Solidification Structure of the Coating Layer on Hot-Dip Zn-11%Al-3%Mg-0.2%Si-Coated Steel Sheet*¹

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The solidification structure of the coating layer on hot-dip Zn-11%Al-3%Mg-0.2%Si-coated steel sheet was studied by means of metallographic examinations together with calculation of phase diagram based on Thermo-Calc. The solidification structure observed, which exhibited a combination of the Zn/Al/MgZn₂ ternary eutectic structure, the primary Al phase, and the MgZn₂ phase, turned out to be different from that predicted under an equilibrium state in the sense that MgZn₂ instead of Mg₂Zn₁₁ was observed under the present condition. Excluding the Mg₂Zn₁₁ phase from the equilibrium phase diagram, the metastable phase diagram was calculated. Excellent agreement was obtained between the calculation and the experiment in terms of the solidification structure of the coating layer. Consequently, MgZn₂ is considered to form easily as the metastable structure known as the Laves phase, because the high cooling rate associated with the present experiment does not provide any potential for peritectic-eutectic reactions, which usually occur in the equilibrium state. Furthermore, MgZn₂, which has a C14-type Laves structure and a high rate of nucleation in the liquid phase, is considered to cause the preferential Zn/Al/MgZn₂ ternary eutectic reactions. [doi:10.2320/matertrans.MRA2008009]

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1. Introduction

Hot-dip galvanized steel sheets are widely used in the markets of construction, electrical appliances, and so on, since they have good corrosion resistance. Particularly in the field of construction, where materials are subjected to a severe outdoor corrosion environment, Zn-5 mass%Al¹⁾ and 55 mass%Al-Zn²⁾ alloy-coated steel sheets have been practically used with corrosion resistance improved owing to the addition of Al. Recently, hot-dip Zn-Al-Mg alloy-coated steel sheets with further corrosion resistance have been developed, and the volume of steels used is soaring.³⁻⁶⁾

Since hot-dip Zn-Al-Mg coating is the solidification of multiple alloys, the solidification structure is more complex than that of hot-dip Zn-Al coating. Furthermore, the solidification structure of hot-dip Zn-Al-Mg coating may differ from the solidification structure expected from the ternary alloy equilibrium phase diagram previously proposed.

It is well known that the coating adhesion or formability of galvanized steel sheet is significantly affected by the alloy type in the coating layer.⁷⁾ It is also reported that the solidification structure affects the corrosion resistance of hot-dip Zn-6 mass%Al-3 mass%Mg-coated steel sheet.⁴⁾

Therefore, it is important to understand each solidification structure in the coating layer and to know the effect on various performances. In this report, to understand the solidification process of hot-dip Zn-Al-Mg coating, the solidification structure was observed and the solidification mechanism using the calculation of phase diagram technique was studied.

2. Test and Calculation Methods of the Phase Diagram

A coating test was carried out using a hot-dip galvanizing simulator, as shown in Fig. 1. A steel sheet with a thickness of 0.8 mm was first reheated to 1053 K for 60 s in an atmosphere of N₂ with 3 vol% H₂, which resulted in a reduction in the surface of the specimen. In the same atmosphere, it was subsequently cooled to 773 K, before being dipped in a coating bath at 723 K for 3 s. The amount of the coated layer on one side was controlled to 70 to 90 g/m² by N₂ wiping and

Fig. 1 Schematic view of the galvanizing simulator.

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Table 1 Number and component elements of the sub-lattice of every phase in the Zn-Al-Mg system.

Phase	Number of sub-lattices	Sub-lattice (i)	Mole fraction of lattice point (a_i)	Component elements	Phase	Number of sub-lattice	Sub-lattices (i)	Mole fraction of lattice point (a_i)	Component elements
Liquid	1	1	1.000	Al, Mg, Zn	MgZn ₂	2	1	0.333	Al, Mg, Zn
Al	1	1	1.000	Al, Mg, Zn			2	0.667	Al, Mg, Zn
Zn	1	1	1.000	Al, Mg, Zn			1	0.400	Mg
Mg	1	1	1.000	Al, Mg, Zn	Mg ₂ Zn ₃	2	2	0.600	Al, Zn
		2	0.611	Al, Zn			1	0.480	Mg
Al ₃ Mg ₂	2	1	0.389	Mg	MgZn	2	2	0.520	Al, Zn
		2	0.611	Al, Zn			1	0.718	Mg
Al ₃₀ Mg ₂₃	2	1	0.418	Mg	Mg ₇ Zn ₃	2	2	0.282	Zn
		2	0.582	Al, Zn			1	0.545	Mg
Al ₁₂ Mg ₁₇	3	1	0.172	Mg	ϕ	2	2	0.455	Al, Zn
		2	0.414	Al, Mg, Zn			1	0.321	Mg
		3	0.414	Al, Mg, Zn			2	0.074	Al, Mg
Mg ₂ Zn ₁₁	2	1	0.154	Mg	τ	4	3	0.593	Al, Mg, Zn
		2	0.846	Al, Zn			4	0.012	Al

Fig. 2 Liquidus surface of the Zn-Al-Mg system.¹¹⁾

cooled at a cooling rate of 10 degrees/s. For the hot-dip coating, a coating bath involving the addition of Al of 11 mass%, Mg of 3 mass%, and Si of 0.2 mass% into the hot-dip Zn was used.

After polishing the cross section, the solidification structure was observed, using a high-resolution field emission scanning electron microscope (FE-SEM). Elements of the solidification structure were also analyzed using an electron probe micro-analyzer (EPMA). Each phase in the solidification structure was identified using X-ray diffraction (XRD) with a Cu target.

Analysis with calculation of phase diagram was also conducted with Thermo-Calc.⁸⁾ Liang *et al.* summarized the interaction parameters in the Al-Mg-Zn ternary alloy based on the sub-lattice model⁹⁾ proposed by Hillert *et al.*, by critically assessing the experimental data in the present systems.¹⁰⁾ In this study, the phase diagram was calculated by incorporating these parameters, obtained from the Al-Mg-Zn ternary system by Liang *et al.*, into Thermo-Calc.

Table 1 shows the number and the component element of the sub-lattice of each phase considered in the Zn-Al-Mg ternary system.¹⁰⁾ As shown in Table 1, the liquid, Al(fcc), Zn(hcp), and Mg(hcp) phases are thought to be a solid solution of Al, Mg, and Zn with a single sub-lattice. On the other hand, the intermetallic compounds of Al-Mg and Mg-Zn are thought to consist of several sub-lattices, most with several mixing constituents as shown in Table 1. Accordingly, Si, which is a trace additive element, was not considered in the phase diagram calculation.

In the present calculation, the thermodynamic parameters for the phases in Table 1 were corrected from Liang *et al.*¹⁰⁾

3. Equilibrium Phase Diagram

Figure 2 shows the equi-liquidus contour lines of the Zn-Al-Mg system prepared by MSIT.¹¹⁾ In Fig. 2, the structure with Zn-4.5 mass%Al-3.5 mass%Mg has a peritectic-eutectic point of $L + \text{MgZn}_2 \rightleftharpoons \text{Mg}_2\text{Zn}_{11} + \text{Al}$. In the structure of

Fig. 3 Cross sectional SEM and EDX images of the coating layer in Zn-11 mass%Al-3 mass%Mg-0.2mass%Si coating. a) SE image, b) Al, c) Mg, d) Zn.

Zn-4 mass%Al-3 mass%Mg, the ternary eutectic point of $L \rightleftharpoons \text{Zn} + \text{Al} + \text{Mg}_2\text{Zn}_{11}$ is present. Therefore, when a metal with this experimental composition, namely, Zn-11 mass%Al-3 mass%Mg containing hyper-eutectic Al, is solidified in an equilibrium state, the solidification structure obtained will be three phases, namely the Zn, Al, and $\text{Mg}_2\text{Zn}_{11}$ phases.

4. Results and Discussion

4.1 EPMA

Figure 3 shows the result of EPMA analysis for the cross section of the coating layer. The solidification structure showed a eutectic structure with strong Zn indication, a structure with strong Al indication, and a structure with strong Mg indication. From the equi-liquidus contour lines in Fig. 2, it is considered that the eutectic structure with strong Zn, which shows a lamellar image in SE, is the ternary eutectic structure, that the structure with strong Al is the Al phase structure crystallized as the primary phase, and that the structure with strong Mg is the Zn-Mg intermetallic compound.

4.2 X-ray diffraction

Figure 4 shows the result of X-ray diffraction of the coating layer. The diffraction peak obtained was only Zn, Al, and MgZn_2 . The peak of $\text{Mg}_2\text{Zn}_{11}$ was not observed. Therefore, the Zn-Mg intermetallic compound observed in Fig. 3 is estimated to be the MgZn_2 phase. As explained in the next section, the ternary eutectic structure is estimated to be Al/Zn/ MgZn_2 .

4.3 Calculated phase diagram

On the equi-liquidus contour lines of the Zn-Al-Mg system

Fig. 4 X-ray diffraction patterns of the Zn-11 mass%Al-3 mass%Mg-0.2mass%Si coating.

in Fig. 2, there is a peritectic-eutectic reaction that crystallizes the $\text{Mg}_2\text{Zn}_{11}$ phase from the liquid phase and the MgZn_2 phase. The $\text{Mg}_2\text{Zn}_{11}$ phase is the stable phase of the Zn-Mg intermetallic compound. Subsequently, the solidification structure predicted from the equilibrium state was calculated with Thermo-Calc. The Zn-Al-Mg ternary equilibrium phase diagram in Fig. 5 shows the calculation results indicating the kind and quality of crystallization in each phase of solidification of the Zn-11 mass%Al-3 mass%Mg alloy with Thermo-Calc.

From Fig. 5, in the equilibrium state, after the Al phase is crystallized as the primary phase, through the eutectic crystallization of the Al and MgZn_2 phases, the peritectic-eutectic reaction that crystallizes the $\text{Mg}_2\text{Zn}_{11}$ phase from the liquid phase and the MgZn_2 phase begins at 638 K. When the entire liquid phase and MgZn_2 phase react with the $\text{Mg}_2\text{Zn}_{11}$ phase, solidification is completed. After

Fig. 5 Calculated change in the kind and quantity of the equilibrium phase in Zn-11 mass%Al-3 mass%Mg alloy.

solidification, precipitation of the Zn phase from the primary Al phase begins at 581 K. The figure also shows a monotectoid reaction, whereby the two phases, namely the Al and Zn phases, are precipitated from the primary Al phase at 550 K. Therefore, the solidification structure estimated in an equilibrium state is considered to be the $\text{Mg}_2\text{Zn}_{11}$ phase crystallized in the peritectic-eutectic reaction, the Zn phase precipitated from the primary Al phase, and the Al and Zn phases precipitated in the monotectoid reaction.

However, in the solidification structure of this experiment, crystals of the MgZn_2 phase, which is the metastable phase, were observed by X-ray diffraction. Since MgZn_2 developed a stable structure called the Laves phase, it was possible that the peritectic-eutectic reaction did not occur with the preparation method of this sample, which features a significant cooling rate. In Fig. 3, since the ternary eutectic structure is observed, no peritectic-eutectic reaction is considered to occur and the ternary eutectic reaction occurs.

Then, a metastable phase diagram excluding the $\text{Mg}_2\text{Zn}_{11}$ phase was calculated using Thermo-Calc and it was compared with the solidification structure of the coating layer experimentally observed. Figure 6 shows the calculation results of a vertical cross section of the metastable phase diagram at $\text{Mg} = 3\%$, excluding the $\text{Mg}_2\text{Zn}_{11}$ in the ternary Zn-Al-Mg system, calculated with Thermo-Calc. Figure 7 shows the calculation results of the kind and quantity of crystallization in each phase of the solidification of the Zn-11 mass%Al-3 mass%Mg alloy in this metastable phase diagram with Thermo-Calc. When the metastable phase diagram is used, after crystallization of the Al phase as the primary phase, and via eutectic crystallization of the Al phase and the MgZn_2 phase, solidification is completed in the ternary eutectic crystallization of the Al, Zn, and MgZn_2 phases. This matches well with the experimentally observed results in Figs. 3 and 4. In other words, the Zn-Mg intermetallic compounds observed in Fig. 3 are considered to be the MgZn_2 phase crystallized together with the Al phase at the $\text{L} + \text{Al} + \text{MgZn}_2$ zone in Fig. 6.

Fig. 6 Calculated metastable phase diagram of the Zn-Al-Mg system at 3 mass%Mg.

Fig. 7 Calculated change in the kind and quantity of the metastable phase in Zn-11 mass%Al-3 mass%Mg alloy.

The ternary eutectic temperature of Zn/Al/ MgZn_2 , in a metastable state and calculated with Thermo-Calc, is 609 K. The difference from 616 K, the ternary eutectic temperature of Zn/Al/ $\text{Mg}_2\text{Zn}_{11}$ at the equilibrium state in Fig. 2, was slight. Based on this result, the free energy of the Zn/Al/ $\text{Mg}_2\text{Zn}_{11}$ ternary eutectic point is lower than that of the Zn/Al/ MgZn_2 ternary eutectic point. However, the difference is minimal. According to the X-ray diffraction result in Fig. 4, no peak of $\text{Mg}_2\text{Zn}_{11}$ was observed and only that of MgZn_2 was observed. For the cooling rate of this sample, the liquid phase was considered to be supercooled under the metastable ternary eutectic temperature. At this temperature, preferential solidification with the Zn/Al/ MgZn_2 ternary eutectic crystallization can be considered to have occurred.

As described above, the phenomenon whereby the Zn/Al/ MgZn_2 ternary eutectic reaction occurs with small supercooling preferentially occurs prior to the Zn/Al/

Fig. 8 SEM images of the ternary eutectic structure and the Al dendrite in the Zn-11 mass%Al-3 mass%Mg-0.2 mass%Si coating. a), b) Low magnification micrograph, c), d) High magnification micrograph.

$\text{Mg}_2\text{Zn}_{11}$ ternary eutectic reaction and the significant supercooling is considered attributable to the difference in the rate of nucleation in the supercooled liquid, which derives from the characteristic crystal structure of MgZn_2 . In other words, the crystal structure of MgZn_2 is a C14-type Laves structure, which is similar to the Frank-Kasper phase.^{12,13)} Since the ratio of the short-range regularity with 12 configuration, which is the local liquid phase structure, is considerable, it is known that the barrier of the nucleus formation energy in the liquid phase is small.¹⁴⁾ In this way, the rate of nucleation of MgZn_2 is considered to be larger and a Zn/Al/ MgZn_2 ternary eutectic reaction is preferably generated.

As previously described, around the solidification completion temperature of the Zn corner of the Zn-Al-Mg alloy, there are three reactions in a narrow temperature range: the peritectic-eutectic point of $\text{L} + \text{MgZn}_2 \rightleftharpoons \text{Mg}_2\text{Zn}_{11} + \text{Al}$ (638 K), the ternary eutectic point of $\text{L} \rightleftharpoons \text{Zn} + \text{Al} + \text{Mg}_2\text{Zn}_{11}$ (616 K), and the ternary eutectic point of $\text{L} \rightleftharpoons \text{Zn} + \text{Al} + \text{MgZn}_2$ (609 K). In the equilibrium state, the peritectic-eutectic reaction and the Zn/Al/ $\text{Mg}_2\text{Zn}_{11}$ ternary eutectic reaction are considered to occur. At the cooling rate used in this experiment, the calculation results with Thermo-Calc revealed that only the Zn/Al/ MgZn_2 ternary eutectic reaction with easy nucleation and small supercooling occurs.

Based on the calculation results in Figs. 6 and 7, it also emerges that the monotectoid reaction that precipitates two phases of the Al and Zn phases from the primary Al phase occurs at 550 K. Therefore, it is considered that the Al phase crystallized at high temperature is observed by two

phases decomposed into the Al and Zn phases at room temperature.

Based on the results above, and the solidification structure observed in Fig. 3, the eutectic structure observed in a lamellar state is the Al/Zn/ MgZn_2 ternary eutectic structure, the structure with strong Al is the Al phase structure, which is crystallized as the primary phase, and that with strong Mg is the MgZn_2 phase structure, which is crystallized as eutectic crystals. Furthermore, the primary Al phase structure is considered to be a structure decomposed into the Al and Zn phases precipitated in the monotectoid reaction.

4.4 Observation of the solidification structure

Figure 8 shows the results of the eutectic structure using high-resolution FE-SEM. The observation result of the ternary eutectic structure with high magnification in Fig. 8 d) shows a lamellar structure decomposed into three phases. The larger the atomic number, the whiter it is when seen under an electron microscope. The white phase is considered to be the Zn phase, the gray phase is the MgZn_2 phase, and the black phase is the Al phase.

On the ternary eutectic structure in Fig. 8 d), the Zn and MgZn_2 phases grow in layers. In the MgZn_2 phase, a mixture of fine Zn and Al phases, developed into a bar shape, is observed in the solidification structure. As shown in Fig. 6, the Al phase solidified at high temperature shows the monotectoid reaction at 550 K, and the Al and Zn phases are precipitated. At room temperature, it is observed by decomposing into the Al and Zn phases. Therefore, the phase with a mixture of the Zn and Al phases in this MgZn_2 phase is solidified as the Al phase in the ternary eutectic reaction.

Fig. 9 Calculated change in the compositions of the Al phase in Zn-11 mass%Al-3 mass%Mg alloy.

Subsequently, the structure is considered to be decomposed into the Zn and Al phases with a monotectoid reaction.

As shown in Fig. 8 c), observation with high magnification showed, similarly, the white Zn phase and the black Al phase that could be precipitated in the monotectoid reaction even in the area in contact with the ternary eutectic structure of the primary Al phase.

Based on Fig. 6, the entire primary Al phase is considered to be decomposed into two phases of the Al phase and the Zn phase. Observation of the division into the Zn phase and the Al phase with FE-SEM is around the final solidification area in contact with the ternary eutectic structure. Due to the fineness of the inside structure, a decomposed condition into the Zn and Al phases was not clearly observed with FE-SEM.

Figure 9 shows the calculation results of the concentration variation in the Al phase of the Zn-11 mass%Al-3 mass%Mg alloy in a metastable state with Thermo-Calc. Based on Fig. 9, the Al phase crystallized as the primary phase starts solidification with a solid solution of Zn to about 40 mass%. As the temperature descends, the solid solution quantity of Zn is increased. During the ternary eutectic reaction that completes solidification, the solid solution quantity of Zn in the Al phase increases to about 80 mass%.

Therefore, in Fig. 8, an area whereby the condition is decomposed into two phases of the Al and Zn phases, respectively, including a monotectoid reaction, is observed with FE-SEM corresponding to areas with a large solid Zn solution. The Al phase in the ternary eutectic structure with a Zn solid solution of about 80 mass% and the final solidification area of the Al phase with a Zn solid solution of almost 80 mass% include a large Zn phase quantity to be precipitated with the monotectoid reaction. A Zn phase of this size, which can be observed with FE-SEM, is considered to be precipitated.

5. Conclusion

The solidification structure of hot-dip Zn-11 mass%Al-3 mass%Mg-0.2 mass%Si coating was observed, and the solidification mechanism was studied using the calculation of phase diagram technique. The following conclusion was reached:

- (1) In the solidification structure, the Al/Zn/MgZn₂ ternary eutectic structure, primary Al phase structure, and MgZn₂ phase structure were observed. It differed from the solidification structure estimated in the equilibrium state.
- (2) The final solidification structure calculated and predicted with Thermo-Calc based on the metastable phase diagram, excluding the Mg₂Zn₁₁ phase, had good agreement with actual coating solidification structure.
- (3) Since MgZn₂ has a stable structure called the Laves phase, using the sample preparation method, which has a large cooling rate, the peritectic-eutectic reaction, which is observed in the equilibrium state, may not have occurred.
- (4) Furthermore, since MgZn₂, which has a C14-type Laves structure, has a large nucleation rate in the liquid phase, the Zn/Al/MgZn₂ ternary eutectic reaction was considered to have preferentially occurred.
- (5) In the primary Al phase and the Al phase of the ternary eutectic structure, a monotectoid reaction occurs at 550 K and the Al and Zn phases are precipitated. At room temperature, the Al phase and the Zn phase were decomposed for observation.

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