zn-Al or 82 wt pct Zn-Al according to Figure 12, and (Zn) first, followed by water quenching. It is seen that the region where the original α'-Al phase was (the second region mentioned above) is now occupied by a mixture of α'-Al + (Zn). This indicates that the high Zn α-Al phase (α'-Al) had
undergone a eutectoid reaction, forming the α'-Al + (Zn) mixture even when the sample was cooled so rapidly by water quenching.

The experiments conducted by López et al. [14] provided strong evidence to show that it was impossible to suppress the eutectoid reaction even with a cooling rate as rapid as water quenching if the α-Al phase had a Zn concentration at or above 77.7 wt pct. Applying this finding to our current study, as the coating samples were cooled by forced air only, suppression of the eutectoid reaction from the high Zn α-Al phase (α'-Al) formed in the coating to a mixture of low Zn α-Al phase (α'-Al) and Zn would then be very unlikely if the Zn concentration in the α-Al phase was sufficiently high.

However, if the Zn concentration in the α-Al phase formed was not high enough, e.g., lower or close to 32.5 wt pct Zn, then the eutectoid reaction possibly would not occur or would be expected to be insignificant.

The Si and MgSi phases were seen to form like single-phase precipitates in the interdendritic region. It was very likely that the α-Al phase formed as a divorced component with the Si and/or MgSi phase contained lower levels of Zn and therefore, it did not decompose to an Al-Zn mixture, whereas the α-Al components formed with the blocky MgZn2 particles and the Zn/MgZn2 lamellar mixtures contained much higher levels of Zn, and therefore, they underwent a eutectoid reaction, forming the observed Al-Zn mixtures.

The computed results obtained in the companion paper [18] had confirmed this. It was found [18] that the Zn concentration in the α-Al phase formed with the formation of Si and MgSi phases was within the range of 26.3 to 41.7 wt pct Zn (~13 to 23 at. pct Zn), whereas the concentration of the α-Al phase formed with the formation of the blocky MgZn2 phase increased rapidly from 41.7 wt pct (~23 at. pct) to 81.2 wt pct Zn (~64 at. pct Zn) and the Zn concentration in the α-Al phase formed with the Zn/MgZn2 lamellar mixture had a constant concentration of 81.2 wt pct Zn (~64 at. pct Zn). The Zn concentrations calculated explained why Si and MgSi phases appeared like single-phase precipitates, whereas the blocky MgZn2 phase and the Zn/MgZn2 lamellar mixtures were surrounded by Al-Zn mixtures in the current study because the Zn concentrations in the z-Al phase formed at different stages were significantly different.

C. Formation of the Large, Blocky MgZn2 Phase and Lamellar Zn/MgZn2 Structure

It has been observed that in the interdendritic region where the MgSi and Si phases were absent, the coating metals essentially contained Al, Zn, and Mg only. To study the solidification behaviour of the molten phase containing essentially Al, Zn, and Mg only, two ternary Al-Zn-Mg liquidus surfaces were computed using the Pandat™ software [25,26] and are shown in Figure 14 for the Zn-rich corners. In computing Figure 14(a), the MgZn11 phase was suppressed, assuming that it was thermodynamically impossible to form. For comparison, the liquidus surface showing the formation of MgZn11 was also computed and shown in Figure 14(b). The computed results in Figure 14(b) were consistent with those shown in the published Al-Zn-Mg liquidus surface [21,27], which was determined under nearly complete equilibrium experimental conditions. From Figure 14(b), it can be seen that, during solidification of an Al-Zn-Mg alloy rich in Al under nearly complete equilibrium conditions, the MgZn2 phase should form as a component of the L → α-Al + MgZn2 reaction first followed by the L → α-Al + Mg2Zn11 reaction, and finally the ternary eutectic reaction L → α-Al + MgZn11 + Zn. In reality, MgZn11 was absent from the coating and even from the ingot sample, and therefore, it was very likely that the binary L → α-Al + Mg2Zn11 and the ternary L → α-Al + Mg2Zn11 + MgZn2 did not occur as a result of the more rapid cooling. Instead, because of the presence of a lamellar Zn/MgZn2 structure, the ternary reaction taking place became L → α-Al + Zn + MgZn2, as shown in Figure 14(a).

To assist in the understanding of the solidification sequence, the composition path obtained from the experimental study [18] is also shown in Figure 14(a). It is seen that with the formation of primary α-Al or the (Al) phase, (Al) + Si, and then (Al) + MgSi + Si, the concentration of Mg in the molten phase increased gradually while the Zn concentration increased much more rapidly, following the dotted line, until its temperature was close to 380 °C (computed temperature is 383.6 °C [18]), where MgZn2 started to form with the α-Al phase, and then the liquid-phase composition path continued to follow the dotted line to the final eutectic point at about 367 °C, where Zn also started to form [18] to complete the solidification process.

The formation of the MgZn2 phase had been confirmed by XRD (X-ray diffraction) analyses conducted previously [4,7] as seen in the XRD pattern obtained by Fujii and Shimoda [7] shown in Figure 15.
In Figure 15, it can be seen that both the MgZn$_2$ and Mg$_2$Si phases were present in the coatings containing 2 pct and 5 pct Mg, but Mg$_2$Zn$_{11}$ was not found. This further supported the SEM/EDS results presented in the current study, showing the presence of MgZn$_2$ rather than Mg$_2$Zn$_{11}$. However, in order to be completely certain about the absence of Mg$_2$Zn$_{11}$, future studies using either the EBSD (electron back-scattered diffraction) or TEM technique or both would be desirable, as when the volume fraction is small, and particularly when it is present at a significant depth in the coating, it would be difficult for the XRD technique to detect its presence.\[28\]

The solidification path shown in Figure 14(a) indicated that the large, blocky MgZn$_2$ phase formed within the temperature range of 383.6 °C to 367 °C via the binary L → γ-Al + MgZn$_2$ reaction. As shown in Figures 5, 9, and 11, the blocky MgZn$_2$ phase has different morphologies from those of Mg$_2$Si and Si. The MgZn$_2$ phase (e.g., in Figure 9) did not occupy the entire interdendritic region, but rather formed as a blocky phase at the centre part of the interdendritic region surrounded by Al-Zn mixtures. As already discussed, the Al-Zn mixtures were originally from the γ'-Al phase formed at high temperatures, and therefore, the surrounding (γ'-Al) phase must have been the γ-Al component, or part of it (with the earlier part being γ-Al), in the L → γ-Al + MgZn$_2$ reaction. As the MgZn$_2$ phase did not develop into a lamellar structure with the γ-Al phase, its formation mechanism must also be a divorced reaction, with the MgZn$_2$ phase nucleating and growing at the centre of the molten phase while the γ-Al phase formed at a different location, either by growing the γ-Al dendrites or forming separately in the molten phase. It could not have formed by surrounding the MgZn$_2$ phase, because if it did, it would have limited the further growth of the MgZn$_2$ phase.

Apart from the divorced eutectic reaction mechanism, in some areas, the eutectic γ-Al component was found to be embedded in the blocky MgZn$_2$ phase, as observed in Figures 4(b), 5(a), 9, and 10(a), indicating that the γ-Al phase could form as isolated particles first but then could be overgrown by the growing MgZn$_2$ phase. The microstructures shown in Figures 4, 5, 9 and 10 also indicated that while the Zn and MgZn$_2$ phases developed into a lamellar structure in the final reaction taking place at about 367 °C (Figure 14(a)), the γ-Al phase also formed as a divorced phase, either at a separate location or growing on the existing dendrite arms. Similar to the situation of the formation of the large, blocky MgZn$_2$, the γ-Al phase could not have surrounded the lamellar Zn/MgZn$_2$ structure either, because if it did, it would have stopped the free growth of the lamellar structure in the liquid also.
Summarizing the discussions above, a schematic illustration showing the formation of the primary $\alpha$-Al dendrites, the Si and/or Mg$_2$Si phases, the blocky MgZn$_2$ and the lamellar Zn/MgZn$_2$ with their divorced $\alpha$-Al components in the 2 pct Mg-55 pct Al-1.6 pct Si-Zn coating on steel is shown in Figure 16. The schematic shows that (a) $\alpha$-Al dendrites formed as the framework of the coating, (b) Si (darker grey) and Mg$_2$Si (purple) then nucleated in the interdendritic regions, mostly at corners and then grew along the interdendritic channels, while the divorced $\alpha$-Al component formed by growing the existing $\alpha$-Al dendrite arms. This was then followed by, (c) the formation of the blocky MgZn$_2$ (lighter grey) phase with its divorced $\alpha$-Al component continuing to grow on the existing $\alpha$-Al dendrite arms, and finally, (d) the formation of lamellar Zn/MgZn$_2$ mixtures (lined), with the divorced $\alpha$-Al component filling the remaining space between the Zn/MgZn$_2$ mixtures and the $\alpha$-Al dendrite arms.

As discussed, when the blocky MgZn$_2$ formed, the $\alpha$-Al component could form as isolated islands inside the MgZn$_2$ phase as well. This mode of reaction is not illustrated in Figure 16. After the completion of solidification, the $\zeta''$-Al component, formed as the eutectic components with the MgZn$_2$ phase and the lamellar Zn/MgZn$_2$ mixtures, in the respective eutectic reactions, then decomposed into Al-Zn mixtures and the composition of the Al-Zn mixture would depend on the temperatures at which the $\alpha$-Al component formed.

V. CONCLUSIONS

The current study examined in detail the microstructure of the 2 pct Mg-55 pct Al-1.6 pct Si-Zn coating on steel and analysed the formation mechanisms of different phases and constituents observed. It was found that:

1. The Al-Zn mixtures observed in the interdendritic region were the products of eutectoid decomposition of the $\zeta''$-Al (high zinc $\alpha$-Al) components associated with the formation of MgZn$_2$ and Zn/MgZn$_2$ mixtures.
2. A new method was successfully developed to differentiate the Si and Mg$_2$Si phases under an optical microscope, with the Mg$_2$Si phase appearing blue or purple, and the Si phase appearing dark grey.
3. Judging from the Al-Si-Mg liquidus projection, Mg$_2$Si should form first, followed by a eutectic reaction forming a mixture of $\alpha$-Al + Mg$_2$Si + Si. This could provide an explanation for the lower volume fraction of Si observed.
4. While thermodynamically, Mg$_2$Zn$_{11}$ was a stable phase to form, it was not observed in the coating. The Mg-Zn phase observed was MgZn$_2$. Fig. 16—Schematic illustration of the divorced binary and ternary eutectic reactions taking place in the interdendritic region of the 2 pct Mg-55 pct Al-1.6 pct Si-Zn coating on steel.
instead, which was seen to develop into two different morphologies, a large blocky MgZn₂ phase and fine precipitates forming a lamellar structure with Zn.

(6) Both blocky MgZn₂ and the lamellar Zn/MgZn₂ mixtures did not occupy the entire space of the interdendritic region, but rather, they were surrounded by the decomposition products of the high Zn α-Al phase components, i.e., Al-Zn mixtures.

(7) All eutectic reactions observed appeared to proceed in a divorced manner with the α-Al components formed at different locations from their eutectic counterparts, most likely via growth of the existing α-Al dendrite arms, with the exception that sometimes it formed as isolated islands embedded in the blocky MgZn₂ phase.

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