Note

Recovery of Zinc from Zn–Al–Fe Melt by Super-gravity Separation

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The removal of iron-containing dross particles and recovery of zinc from galvanizing dross by super-gravity separation was investigated using a model Zn–Fe–Al alloy. After super-gravity separation, the high purity molten zinc went through the filter, while the residue mainly consisting of dross particles was intercepted by the filter and separated from the molten zinc. The effects of gravity coefficient and separating temperature on zinc recovery and iron removal were investigated. The preliminary results show the super-gravity separation is a promising method of recovering zinc from galvanizing dross.

KEY WORDS: super gravity; galvanizing dross; zinc recovery; separation; iron removal.

1. Introduction

Galvanizing dross is one of the major by-products in hot dip galvanizing process.¹⁾ It is mainly composed of free zinc and iron-containing dross particles (Al–Fe–Zn intermetallic compounds) which are formed by reactions between the immersed steel and molten zinc and aluminum in the galvanizing bath.^{2,3)} The galvanizing dross is a kind of valuable secondary resource due to its large quantity and high levels of zinc (over 90%), motivating the search for processes to allow its cost-effective recycling. The conventional processes of recovering zinc from galvanizing dross include pyrometallurgical and hydrometallurgical processes. In general, the pyrometallurgical routes are high energy-consuming and require large capital investments;^{4,5)} while the hydrometallurgical processes are usually quite complex and consume a great deal of lixiviating reagent.⁶⁾ So far, super-gravity separation has been successfully applied in removing impurities from alloy melt^{7,8)} and recovering valuable elements from different kinds of slag.^{9,10)} Inspired by these applications, this study examined the application of the method in recovering zinc from galvanizing dross. At the galvanizing temperatures (440–460°C),¹¹⁾ the solid dross particles are possibly removed from the molten zinc under super-gravity field, and the purified zinc could be directly return to the galvanizing bath to coat products (if the iron

content is lower than 0.1 wt%).¹⁾ To minimize uncertainty associated with the inherent heterogeneity of industrial galvanizing dross, a Zn–Al–Fe alloy containing 6 wt% Al and 2 wt% Fe was used as a model galvanizing dross. The aims of the study were to improve our fundamental understanding of the direct separation of zinc melt from the dross particles and to demonstrate the technical feasibility of recovering zinc from galvanizing dross by super-gravity separation.

2. Experimental

The Zn–Al–Fe alloy used in this study had a composition of 92 wt% Zn, 6 wt% Al and 2 wt% Fe. The Zn–Al–Fe alloy was prepared with 20.0 g of Zn (99.99 wt%), 1.304 g of Al (99.99 wt%) and 0.435 g of Fe (99.99 wt%) as starting materials in a quartz crucible (I.D. 18 mm) heated in an induction furnace under an argon atmosphere at 700°C for 1 h, then cooled to 460°C for 5 h.

The super-gravity field was generated by a centrifugal apparatus as depicted in Fig. 1. A resistance heating furnace balanced with a counterweight across the rotation axis was fixed onto a centrifugal rotor. The temperature of the heating furnace was controlled by a program controller with a type-R thermocouple. Furthermore, the gravity coefficient (G) was calculated via Eq. (1).

$$G = \frac{\sqrt{g^2 + (\omega^2 r)^2}}{g} = \frac{\sqrt{g^2 + \left(\frac{N^2 \pi^2 r}{900}\right)^2}}{g} \dots\dots\dots (1)$$

where g is the normal-gravitational acceleration, 9.8 m/s²; ω denotes the angular velocity, rad/s; r is the distance from the axis to the center of sample, 0.25 m in this work; N denotes the rotating speed, r/min.

The prepared Zn–Al–Fe alloy sample was placed into an upper graphite crucible (I.D. 20 mm and H. 60 mm) with several holes (D. 0.75 mm) at the bottom. A layer of carbon fiber felt (CFF) with a thickness of 4 mm was applied at the bottom of the crucible as the filter medium. The CFF supplied by Jing Long Te Tan Ltd in China has the bulk density of 0.171 g/cm³, real density of 1.82 g/cm³ and average fiber diameter of 17 μm. Another lower graphite crucible (I.D.

Fig. 1. Schematic diagram of the centrifugal apparatus: 1 counterweight, 2 centrifugal axis, 3 resistance heating furnace, 4 Zn–Al–Fe alloy sample, 5 filtered zinc, 6 graphite crucible, 7 filter, 8 type-R thermocouple, 9 resistance coil, 10 temperature controller.

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20 mm and H. 20 mm) was used to contain the molten zinc which flew through the filter. The sample was then heated in the resistance heating furnace at the target temperatures (425–665°C) for 15 min, after which the centrifugal apparatus was started and adjusted to the desired rotating speed to conduct isothermal separation for 5 min. Preliminary experiments show that the lowest temperature, which is 5°C higher than the melting point of zinc, was enough to appropriately melt the samples used, and the molten zinc flowed through the filter nearly completely within the first minute of rotation. Then the centrifugal apparatus was shut off and the sample was water quenched. Comparatively, the parallel experiment was conducted at 425°C for 5 min in normal gravity. The filtered zinc (went through the filter) and residue (intercepted by the filter) were sectioned into two parts along the longitudinal center axis. One part was polished for SEM analysis, and the other was used to determine the chemical composition by ICP-OES.

To evaluate the separation efficiency under different conditions, three parameters were defined, including mass fraction of filtered zinc (W_{zinc}), recovery rate of zinc (R_{zinc}) and removal rate of iron (η_{iron}). W_{zinc} is defined as ratio of the mass of filtered zinc (m_{fz}) to the mass of the original Zn–Al–Fe sample (m_o). R_{zinc} and η_{iron} were calculated via Eqs. (2) and (3), respectively.

$$R_{zinc} = \frac{m_{fz} \times w_{zinc_fz}}{m_o \times w_{zinc_o}} \times 100\% \quad (2)$$

$$\eta_{iron} = \left(1 - \frac{m_{fz} \times w_{iron_fz}}{m_o \times w_{iron_o}} \right) \times 100\% \quad (3)$$

where w_{zinc_fz} and w_{zinc_o} denote the mass fraction of zinc in the filtered zinc and original Zn–Al–Fe sample, respectively. w_{iron_fz} and w_{iron_o} are the mass fraction of iron in the filtered zinc and original Zn–Al–Fe sample, respectively.

3. Results and Discussion

Figure 2 indicates the cross section of the samples obtained by super gravity at separating temperature $T = 425^\circ\text{C}$ and different gravity coefficients. Under normal gravity, the whole parallel sample remained on the filter and no separation occurred. When the gravity coefficient was higher than 15 (Figs. 2(b)–2(d)), part of zinc went through the filter into the lower crucible, with the residue intercepted on the filter. **Figure 3** shows the microstructure of the parallel sample and the residue and filtered zinc obtained at $T = 425^\circ\text{C}$ and $G = 400$. Figures 3(a), 3(b), 3(c) and 3(d) refer to areas ‘A’, ‘B’, ‘C’ and ‘D’ marked in Fig. 2, respectively. As shown in Figs. 3(a) and 3(b), in the parallel sample, the dross particles (dark gray) were distributed in the alloy matrix consisting of a zinc-rich phase (η , light gray) and a eutectic type phase (middle gray).²⁾ Point analysis by EDS of 30 random dross particles indicated that these particles had an average chemical formula of $\text{Fe}_2\text{Al}_5\text{Zn}_{0.67}$. Besides, there were more dross particles in the upper part (Fig. 3(a)) compared to the lower part (Fig. 3(b)) due to the lower density of the dross particles than the alloy matrix.¹²⁾ As shown in Fig. 3(c), after super-gravity separation, the dross particles were intercepted by the filter and gathered in the

Fig. 2. Macrographs of the samples obtained by super-gravity separation at $T = 425^\circ\text{C}$ and different gravity coefficients. (a) $G = 1$; (b) $G = 15$; (c) $G = 400$; (d) $G = 1\,000$.

Fig. 3. Back-scattered electron images of four different typical regions in Fig. 2. (a) Upper part of the parallel sample; (b) lower part of the parallel sample; (c) residue obtained at $T = 425^\circ\text{C}$ and $G = 400$; (d) filtered zinc obtained at $T = 425^\circ\text{C}$ and $G = 400$.

residue. After super-gravity separation, the filtered zinc was significantly purified and hardly any dross particle was observed in the filtered zinc (Fig. 3(d)).

The chemical composition of the filtered zinc and separation efficiencies obtained at different gravity coefficients were presented in **Table 1** and **Fig. 4(a)**, respectively. After separation at 425°C , the filtered zinc obtained a very low content of iron (average 0.0059 wt%) and η_{iron} reached a quite high value (average 99.7 wt%). As indicated in Fig. 4(a), W_{zinc} and R_{zinc} increased with increasing gravity coefficient, since more molten zinc flowed through the filter into the lower crucible. After separation at $G = 400$ and $T = 425^\circ\text{C}$, R_{zinc} and η_{iron} reached 86.6 wt% and 99.7 wt% respectively. To filter the molten zinc, the centrifugal pressure (P_c , proportional to the angular velocity and the amount of molten zinc above the filter medium)¹³⁾ acting on the surface of filter medium should be larger than the filtration resistance (P_r) offered by the filter medium. P_r can be described by the capillary law:

$$P_r = -\frac{4\sigma \cos\theta}{d} \quad (4)$$

Fig. 4. Variation in separation efficiency including W_{zinc} , R_{zinc} and η_{iron} with (a) gravity coefficient at $T = 425^{\circ}\text{C}$ and (b) separating temperature at $G = 400$.

Table 1. Chemical composition of the filtered zinc obtained at different conditions.

Gravity coefficient	Separating temperature, $^{\circ}\text{C}$	Composition of filtered zinc, wt%		
		Zn	Al	Fe
15	425	96.8	3.17	0.00451
100	425	96.8	3.24	0.00598
400	425	96.7	3.25	0.00608
700	425	96.6	3.43	0.00579
1 000	425	96.5	3.52	0.00715
400	465	96.8	3.17	0.00752
400	515	96.6	3.35	0.0122
400	565	96.8	3.22	0.0178
400	615	96.5	3.48	0.0202
400	665	96.6	3.42	0.031

where σ is the surface tension of molten zinc, θ denotes the wetting angle and d is the effective opening diameter of the filter medium. When G was over 15, P_c exceeded the P_r caused by the CFF and the molten zinc started to pass through the CFF. With the proceeding of the filtration, the amount of the molten zinc above the filter medium decreased steadily, lowering P_c . And the dross particles were gradually deposited above the CFF and served as another filter medium for subsequent filtration, which gradually decreased the effective opening diameter (d in Eq. (4)) and increased P_r . When P_r was higher than P_c , the filtration of molten zinc was stopped and the residue zinc was kept in the interstices of the dross particles, as shown in Fig. 3(c). Increasing gravity coefficient can improve P_c and overcome higher P_r , therefore, more molten zinc can pass through the filter medium, resulting in the higher W_{zinc} and R_{zinc} (Fig. 4(a)).

The effects of separating temperature on the chemical composition of the filtered zinc and separation efficiencies were shown in Table 1 and Fig. 4(b), respectively. With increasing T from 425°C to 665°C , both W_{zinc} and R_{zinc} increased slightly, but η_{iron} decreased gradually from 99.7 wt% to 98.7 wt%, resulting from the higher iron content in the filtered zinc at higher separating temperatures (Table 1). Increasing temperature reduced σ and $\theta^{(4,15)}$ in Eq. (4) and decreased P_r correspondingly, benefiting the filtration of molten zinc. But increasing temperature also increased the solubility of iron in molten zinc,⁽¹⁶⁾ so more iron impurities passed through the filter and deteriorated the quality of

filtered zinc at higher temperatures.

After super-gravity separation, the filtered zinc obtained quite low content of iron impurities and can be directly used as fresh galvanizing zinc to coat products. And the residue could be further recycled by the conventional methods more economically, because the amount of the residue significantly reduced in comparison with the original sample.

4. Conclusions

The feasibility of zinc recovery from a Zn–Al–Fe alloy by super-gravity separation was demonstrated. The molten zinc went through the filter, while the dross particles were intercepted by the filter and effectively separated from the molten zinc. After separation at $G = 400$ and $T = 425^{\circ}\text{C}$, zinc recovery was 86.6 wt% and up to 99.7 wt% of iron was concentrated in the residue. Increasing gravity coefficient and separating temperature benefited the zinc recovery, while lowering separating temperature reduced the content of iron impurities in the obtained filtered zinc.

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