

Removal of Iron from Commercial Aluminum by Electroslag Refining

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The present study aims at development of a novel method for iron removal from commercial aluminum by electroslag refining. Cast electrodes of commercial aluminum were electroslag refined using KCl-NaCl-Na₃AlF₆ slag containing 10wt.%Na₂B₄O₇. The Fe content decreased from 0.42% to 0.20wt.% after electroslag refining. The chemical reaction between melt and slag to form Fe₂B in the electroslag refining process is the main reason for the reduction in Fe. Thermodynamic calculation theoretically accounts for the formation of Fe₂B in the electroslag refining process.

Keywords: *Electroslag refining; Aluminum; Iron; Purification*

1. Introduction

Iron, as one of the main impurities in aluminum, is always present in alloys made from commercially pure base material[1-2]. The maximum equilibrium solid solubility of iron in aluminum is very low(at 0.05wt%), and iron is usually present therefore in the form of Fe-rich intermetallic compounds together with other alloying elements, such as silicon, manganese and copper[3-4]. These compounds, which are very hard and brittle and have a relatively low bond strength with the matrix, act as stress raisers which contribute to the deterioration of the mechanical properties of aluminum alloy[5-6].

From the former investigations[7-9], it is clear that iron removal from aluminum alloy can be carried out by the formation, sedimentation and filtration of intermetallic phases. However, the essence of the process is the utilization of manganese to form intermetallics rich in Fe, Mn, Si and Al, which aggregates in the sedimentation process and can be removed by filtration. But the manganese is also one of the most harmful impurities for aluminum alloy, so the addition of Mn should be avoided if possible. Moreover, the elimination of iron in the process is influenced by the Mn/Fe ratio and the processing temperature. Therefore, this method is very limited in application.

Electroslag refining[10] is a secondary refining process already well established for ferrous materials. In the refining process, a slag or flux is used both as a heat source and as a refining medium. The molten droplets formed at the tip of the electrode fall through the molten slag, and collect in a pool on the baseplate to solidify. Refining takes place because of the reaction between the metal and the slag in the process. By suitable choice of slags, chemical reaction can be encouraged, such as removal of impurity elements to very low levels.

In view of its potential for removal of impurity elements, an attempt has been made to study the possibility of using electroslag refining for removal of iron from commercial aluminum. This paper discusses the effect of electroslag refining on the elimination of iron and the reaction mechanism of iron and molten slag.

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2. Experimental

The material used in the experiment was commercial purity aluminum in which the iron content was adjusted to 0.42wt.%. The composition of the material is given in Table 1. The slag used was a mixed chloride-fluoride flux, containing 47wt.%KCl, 30wt.%NaCl and 23wt.%Na₃AlF₆. In addition, the Na₂B₄O₇ was added to the slag for the removal of iron and the addition of Na₂B₄O₇ was 10wt.% of the slag.

Table 1 The composition of the commercial purity aluminum

Impurity elements	Fe	Si	Ca	Cu	Na	B	Zn	Al
Content (wt %)	0.4218	0.0425	0.0270	0.0059	0.0312	0.0048	0.0113	Balance

The electroslag remelting experiments were carried out in a 60 KVA single phase AC unit using straight polarity. Figure 1 is schematic illustration of the electroslag remelting unit. Before the electroslag remelting experiments, the commercial purity aluminum was cast to electrodes of 40 mm diameter and 80 cm length, and the flux was pre-fused at 250°C in a oven. In the remelting process, the solid starting technique was used through the arc striking agent. A 0.5 kg mass of slag was melted to form the slag bath and the molten slag was super-heated to 740°C in the remelting process. The electrodes were immersed to obtain ingots of 80 mm diameter and 25-30 cm length under a voltage of 10-15 V and a current of 600-700 A. Finally, the sludge was collected for X-ray diffraction (XRD) analysis, and aluminum samples for metallographic observation and spectrum analysis were taken from the ingots.

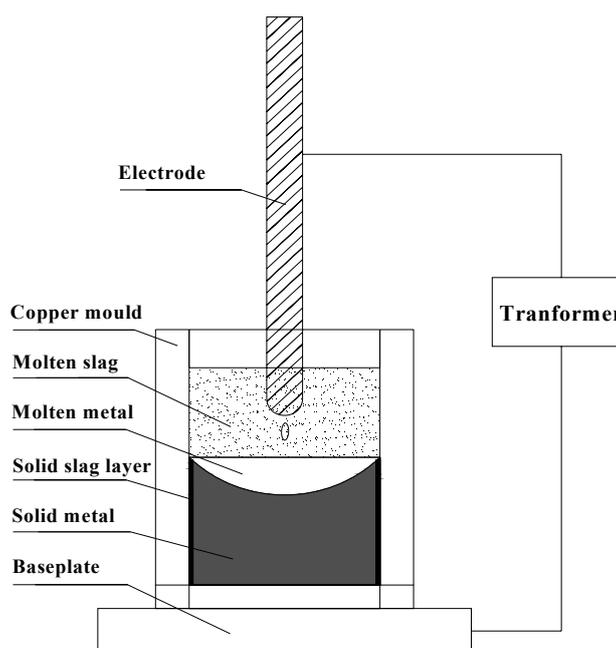


Fig.1. schematic illustration of the electroslag remelting unit

The chemical compositions of the aluminum sample were analysed with an ICP_AES machine (ICP, Iris Advantage 1000). Metallographs were observed by scanning electron microscopy (SEM, JSM-6460). The original NaCl and KCl in the sludge were removed through a deionized water filter process and phases in the sludge were detected with an X-ray diffractometer (XRD, D/MAX 2550VL/PC).

3. Results and discussion

Table 2 The Fe concentration of the aluminum samples before and after purification

Element concentration	Fe (wt %)
Before purification	0.4218
After purification sample No.1	0.1932
After purification sample No.2	0.2066

Table 2 shows the Fe concentration in aluminum before and after electroslag refining. The Fe content of the aluminum sample decreased to about 0.20% from 0.42% of the unpurified sample. The result indicates that the rate of Fe reduction is more than 50% through electroslag refining. The microstructure of the aluminum sample before and after electroslag refining is shown in Figure 2. The Al-Fe binary phase at grain boundaries becomes less and thinner after purification, as shown in Figure 2(b).

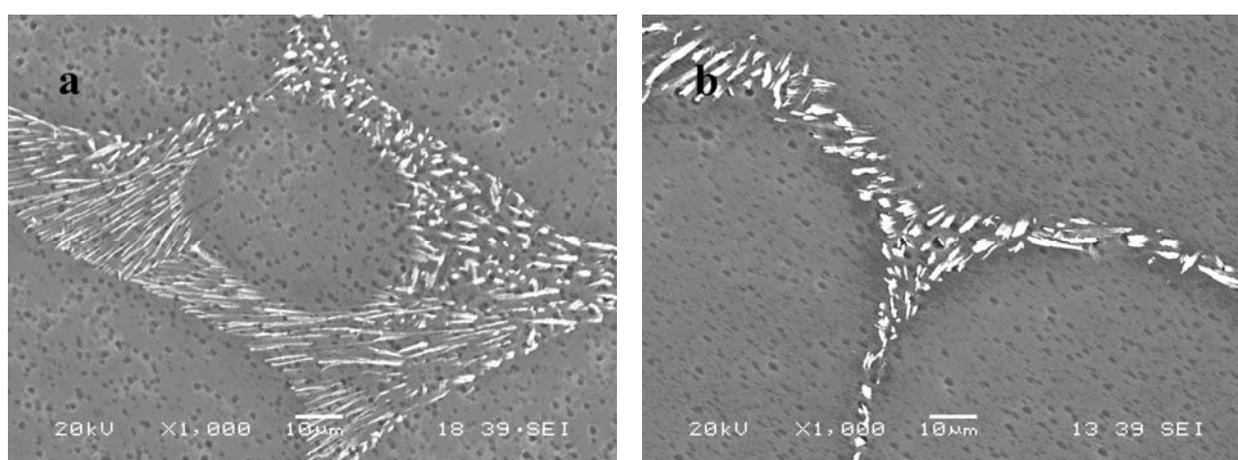


Fig. 2. SEM micrographs of the aluminum sample: (a) before purification (b) after purification.

The X-ray diffraction analysis of the collected molten sludge is shown in Fig 3. The elpasolite (K_2NaAlF_6) phase and intermetallic compound Fe_2B were found in the molten sludge. The elpasolite phase was a resultant of AlF_6^{-3} combined with Na^{+1} and K^{+1} , because Na_3AlF_6 , KCl , $NaCl$ were resolved into Na^{+1} , AlF_6^{-3} , K^{+1} and Cl^{-1} in the molten flux. The iron boride phase may form as

a result of chemical reaction between the iron and $\text{Na}_2\text{B}_4\text{O}_7$ in the molten flux and subsequently be captured by the molten flux during the electroslag refining process. The melting point of Fe_2B is 1389°C higher than the temperature of this molten flux [11]. Therefore, the formed particulate iron boride can be captured by the molten flux and was finally removed with the sludge, which accounts for the reason why the electroslag refining can reduce the Fe content in the aluminum.

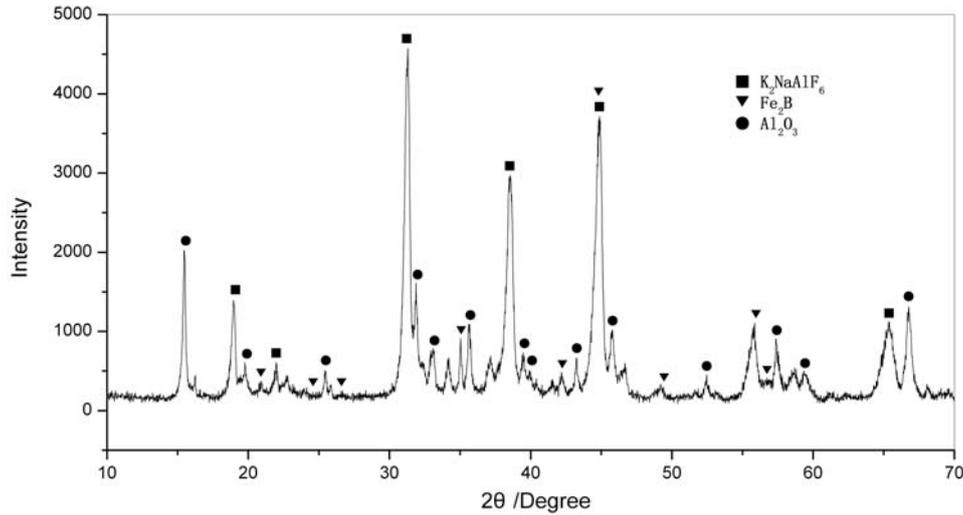
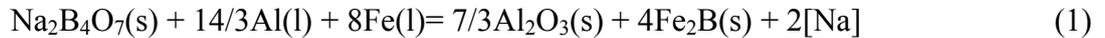


Fig.3. X-ray diffraction spectra of the molten sludge

In this chemically complicated flux-melt system, the following reaction may take place to produce Fe_2B among $\text{Na}_2\text{B}_4\text{O}_7$, Fe and Al.



In Eq. (1), s, l and g represent solid, liquid and gas, respectively. Under practical conditions, the Gibbs free energy of reaction (1) should be calculated by Eq. (2)

$$\begin{aligned} \Delta G_{1013\text{K}} &= \Delta G_{1013\text{K}}^0 + RT \ln \frac{\alpha_{\text{Al}_2\text{O}_3}^{7/3} \alpha_{\text{Fe}_2\text{B}}^4 \alpha_{\text{Na}}^2}{\alpha_{\text{Al}}^{14/3} \alpha_{\text{Fe}}^8 \alpha_{\text{Na}_2\text{B}_4\text{O}_7}} \\ &= \Delta G_{1013\text{K}}^0 + RT \ln \frac{[\text{Na}]_{\text{Mole}}^2}{[\text{Al}]_{\text{mole}}^{14/3} [\text{Fe}]_{\text{mole}}^8} \end{aligned} \quad (2)$$

where $\alpha_{\text{Al}_2\text{O}_3}$, $\alpha_{\text{Fe}_2\text{B}}$, $\alpha_{\text{Na}_2\text{B}_4\text{O}_7}$, α_{Al} , α_{Fe} and α_{Na} are activities of Al_2O_3 , Fe_2B , $\text{Na}_2\text{B}_4\text{O}_7$, Al, Fe and Na in the molten droplets, respectively. $\alpha_{\text{Al}_2\text{O}_3}$, $\alpha_{\text{Fe}_2\text{B}}$, and $\alpha_{\text{Na}_2\text{B}_4\text{O}_7}$ can be considered as 1 for solid state matter. For simplification, α_{Al} , α_{Fe} and α_{Na} are replaced by their approximately mole atomic concentration, i.e. $[\text{Al}]_{\text{mole}}$, $[\text{Fe}]_{\text{mole}}$ and $[\text{Na}]_{\text{mole}}$ respectively. In this experiment, the weight concentration of Al and Fe in the aluminum are 99.4555wt.% and 0.4218wt.%, and the addition of $\text{Na}_2\text{B}_4\text{O}_7$ was 10wt.% of the slag. Thus, $[\text{Al}]_{\text{mole}}$, $[\text{Fe}]_{\text{mole}}$ and $[\text{Na}]_{\text{mole}}$ can be calculated as

$$[\text{Al}]_{\text{mole}} = \frac{0.994555/27}{0.994555/27 + 0.004218/56} = 0.997959 \quad (3)$$

$$[Fe]_{mole} = \frac{0.004218/56}{0.994555/27 + 0.004218/56} = 0.002041 \quad (4)$$

$$[Na]_{mole} = \frac{(10\% \times \frac{23 \times 2}{23 \times 2 + 11 \times 4 + 16 \times 7})/23}{0.994555/27 + 0.004218/56} = 0.026824 \quad (5)$$

In Eqs. (3)-(5), 27, 56, 23, 11 and 16 are the atomic weights of Al, Fe, Na, B and O, respectively.

The standard Gibbs free energy at the temperature of 1013K, ΔG_{1013K}° , can be calculated by Eq. (6), based on Gibbs free energy function (Φ_T) Method.

$$\Delta G_{1013K}^{\circ} = \Delta H_{298K}^{\circ} - T\Delta\Phi'_{1013K} \quad (6)$$

Using the standard Φ_{1013K}' and H_{298K}° data of the substance shown in Table 3[12], ΔG_{1013K}° of the reaction (1) can be calculated to be $-839614 \text{ J}\cdot\text{mol}^{-1}$.

Table 3 Thermodynamic data of the reaction (1)

Substance	Al ₂ O ₃	Fe ₂ B	Na	Na ₂ B ₄ O ₇	Al	Fe
$\Phi_{1013K}'(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	103.136	96.990	71.182	305.135	43.108	42.632
$H_{298K}^{\circ}(\text{J}\cdot\text{mol}^{-1})$	-1675274	-71128	0	-3276490	0	0

Substituting T with 1013K, R with $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $[Al]_{mole}$ with 0.997959, $[Fe]_{mole}$ with 0.002041, $[Na]_{mole}$ with 0.026824 and ΔG_{993K}° with $-839614 \text{ J}\cdot\text{mol}^{-1}$ in Eq. (2), the Gibbs free energy of the reaction (1) should be

$$\Delta G_{1013K} = -483131 \text{ J}\cdot\text{mol}^{-1} \quad (7)$$

The negative value of ΔG_{1013K} indicates that the reaction (1) can spontaneously take place in the flux-melt system. Therefore, thermodynamic calculation theoretically accounts for the formation of Fe₂B in the electroslag refining process.

Moreover, as the remelting current enters the molten slag in the electroslag refining process, it interacts with its induced magnetism to create the electromagnetic force. The electromagnetic force has a function of stirring to the molten slag. Therefore, when the metal pass through the slag drop by drop in the electroslag refining process, the reaction interface between melt and slag is improved greatly and the reaction (1) is enhanced to great degrees.

4. Conclusions

Electroslag refining decreases the Fe content in commercial aluminum from 0.42% to 0.20 wt.%(more than a 50% reduction in Fe content). The chemical reaction between melt and slag to form Fe₂B in the electroslag refining is the main reason for the reduction in Fe. Thermodynamic calculation accounts for the formation of Fe₂B in the electroslag refining process.

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