Role of TiAl_3 Fine Precipitate in Nucleation of the Primary Al Dendrite Phase during Solidification in Hot-Dip Zn-11%Al-3%Mg-0.2%Si Coated Steel Sheet*

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The primary Al phase crystallizes preferentially on TiAl_3 fine precipitate during the solidification process of hot-dip Zn-11 mass%Al-3 mass%Mg-0.2 mass%Si coating, which leads to the formation of fine dendrite structures by the small amounts of Ti added to the coating bath. TiAl_3 is thought to act as heterogeneous nucleation sites of the primary Al phase. Detailed TEM observation of the sectioned specimen by a micro-sampling unit equipped with an FIB system revealed that the TiAl_3 fine precipitate is not a single crystal but polycrystals. However, a crystallographic relationship exists between the TiAl_3 phase and the surrounding Al phase, namely, $[001]_{\text{TiAl}_3} // [001]_{\text{Al}}$, $[010]_{\text{TiAl}_3} // [010]_{\text{Al}}$ and $[100]_{\text{TiAl}_3} // [100]_{\text{Al}}$. High-resolution TEM observation of the interface indicates a good coincident relationship between the Al matrix and the precipitate. Therefore, the primary Al phase nucleated heterogeneously on the surface of the TiAl_3 phase. Furthermore, detailed TEM observation revealed a monotectoid reaction by the primary Al phase to the extremely fine Al and Zn phases.

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1. Introduction

Hot-dip galvanized steel sheets present excellent corrosion resistance and are thus widely used in industries such as construction and consumer electronics. Particularly in the construction industry, materials are frequently utilized within severely corrosive environments, such as outdoors. For example, Zn-5 mass%Al hot-dip coated steel sheets¹⁾ and Zn-55 mass%Al hot-dip coated steel sheets²⁾ are often utilized, in which the corrosion resistance is improved by adding Al. In addition, recently Zn-Al-Mg hot-dip coated steel sheets with improved corrosion resistance through the addition of Mg have been developed and are widely used.³⁻⁶⁾

The Zn-Al-Mg coating is of a ternary eutectic-type alloy, and in the hypereutectic composition of Al, the Al phase-like dendrites are crystallized in the form of primary crystals. In our previous paper,⁷⁾ details of the solidification mechanism were discussed by observing the solidification structure of the hot-dip Zn-11 mass%Al-3 mass%Mg-0.2 mass%Si coating using high-resolution field emission scanning electron microscope (FE-SEM) analysis, together with calculation of the phase diagram. The solidification structure of the coating correlated well with the metastable phase diagram of the Zn-Al-Mg system, while the solidification terminated at the ternary eutectic of Zn/Al/MgZn₂ via the eutectic of the Al and MgZn₂ phases, after crystallizing the Al phase-like dendrites as primary crystals.⁷⁾

Moreover, it also emerged that the primary Al phase, solidified at elevated temperatures, had a Zn of 40–80 mass% in a solid solution, and was to be decomposed into two phases of the Al and Zn phases due to a monotectoid reaction at 550 K.⁷⁾ Nevertheless, the microstructure according to the

monotectoid reaction was too fine to observe clearly, in terms of the phase decomposition of the primary Al phase into the Al and Zn phases through FE-SEM.

On the other hand, it emerged that the dendrite structure of the primary Al phase was refined when a small amount of Ti was added to the hot-dip Zn-11 mass%Al-3 mass%Mg-0.2 mass%Si coating.⁸⁾ It is important when improving product properties to refine the coating structure, and the basic background of this study lies in examining the control factors for the solidification structure refinement. Based on the analysis results of crystal orientations by electron back scattering diffraction pattern (EBSD) presented in a previous paper,⁸⁾ TiAl_3 , formed by the Ti addition, was expected to act effectively as a nucleation site for the primary Al phase, since the TiAl_3 (D0₂₂) and Al phases (FCC) have excellent lattice coherency.

Regarding the aluminum alloy used for casting, it has already been reported that the solidification structure is refined by numerously dispersing intermetallic compounds, such as TiAl_3 .⁹⁾ However, there are many parts yet to be elucidated when considering the crystallographic conditions required for the nucleation site of Al phase dendrites. In this paper, focus was placed on elucidation of the complete microstructure of the coating through analysis using a transmission electron microscope (TEM) and by obtaining greater understanding concerning the nucleation mechanism of the primary Al phase on the TiAl_3 phase.

2. Experimental Procedure

Coated steel sheets used for testing were prepared by utilizing the hot-dip galvanizing simulator, shown in Fig. 1. The testing materials were prepared with mild steel sheets 0.8 mm thick, the temperature of which was elevated up to 1,053 K in an atmosphere comprising 3 vol% of H₂ balanced

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Fig. 1 Schematic view of galvanizing simulator.

by N_2 , whereupon they were subsequently retained for 60 s to reduce their surfaces, then cooled back down to 773 K under the same atmosphere, and finally immersed in the desired hot-dip coating bath. As for the hot-dip coating method, immersion in a coating bath of Zn-11 mass%Al-3 mass%Mg-0.2 mass%Si with added Ti at 100 mass ppm for 3 s at a bathing temperature of 723 K was employed. After coating, the materials were wiped with N_2 gas to adjust the coating amount to $70\text{--}90\text{ g/m}^2$, which was followed by cooling to room temperature at a rate of 10 K/s.

Sectional structure observation using TEM was performed utilizing the same specimens as in the crystal orientation analysis conducted by the EBSD method in the previous paper.⁸⁾ As for the solidification structure, coating layers were chemically polished to a depth of several μm from the surface before analyzing the crystal orientations of the TiAl_3 and its surrounding Al, in order to provide a specific region for TEM observation. For the transmission electron microscope, a FE-TEM (the HF-200, from Hitachi Co., Ltd.), equipped with a field-emission electron gun carrying an

energy dispersive spectroscopy (EDS) system, was used under the conditions of an accelerating voltage of 200 kV. In addition, a specific region including the primary Al phase nucleated on the TiAl_3 and its surroundings was prepared using a focused ion beam (hereafter, “FIB”) processing method,¹⁰⁾ in order to produce a thin film. The FIB equipment utilized was an FB-2000A equipped with a micro-sampling function.

3. Results and Discussion

3.1 Analysis of the microstructure of the primary Al phase and the monotectoid reaction

As indicated in the previous paper, the coating solidification structure becomes refined by adding a small amount of Ti.⁸⁾ This process has high reproducibility, and an example of the refinement obtained is shown using the optical micrograph in Fig. 2(a). The specimen in this figure is a Zn-11 mass%Al-3 mass%Mg-0.2 mass%Si coating with added Ti of 100 mass ppm, as in the previous paper. Figure 2(b) shows the results of observation by magnifying the central part of the Al dendrite with the SEM revealing the nucleation of the primary Al phase on the TiAl_3 , together with the ternary eutectic structure of Zn/Al/MgZn₂.

Since the coating layer has an approximate thickness of $10\mu\text{m}$, a dendrite arm having its own thickness of $5\text{--}7\mu\text{m}$ hardly grows in the thickness direction, but does so principally in that of the inner face. For this reason, polishing the surface even slightly enables us to observe the center of the dendrites easily, as shown in Fig. 2(a). Furthermore, as shown in Fig. 2(b), it is characteristic that TiAl_3 may be observed at almost every dendrite center. In addition, in the SEM image of Fig. 2(b), the Al phase was observed as black with strong contrast.

The TEM micrograph shown in Fig. 3 from the normal direction to the sheet surface was obtained at the center of the Al phase, where a primary dendrite arm spread out in four directions, as shown in Fig. 2(b). The result indicates that the normal directions to the sheet surface of the Al phase and TiAl_3 precipitate are commonly aligned with $\langle 100 \rangle$ orientation. The TiAl_3 of the specimen shown in Fig. 3

Fig. 2 The ternary eutectic structure and the Al dendrites in the Zn-11 mass%Al-3 mass%Mg-0.2 mass%Si-100 mass ppm Ti coating. (a) Optical micrograph, (b) SEM image showing TiAl_3 in Al dendrite.

Fig. 3 TEM bright field image of Al phase and TiAl_3 , that with their $\{100\}$ orientation parallel to the sheet surface.

appears to be one piece, as in Fig. 2, when observed by SEM, and lies in the same crystal orientation (namely $\{100\}$ normal to the sheet surface), as revealed by the EBSD method. Nevertheless, TEM observation revealed directionally aligned polycrystals, as indicated in Fig. 3, and it was additionally confirmed that all these TiAl_3 precipitates have a smooth interface.

Furthermore, in the TEM bright field image shown in Fig. 3, while the Al phase presents a complicated contrast

and the extremely fine precipitates presumably correspond to two decomposing phases, their precipitation contrast gradually weakened as they left TiAl_3 precipitates to change into a tweed-like structure. This may be interpreted as the precipitation of the Zn phases as a result of the monotectoid reaction at 550 K, where the Zn-rich Al phase decomposes into the Al and Zn phases.⁷⁾

Figure 4 shows a magnified bright field image of a TiAl_3 crystal, along with the primary Al phase in Fig. 3, together with the EDS analysis results of each phase. Initially, the peaks of Si, as well as Al and Ti, were observed in Fig. 4(a) in region “a”, which was identified as a TiAl_3 precipitate through the EBSD method in the previous paper. Moreover, the existence of Cu on the same EDS chart is due to the generation of a characteristic X-ray from the Cu support stand carrying specimens. The crystals could be identified crystallographically as TiAl_3 intermetallic compounds;⁸⁾ however, when these EDS analysis results are taken into account, it may be more correct to state that the intermetallic compounds are identified as $\text{Ti}(\text{Al}, \text{Si})_3$, in which part of the Al was substituted by Si.

From the surrounding parts of the TiAl_3 , the EDS spectrums were obtained, namely, from region “b”, characterized by black contrast, and from region “c”, characterized by white contrast, as shown in Figs. 4(b) and (c), respectively. In either of these, the peaks of Al and Zn contained Zn and Al, mainly in regions “b” and “c”, respectively.

Fig. 4 TEM bright field image of Al phase and TiAl_3 together with, (a) EDS analysis of point a in photo, (b) EDS analysis of point b in photo and (c) EDS analysis of point c in photo.

Fig. 5 Diffraction pattern of TiAl_3 and that of Al nucleated on TiAl_3 , (a) superimposed diffraction pattern of Al and TiAl_3 , (b) key diagram of (a), (c) diffraction pattern of TiAl_3 and (d) diffraction pattern of Al.

Furthermore, the crystal orientations of the Al-rich phases, which were characterized by white contrast, were confirmed through the dark field method to be aligned, forming a matrix—the same as that shown by the results using the EBSD method. In addition, the Zn-rich phases characterized by black contrast became precipitated like sheets aligned in two directions, indicating that the Zn phases precipitated through phase decomposition according to the monotectoid reaction from the primary Al phase.

3.2 Crystal orientation analysis of TiAl_3 and the primary Al phase

The primary dendrite arms of the Al phase shown in Fig. 2(b) spread out in four directions, and the crystal orientation relationship between this Al phase and the nuclei TiAl_3 was examined using the EBSD method mentioned in the previous paper.⁸⁾ Namely, the normal directions with respect to the sheet surface of both the TiAl_3 precipitates and the Al phase are commonly $\langle 100 \rangle$ oriented. In addition, as shown in Fig. 2(b), the interfaces between the TiAl_3 precipitates and Al phases are inclined at an angle of approximately 45° to the growth direction of the primary dendrite arms. This implies that, since the normal directions with respect to the sheet surface of Al phases and TiAl_3 precipitates are commonly $\langle 100 \rangle$ oriented, the direction of growth of the primary dendrite arms is of a $\langle 110 \rangle$ orientation. In this paper, in order to re-examine the orientation relationship and investigate the structure of the interface between the TiAl_3 precipitate and the Al phase in detail, thin-film

specimens parallel to this observational plane were prepared for TEM analysis.

In the results of crystal orientation analysis by EBSD, TiAl_3 represents the same crystal orientation as far as a certain nuclei is concerned, which indicates that the TiAl_3 precipitate appearing to be polycrystals consists of a group of the common crystal orientations aligned at least normal to the sheet surface. When similar observations were performed by increasing the sample number, there were two cases of both—a single crystal and a group of polycrystals, with TiAl_3 precipitates in the Al phase.

In crystal orientation analysis using solely the EBSD method, as reported in the previous paper, since TiAl_3 precipitates presented the same crystal orientation to hence appear as single crystals, the TiAl_3 phase was considered to be a nucleation site of the Al phase, whereby the crystal orientation of the TiAl_3 precipitates coincides with that of their surrounding Al phases.⁸⁾ Nevertheless, because there are cases where TiAl_3 precipitates were also observed as polycrystals, as confirmed by this TEM observation, a more detailed analysis is considered necessary to elucidate the relationship between the crystal orientation of TiAl_3 precipitates and their surrounding Al phases. Accordingly, in this paper, a detailed analysis regarding crystal orientations between one of the polycrystals and its surrounding Al phase, observed in Fig. 3, was conducted.

Figures 5(a) and (b) show the electron diffraction patterns measured at the interface region, where the patterns from the TiAl_3 phase (a) and the Al phase (c) in Fig. 4 were detectable

Table 1 Crystal lattice structures of TiAl_3 and Al.

	Crystal Structure	Lattice Constant, nm		Strukturbericht Designation
		a	c	
Al	Cubic	0.4494		A1(FCC)
TiAl_3	Tetragonal	0.38537	0.85839	D0 ₂₂

simultaneously. The superimposed results were indexed in Figs. 5(a) and (b). In addition, the individual electron diffraction patterns from the TiAl_3 phase (a) and Al phase (c) in Fig. 4—along with the analysis results—are shown in Figs. 5(c) and (d).

The intermetallic compounds of Ti and Al existing in the center of the Al phases were identified again as TiAl_3 by analyzing the diffraction pattern in Fig. 5(c). As for the lattice constants used here, the values described in PDF database 37-1449 of the ICDD shown in Table 1 were employed. Moreover, the lattice constant between the intermetallic compounds of Ti-Al, in which Si was detected by the EDS spectrum, are assumed to be the same as those of TiAl_3 , so that the solid solution of Si does not affect the lattice constants of the intermetallic compounds of Ti-Al. Therefore, the diffraction spots shown in Fig. 5(c) can be indexed as indicated in the figure.

Al phases were also similarly analyzed using the lattice constants described in the PDF database 4-0787, listed in Table 1. However, the lattice constant of the Al phase with Zn in a solid solution has already been measured and reported in the previous paper,⁸⁾ and the Al phase has lattice constants within a variance of 1%, despite containing Zn in a solid solution. For this reason, the diffraction spots shown in Fig. 5(d) can be identified as that of Al and are indexed as shown in the figure.

The electron diffraction patterns in Fig. 5(a) coincide with those in Figs. 5(c) and (d) that are superimposed, thereby, it is concluded that they are: $(010)_{\text{TiAl}_3} // (010)_{\text{Al}}$ or $[010]_{\text{TiAl}_3} // [010]_{\text{Al}}$, $[100]_{\text{TiAl}_3} // [100]_{\text{Al}}$, and $[001]_{\text{TiAl}_3} // [001]_{\text{Al}}$. In addition, the electron diffraction pattern obtained from the interface enables us to verify the simple addition of the respective diffraction patterns from the TiAl_3 precipitates and their surrounding Al phases; hence, the conclusion that there is no formation, such as a reaction layer (a second layer), at the interface area. To clarify this aspect, high-resolution TEM observation of the interface was attempted with incident electron beam conditions.

Figure 6 shows a lattice image at the interface between the Al phase and TiAl_3 . The lattice image at the interface in Fig. 6, which was observed right down to Fig. 3, indicates that the TiAl_3 phase on the right side in Fig. 6 satisfies the exact incident condition of the crystal zone axis. On the other hand, as for the electron diffraction images of the Al phases on the left side, nothing other than the lattice images in only one direction could have been obtained.

The high-resolution TEM image in Fig. 6 reveals that (001) lattice faces are observed on the Al side and crystal structure images of $\langle 010 \rangle$ incidence are observed on the TiAl_3 side. Moreover, the interface, which has no second phase, such as a reaction layer, is semi-coherent in the

Fig. 6 Lattice image of Al dendrite and TiAl_3 .

sense that dislocation was emitted from the interface (as discussed later). In addition, since the interface of the TiAl_3 phases is smooth, it seems that the $(001)_{\text{TiAl}_3}$ of the TiAl_3 s solidified to become an actual surface. Accordingly, the Al phase that heterogeneously nucleated on the $(001)_{\text{TiAl}_3}$ grew epitaxially.

As shown in the previous paper, when the Al phase with $(001)_{\text{Al}}$ is heterogeneously nucleated on the TiAl_3 with $(001)_{\text{TiAl}_3}$, the lattice registry between the $d(100)_{\text{TiAl}_3}$, of 0.3854 nm, and the $d(100)_{\text{Al}}$, of 0.4049 nm, becomes approximately 5%; thus, the dislocation is presumably generated from the interface in order to relax this strain.⁸⁾ Strict monitoring of corresponding lattices showed that atom layers shifted by one layer in every 20 or so. However, because there is the problem of the joint faces being slightly inclined, a detailed discussion is omitted here. Nevertheless, it is obvious that the interface maintains comparatively good coherency. A quantitative evaluation on such interfaces will become possible in the near future owing to high-resolution TEM images.

4. Conclusion

Regarding the solidification structure of the Ti-added hot-dip Zn-11 mass%Al-3 mass%Mg-0.2 mass%Si coating, we examined the crystal orientation relationship between the primary Al phases and their nuclei, TiAl_3 precipitates, through TEM observation, and drew the following conclusions:

(1) Peaks of Al, Ti, and Si were observed in the EDS spectrums of intermetallic compounds existing in the center of the primary Al phases; thus, these intermetallic compounds were identified as Ti(Al, Si)_3 .

(2) A number of fine precipitates, such as those plate-sized measuring several hundred nanometers, were observed in the Al dendrite phases. This is due to the Zn phases being precipitated below a monotectoid reaction temperature of 550 K or less by phase decomposition from the primary Al phases.

(3) The TiAl_3 observed by TEM was not of a single crystal but of polycrystals having mutual $\langle 100 \rangle$ orientations.

(4) The result of electron diffraction by TEM analysis, just as in the analysis results from the EBSD method, revealed an orientation relationship between TiAl_3 and the primary Al phase of $[010]_{\text{TiAl}_3} // [010]_{\text{Al}}$, $[001]_{\text{TiAl}_3} // [001]_{\text{Al}}$, and $[100]_{\text{TiAl}_3} // [100]_{\text{Al}}$.

(5) The interface of Al/ TiAl_3 was observed by high-resolution TEM, which revealed that no reaction layers existed in the interface and that the interface is semi-coherent.

(6) Consequently, it is understood that the Al phases heterogeneously nucleated on TiAl_3 and grew epitaxially.

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