Structural and Mechanical Characterizations of Top Dross in a Molten Zinc Bath

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1. Introduction

In a molten zinc bath in a continuous galvanizing line (CGL), top dross particles crystallize as Fe–Al–Zn intermetallic compounds. These particles easily adhere to the steel sheets causing surface defects. Therefore, controlling the top dross particles is a key issue. Our study focused on the structural and mechanical characterizations of the top dross particles using an electron probe micro analyzer, X-ray diffraction, electron back scattering diffraction, Vickers hardness measurements, and nano-indentation measurements.

The following results were obtained: (1) The crystal structure of the top dross particles Fe₃Al₂Znₓ, having 37–38 wt% Fe, 44–45 wt% Al, and 18–19 wt% Zn belongs to the orthorhombic system with lattice constants of a = 7.61 Å, b = 6.68 Å, and c = 4.23 Å. The a-axis of Fe₃Al₂Znₓ becomes shorter, while its b- and c-axes become longer compared to those of the binary Fe₂Al₅. (2) The coarsening of the top dross particles with the faceted interface was postulated to occur as a result of the driving force provided by the anisotropic energy between the top dross particles and molten Zn, rather than via the aggregation mechanism. (3) The hardness and the elastic modulus of the top dross particles are the lowest in the [001] orientation, similar to Fe₂Al₅ and are lower than those of Fe₂Al₅. (4) The fracture toughness of the top dross particles is approximately 1.1 MPa·m¹/², which is slightly lower than that of Fe₂Al₅.

KEY WORDS: top dross; molten zinc; crystal structure; mechanical properties; Fe₃Al₂Znₓ; intermetallic compounds; electron back scattering diffraction.

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1. Introduction

In a molten Zn bath of the Sendzimir-type continuous galvanizing line (CGL), dissolved Fe from a sheet steel reacts with Zn and Al in a bath and forms crystallized products (dross) with high melting temperature. These dross particles are well-known to easily adhere to the steel sheets, thereby causing surface defects. Despite the industrial importance of controlling dross particles for the purpose of stably manufacturing high-quality galvanized steel sheets, there appears to be a scarce amount of research into the structural and mechanical characteristics of dross. Top dross particles that float in a Zn bath, considered as the most crystallized product among the dross particles, are reported to be Fe₃Al₂Znₓ.1) With regard to the top dross particles, Tang3) and Arioka et al.3) have had reports thereon. Tang3) reported on the crystallization conditions of the top dross particles by constructing a ternary phase diagram at the Zn-Rich corner showing the state of the Zn bath in CGL, he examined the crystallization conditions. As a result, it was clarified that the top dross particles became crystallized at an Al concentration of 0.14 wt% or more in a molten Zn bath. Arioka et al.3) developed a method for extracting the top dross particles from Zn, observed their 3D shape, and concluded that the top dross particle is the polyhedron structure with 14 facets planes. However, in the previous studies, there was no report on the findings from the following three viewpoints. First, we discuss the viewpoint of the crystal structure of top dross particles. The schematic diagram of the crystal structure of binary Fe₂Al₅ is shown in Fig. 1.4) It has been reported that partially occupied Al sites are present along the c-axis (c-axis chain) and that they are of two types, whose occupancy ratios are 0.32 and 0.24, respectively. Hereinafter, Al sites with occupancy ratios of 1.0, 0.32, and 0.24 will be referred to as AlI, AlII, and AlIII, respectively. Recently, crystal structure analysis of Fe₂Al₅ has been actively performed and it has been reported5) that the partial occupation of Al atoms (AlII, AlIII) along the c-axis of the orthorhombic parent lattice takes place in an ordered...
manner and that there exists a tripled superlattice structure as the low temperature phase of $\eta$-Fe$_2$Al$_5$ (designated as $\eta'$). Moreover, the $\eta'$ phase is reported to primarily exist at the Fe-lean side of the $\eta$-Fe$_2$Al$_5$ phase.\textsuperscript{5)\textsuperscript{6)} However, the crystal structure of the top dross particles containing about 20 wt% (15 at%) of Zn has never been determined. Moreover, there is no report even on the lattice constant. Second, it has been reported\textsuperscript{6)} that the top dross particles are coarsened by the grain growth mechanism during the rapid cooling of the molten Zn bath using the in-situ synchrotron X-ray measurement. However, the coarsening process of the top dross particles is not clear during isothermal holding at a certain temperature. In other words, it is unknown whether the coarsening of the top dross particles is due to the aggregation mechanism or to the growth mechanisms driven by the chemical free energy or the interfacial energy between the top dross and the liquid Zn phase. Third, the relationship between crystal orientation and mechanical properties (e.g., hardness, elastic modulus, and fracture toughness) of Fe$_2$Al$_5$ has already been reported.\textsuperscript{7)} However, there exists no report on the top dross (Fe$_2$Al$_5$Zn$_x$) and the crystal anisotropy of mechanical properties (e.g., hardness, elastic modulus, and fracture toughness). Therefore, in the present study, we focused on the aforementioned viewpoints and investigated the structural and mechanical characterizations of the top dross particles, especially the chemical composition, crystal structure, coarsening mechanism of top dross, and the mechanical properties thereof. In order to obtain information regarding the first viewpoint, the chemical composition was measured using an Electron Probe Micro Analyzer (EPMA), while the crystal structure was analyzed using X-ray diffraction. In our investigation with regard to the second viewpoint, phase identification and crystal orientation analysis were performed using Scanning Electron Microscopy-Electron Back Scattering Diffraction (SEM-EBSD). In particular, we attempted first an analysis of the top dross particles using EBSD. Lastly, in our research regarding the third viewpoint, hardness, elastic modulus, and fracture toughness were measured using Vickers hardness measurement and nano-indentation methods, taking crystal anisotropy into consideration.

2. Experimental Procedure

2.1. Method for Preparing Top Dross Particles (Fe$_2$Al$_5$Zn$_x$)

The top dross particles were prepared using the same method as reported by Arioka \textit{et al.}\textsuperscript{3)} About 10 kg of Zn (99.99 wt%) was dissolved in a graphite crucible (top diameter: 135 mm, height: 100 mm, and bottom diameter: 85 mm) and held in a bath at a temperature of 460°C in the atmosphere. Pure Al balls with 0.5% of the total weight and a diameter of about 20 mm were added to this Zn bath. After confirming the dissolution of Al, 0.5% of the total weight of Fe (extremely low carbon steel mass-produced as galvannealed steel sheets), finely cut into 0.5 mm square pieces, was added. Table 1 shows the chemical compositions of extremely low carbon steel. The abovementioned state was maintained for one day to make the top dross particles. The concentration of the liquid phase in this Zn bath after being kept for one day is as follows: Al with 0.140 wt% and Fe with 0.32 wt% — which was in good agreement with the triple point of the phase diagram by Tang.\textsuperscript{8)} Therefore, it can be considered that this Zn bath is under a condition that Al and Fe are supersaturated and that the top dross particles are easily crystallized.

| Element | C | Si | Mn | P | S |
|---------|---|----|----|---|---|
| wt%     | 0.01 | 0.01 | 0.14 | 0.01 | 0.01 |

Table 1. Chemical composition of extremely low carbon steel (mass%).

2.2. Method for Sample Collection

Since the state of the top dross particles changes very quickly during cooling, sufficient attention was given to the method of freezing the samples. First, using a glass pipette, as shown in Fig. 2(a), the top dross was sucked and collected from the surface of the Zn bath in a laboratory. Second, the collected melt was dropped into a copper mold, as shown in Fig. 2(b), and rapidly cooled. The cooling rate near the contact surface between the droplet and the copper mold was estimated to be about 10 000°C/s. Third, the rapidly cooled surface was ground by 0.5 mm in the depth direction and then the ground surface was used for observation.

2.3. Method for Analyzing Top Dross Particles (Fe$_2$Al$_5$Zn$_x$)

Element analysis using EPMA was performed to identify the type of the top dross particles from their chemical composition. A JXA8900RL instrument, operated at an accelerating voltage of 15 kV, was used for the elemental analysis. X-ray diffraction was conducted to analyze the crystal structure of the top dross particles. A Rigaku SmartLab X-ray diffractometer, with a rotating anode system comprising a Cu X-ray source, was operated at a tube voltage of 40 kV and a tube current of 36 mA. We likewise attempted to analyze the top dross particles using SEM-EBSD; the SEM was operated at an accelerating voltage of 25 kV. The software OIM Analysis ver. 7 (TSL Solutions) was used in the EBSD analysis. Herein, the fitting method used was a general one to trace the representative Kikuchi lines and to measure their widths for the purpose of determining the corresponding Miller indices.
2.4. Method to Measure Mechanical Properties of Top Dross Particles (Fe$_2$Al$_5$Znx)

In order to investigate the relationship between the crystal orientation and the hardness of the top dross particles, the Vickers hardness of the top dross particles whose crystal orientations were already analyzed using EBSD was evaluated. We found that, on the one hand, when the measurement was performed with a load of 490 mN, the top dross particles were sometimes broken. On the other hand, when the measurement was performed with a load of 49 mN, the hardness values scattered. Therefore, the measurement was performed with a load of 98 mN, a maximum load at which stable hardness values were obtained and the top dross particles were not broken.

For the evaluations of the elastic modulus and fracture toughness, the same method as that of Tsukahara et al. was utilized. That is, the elastic modulus was measured using a nano-indentation hardness test, while the fracture toughness was measured using the Indentation Fracture (IF) method via a Vickers hardness test. Figure 3 shows the parameters required for measuring the elastic modulus ($E$) and fracture toughness ($K_{IC}$). $E$ was determined using the load-displacement curve obtained using a nano-indentation hardness test equipped with a Barkovich-type indenter. The plastic deformation $h_1$ (m) and the elastic deformation $h_2$ (m) were measured using the slope after reaching the maximum load $P_{max}$ (N), and then $E$ was calculated using the Eqs. (1) and (2) (Fig. 3(a)).

$$ E = \frac{\sqrt{E}}{2\sqrt{A}} \times \frac{P_{max}}{h_2} \quad \text{(1)} $$

$$ A = 24.5h_1^2 \quad \text{(2)} $$

The unit of $E$ is Pa.

The fracture toughness ($K_{IC}$) was calculated using Eq. (3) (Fig. 3(b)). The average crack length $l$ (m), hardness $H_v$ (MPa), and load $P$ (MN) were obtained when cracks were introduced from the four corners of the indent using the Vickers test.

$$ K_{IC} = 0.0937 \left( \frac{H_vP}{4l} \right)^{1/2} \quad \text{(3)} $$

The unit of $K_{IC}$ is MPa·m$^{1/2}$. The calculation of $K_{IC}$ using Eq. (3) assumes the occurrence of the Palmqvist-type cracks from the four corners of the Vickers indent. Figure 3(c) shows an optical micrograph of the cracks introduced by the Vickers hardness indent. Furthermore, Fig. 3(d) shows an optical micrograph of the cracks after polishing the specimen so that the indent does not disappear. As shown in Fig. 3(d), a gap between the indent and the cracks was confirmed. Therefore, the crack of the top dross particles in the present study satisfied the condition of the Palmqvist-type crack.

3. Experimental Results and Discussion

3.1. Analyses of Chemical Composition and Crystal Structure of Top Dross Particles (Fe$_2$Al$_5$Znx)

3.1.1. Analysis of Chemical Composition Using EPMA

Figure 4 shows the result of analyzing the chemical comp-
position of the top dross particles using EPMA. Figure 4(a) shows the EPMA compositional image of the sample, where the black angular inclusions are the top dross particles and the surrounding white background is the solidified liquid Zn phase. It was found that the composition of the top dross particles is almost constant, regardless of their sizes, and that the variation in chemical compositions of each top dross particle is small. The compositions of the top dross particles are 37 to 38 wt% (25.4 to 26.1 at%) Fe, 44 to 45 wt% (62.6 to 64.1 at%) Al, and 18 to 19 wt% (10.6 to 11.2 at%) Zn. According to the phase diagram of the Fe–Al binary system, the Fe and Al concentrations of the Fe$_2$Al$_5$ phase are 45 to 46 wt% (28.4 to 29.1 at%) and 54 to 55 wt% (70.6 to 71.9 at%), respectively. Using the thermodynamic database constructed by Nakano et al., we calculated the Fe–Al–Zn ternary phase diagram (Fig. 5). As shown clearly in Fig. 5, the Fe concentration of the Fe$_2$Al$_5$ phase equilibrated with the liquid Zn phase is 33.5 to 34 wt% (24.0 to 24.3 at%), the Al concentration is 40.5 to 41 wt% (60.1 to 60.5 at%), and the Zn concentration is 25 to 26 wt% (15.2 to 15.9 at%). The atomic ratio of Al to Fe in the top dross (Al/Fe) obtained from the experiment was 2.40 to 2.52, which is close to the value of 2.43 to 2.53 obtained in the Fe–Al binary phase diagram and 2.43 to 2.53 thermodynamically calculated in the Fe–Al–Zn ternary phase diagram. These results suggest that the atomic ratio of Al to Fe in the top dross particles is close to the stoichiometric ratio (i.e., 2.5) of Fe$_2$Al$_5$ and that the top dross particles presumably have a similar crystal structure to that of Fe$_2$Al$_5$ in the binary Fe–Al system. As described above, the Zn concentration of the top dross particles obtained experimentally was 18 to 19 wt%, whereas the calculated Zn concentration dissolved in the Fe$_2$Al$_5$ phase in equilibrium with the liquid Zn phase in the Fe–Al–Zn ternary system was 25 to 26 wt%. The reason for the difference between the two has not yet been elucidated as of the present and will be addressed in the future.

The following two cases are assumed for the possible positions of Zn atoms in the top dross particles. One case is that the crystal structure wherein Zn atoms exist in the partially occupied sites of Al atoms (Al$^{I}$ and Al$^{III}$ in Fig. 1) along the c-axis direction without changing the atomic arrangement of Fe and Al(Al$^{II}$ in Fig. 1). The other case is that the crystal structure in which some of the Fe and Al atoms (Al$^{I}$, Al$^{II}$, Al$^{III}$) are replaced by Zn atoms wherein most of the Zn atoms replace Al atoms. In order to determine the accurate crystal structure of the top dross par-
particle $\text{Fe}_2\text{Al}_5\text{Zn}_x$, further research exploiting XAFS (X-ray Absorption Fine Structure) or first-principles calculation would be necessary, which would be a possible future subject of study.

3.1.2. Analysis of Crystal Structure by X-ray Diffraction
The phases were identified using X-ray diffraction to analyze the crystal structure of the top dross particles. The result is shown in Fig. 6. It was confirmed that the X-ray diffraction peaks consisted of the peaks from top dross particles in addition to the strong peaks of the Zn phase and the peak of the CoK$\beta$ line of Zn (100). The peaks of the top dross particles shifted from the peaks (red line in Fig. 6) of the orthorhombic $\text{Fe}_2\text{Al}_5$ (lattice constants: $a = 7.656 \, \text{Å}$, $b = 6.415 \, \text{Å}$, $c = 4.218 \, \text{Å}$) present in the Fe–Al binary system. When the lattice constants were rigorously determined by the Pawley method$^{12}$ based on the orthorhombic space group (Cmcm)$^9$ and peak positions of $\text{Fe}_2\text{Al}_5$, the lattice constants of the top dross were obtained as $a = 7.61 \, \text{Å}$, $b = 6.48 \, \text{Å}$, and $c = 4.23 \, \text{Å}$. Furthermore, the theoretical peak pattern (peak intensity) was calculated via the Rietveld analysis using the newly determined lattice constants and the atomic coordination$^{11}$ of the binary $\text{Fe}_2\text{Al}_5$. The blue lines in Fig. 6 are the results. The peak pattern as well as peak intensity finally obtained using the Rietveld analysis were in good agreement with those experimentally obtained by X-ray diffraction of the top dross particles. Consequently, it is considered that the top dross particles presumably have the same crystal structure as that of the binary $\text{Fe}_2\text{Al}_5$; however, the lattice constant is slightly changed by containing Zn. As such, the lattice constants of the top dross particles containing Zn are $a = 7.61 \, \text{Å}$, $b = 6.48 \, \text{Å}$, and $c = 4.23 \, \text{Å}$ as described above. The $a$ axis of the top dross particles becomes shorter, while the $b$ and $c$ axes become longer compared to those of the binary $\text{Fe}_2\text{Al}_5$ ($a = 7.656 \, \text{Å}$, $b = 6.415 \, \text{Å}$, $c = 4.218 \, \text{Å}$). Moreover, Sakidja et al.$^{13}$ reported that the Al occupancy of the partially occupied Al sites along the $c$-axis increases when the Al concentration in the binary $\text{Fe}_2\text{Al}_5$ increases, resulting in the $a$-axis becoming short and the $b$- and $c$-axes becoming long. Therefore, it was suggested that the top dross particles might have a shorter $a$-axis and longer $b$- and $c$-axes due to the location of Zn atoms in the partially occupied Al sites along the $c$-axis. The verification and reasons for this speculation will be addressed in the future.

3.2. Analysis of Coarsening Mechanism of Top Dross Particles ($\text{Fe}_2\text{Al}_5\text{Zn}_x$)
Here, EBSD was used for analyzing the coarsening mechanism of the nucleated top dross particles.

3.2.1. Measurement of Kikuchi Line by EBSD
The Kikuchi line of the top dross particles was measured using SEM-EBSD. The result is shown in Fig. 7(a). A relatively clear Kikuchi line was obtained, which made it possible to identify phases and analyze crystal orientations using EBSD.

3.2.2. Analysis of Kikuchi Line Using EBSD
The Kikuchi line was fitted using the newly determined lattice constant data of the top dross particles obtained in the present study. The result is shown in Fig. 7(b). The predicted Kikuchi line pattern and the actually obtained Kikuchi line pattern match well, indicating that the fitting of the Kikuchi line of the top dross particles is possible with high accuracy. In other words, it was found that the phase identification and orientation analysis were possible with EBSD.

3.2.3. Observation of Top Dross Particles by EBSD and Its Coarsening Mechanism
Figure 8 shows the results of the phase identification and crystal orientation analysis of the top dross particles conducted using the method described in Section 3.2.2. It is evident that the top dross particles coarsened to about 50 to 100 $\mu$m in size and that the fine top dross particles are simultaneously mixed. The coarse top dross particles have facets and show the same crystal orientation for each individual particle. Therefore, it is assumed that the top dross particles did not coarsen to about 100 $\mu$m by a mechanism of agglomeration, but rather coarsened to minimize the total interfacial energy, where the facet plane with the lowest interfacial energy between the top dross particle and liquid Zn phase is maintained. The coarsening of the top dross particles occurred when the Zn bath containing Fe and Al was held for a long time. Therefore, it is difficult to imagine the coarsening mechanism that presume the chemical free energy as the driving force. On the other hand, Fig. 8 allows us to infer that the coagulation of some top dross particles might proceed simultaneously. However, the experimental fact that the coagulation process hardly occurs implies that the interfacial energy between the top dross particles with special crystallographic facet planes and the liquid Zn phase is relatively low. Thus, the analysis using EBSD revealed, for the first time, that the coarsening mechanism of the top dross particles is driven by the anisotropic interfacial energy. The time-dependent change of the top dross particles based on the detailed investigation into the nucleation and growth process will be discussed in the future.

3.3. Analysis of Mechanical Properties of Top Dross Particles ($\text{Fe}_2\text{Al}_5\text{Zn}_x$)
The hardness, elastic modulus, and fracture toughness of the top dross particles ($\text{Fe}_2\text{Al}_5\text{Zn}_x$) analyzed using EBSD in section 3.2 were measured. The effects of Zn in $\text{Fe}_2\text{Al}_5$ on its basic mechanical properties and its crystal anisotropy were investigated.

3.3.1. Vickers Hardness
Vickers hardness measurements conducted for many top dross particles as shown in Fig. 9. The load was 98 mN, and the size of the indentation was controlled to be smaller than 1/3 of the size of the top dross particle in order to improve the accuracy. Although the thickness of the top dross particles in the depth direction has not been sufficiently studied this time, the top dross particles are expected to have sufficient thickness as described in the paper by Arioka et al.$^3$ Figure 10 shows the average hardness and its standard deviation for each crystal orientation of the top dross particles. The coefficient of variation was less than 6.5% for any top dross particles. The hardness of the crystal$^5$ in Fig. 10 near the [100] orientation of the top dross particle is 714
Fig. 6. X-ray diffraction patterns showing the existence of Fe$_2$Al$_5$Znx phase in the top dross of molten Zn. The arrows indicate the diffraction peaks of Fe$_2$Al$_5$Znx. The red and blue lines indicate both the diffraction angles and intensities of Fe$_2$Al$_5$ and Fe$_2$Al$_5$Znx, based on the Rietveld method, respectively.

Fig. 7. (a) EBSD Kikuchi patterns of a Fe$_2$Al$_5$Znx phase dross particle. (b) Fitting result of the Kikuchi pattern using the newly proposed lattice parameters for top dross.

Fig. 8. EBSD (a) image quality map, (b) phase map, and inverse pole figure maps of (c) Fe$_2$Al$_5$Znx phase dross particles and (d) Zn.
Hv, while the hardness of the crystal ① near the [010] is 754 Hv. On the other hand, the hardness of the crystal ⑦ close to [001] was considerably low as 616 Hv, indicating that the [001] orientation tended to be softest. This is a similar trend to the result of binary Fe$_2$Al$_5$ measured by Tsukahara et al. ⑥ The softest [001] orientation is presumably due to the existence of vacancies and Zn atoms in partially occupied Al sites along the c-axis. Furthermore, it is revealed that the hardness of the top dross particles is significantly soft when compared with the hardness value of 780 to 810 Hv of the binary Fe$_2$Al$_5$. The cause of such characteristics of the top dross particles containing Zn considering the location of Zn atoms in Fe$_2$Al$_5$ will be discussed in future.

### 3.3.2. Elastic Modulus

The measurement of the elastic modulus was performed using a nano-indentation hardness test method. Referring to the paper by Tsukahara et al., ⑦ the test was conducted under the condition of the maximum load ($P_{\text{max}}$) of 9.8 mN. Nano-indentation tests were performed on grains with [100], [010], and [001] orientations, and the resulting load-displacement curves are shown in Fig. 11. The elastic modulus ($E$) evaluated using the Eq. (1) is 217 GPa in the [100] orientation and 235 GPa in the [010] orientation. On the other hand, $E$ in the [001] orientation is 204 GPa. Although the number of measurements was one this time, the elastic modulus in the [001] orientation tends to be significantly lower than those of the other orientations. This tendency is similar to the case of hardness, indicating the anisotropy in mechanical properties. Elastic anisotropy of the top dross is qualitatively similar to that of the binary Fe$_2$Al$_5$ reported by Tsukahara et al., ⑦ which is speculated to be caused by the atomic arrangement of vacancies and Zn atoms in the partially occupied Al sites along the c-axis. According to Tsukahara et al., ⑦ the value of $E$ of the binary Fe$_2$Al$_5$ is 253 GPa in the orientation close to the [100] and is as low as 222
GPa in the orientation close to the [001]. Therefore, the top dross particles containing Zn was confirmed to exhibit lower elastic modulus as well as hardness than those of Fe₂Al₅.

3.3.3. Fracture Toughness

Figure 12 shows the crack behaviors when a Vickers indenter was pressed along the [100], [010] and [001] orientations with a load of 490 mN. Only in the [001] orientation, cracks opened in four directions as shown in Fig. 11(a) and the fracture toughness value (K_{IC}) obtained using the Eq. (2) was 1.1 MPa · m^{1/2}. However as shown in Figs. 11(b) and 11(c), the K_{IC} value was not determined in the [010] and [001] orientations because cracks did not occur in four directions, but occurred only in two or three directions. The same tendency was confirmed even after three tests. Compared with the K_{IC} (1.3 MPa · m^{1/2}) of Fe₂Al₅ reported by Tsukahara et al., it is such that the concentrations of Fe, Al and Zn are 37 to 38 wt%, 44 to 45 wt%, and 18 to 19 wt%, respectively.

Moreover, the variation in the concentrations of these elements hardly depends on the size of the top dross particles. The same tendency was confirmed even after three tests. Compared with the K_{IC} (1.3 MPa · m^{1/2}) of Fe₂Al₅ reported by Tsukahara et al., it is such that the concentrations of Fe, Al and Zn are 37 to 38 wt%, 44 to 45 wt%, and 18 to 19 wt%, respectively.

The elastic modulus values of the top dross particles tend to be lower in all directions compared to those of the binary Fe₂Al₅. The fracture toughness of the top dross particles in the [001] orientation tends to be slightly lower than that of the binary Fe₂Al₅. No crystal anisotropy of fracture toughness was previously reported in the binary Fe₂Al₅, while the crack behavior of the top dross particles depends on crystal orientations.

4. Conclusions

The following findings were obtained for the top dross particles (Fe₂Al₅Znₓ) floating in the molten Zn bath.

(1) The chemical composition of the top dross particles is such that the concentrations of Fe, Al and Zn are 37 to 38 wt%, 44 to 45 wt%, and 18 to 19 wt%, respectively. Moreover, the variation in the concentrations of these elements hardly depends on the size of the top dross particles.

(2) The crystal structure of the top dross particles is orthorhombic even when it contains Zn. The lattice constants are \(a = 7.611 \, \text{Å}, b = 6.48 \, \text{Å}, \text{and} \ c = 4.23 \, \text{Å}.\) Compared with those of the binary Fe₂Al₅, the a-axis is shorter, while the b- and c-axes are longer.

(3) The top dross particles consist of a mixture of fine ones with about 1 µm and coarse ones up to 100 µm. The orientation analysis using EBSD revealed that a coarse grain has the same orientation with clear facet planes, which suggests that coarsening is caused by the growth mechanism driven by the anisotropic interfacial energy between the top dross and liquid Zn phase, not by the aggregation mechanism.

(4) Similar to the binary Fe₂Al₅, the top dross particles have the lowest hardness in the [001] orientation. Moreover, the hardness values of the top dross particles in all directions tend to be significantly lower than those of the binary Fe₂Al₅.

(5) Similar to the binary Fe₂Al₅, the top dross particles have the lowest elastic modulus in the [001] orientation. The elastic modulus values of the top dross particles tend to be lower in all directions compared to those of the binary Fe₂Al₅.

(6) The fracture toughness of the top dross particles in the [001] orientation tends to be slightly lower than that of the binary Fe₂Al₅. No crystal anisotropy of fracture toughness was previously reported in the binary Fe₂Al₅, while the crack behavior of the top dross particles depends on crystal orientations.

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