A Novel Method to Remove Iron Impurity from Aluminum

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A novel method for iron removal from aluminum by electroslag refining using KCl-NaCl-Na$_3$AlF$_6$ flux containing P was studied. After electroslag refining, the Fe content in commercial purity aluminum decreased from 0.48% to 0.30 mass%, and the mechanical properties of commercial purity aluminum were improved, especially in tensile elongation increased by 33%. XRD and TEM analysis of the sludge indicated that the reaction between the melt and the molten slag to form Fe$_3$P in the electroslag refining process was the main reason for iron reduction. The thermodynamic phase diagram calculation for Al-Fe-P system accounts for the formation of Fe$_3$P theoretically in the electroslag refining process. [doi:10.2320/matertrans.M2011108]

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1. Introduction

Aluminum is the second-largest metal material and has a highest recovery rates among the metals. The remained impurities from the environment, which are difficult or costly to be removed entirely, damage the performance of the recycled metals. Besides silicon, Iron is the most harmful impurities in aluminum, and is always present in alloys made from commercially pure base material.1,2 Because the maximum equilibrium solubility of iron in solid aluminum is very low (at 0.05 mass%), most iron forms Fe-rich intermetallic compounds together with other elements, which appear as needles or plateles in the microstructure. These compounds, which are very hard and brittle, act as stress raisers which seriously degrade the mechanical properties of aluminum alloys.3–5

Among the iron removal methods employed, the most popular strategy adopts the precipitation and separation of Fe-rich phases from the liquid Al melt,6–8 and also requires the addition of other elements, such as Mn, Cr, etc.9–12 However, many additives are harmful to the Al alloys. Zone refining,13 which is based on the theory of unidirectional solidification, is also an effective method to remove impurities from metal, but it is adapted to the high-purity aluminum, not to the large-scale product. Although three-layer liquid electrolysis is an effective way to purify aluminum on a large scale, it is costly. So it makes sense to find a new way to remove the iron impurity from aluminum rapidly and economically.

Electroslag refining (ESR) is a secondary refining process which has already been well established for producing steels and other high performance alloys.14–16 In the process, high current is applied through a resistive slag layer, and the heat generated within the slag melts a consumable electrode. Metal droplets formed at the tip of the electrode, drop through the molten slag, and solidify in a mould to form the ingot. Refining takes place in the slag bath because of the reaction between the metal droplets and the molten slag. By suitable choice of slags, removal of impurity elements can be encouraged by chemical extraction with the slag. Stoephasius and Reitz have investigated the removal of the main impurities out of titanium and titanium-aluminum alloys by electroslag refining using a CaF$_2$-based active slag.16

In the present work, electroslag refining was applied to commercial aluminum for removal of iron impurity. The effect of electroslag refining on the iron removal using KCl-NaCl-Na$_3$AlF$_6$ flux containing P and the reaction mechanism between the melt and the molten slag were investigated.

2. Experimental

The material used in the experiment was commercial purity aluminum in which the iron composition was adjusted to 0.48 mass%. The slag used was a mixed chloride-fluoride flux, containing 47 mass% KCl, 30 mass% NaCl and 23 mass% Na$_3$AlF$_6$. In addition, the AIP was added to the flux for the removal of iron and the addition of AIP was 10 mass% of the flux. The melting point of the slag is ~610°C, and the density of the slag is 1.90 g cm$^{-3}$ at 750°C.

The electroslag refining experiments were carried out in a 60 KVA single phase AC unit. Figure 1 is the sketch of the electroslag refining apparatus. Before the electroslag refining experiment, a 2.7 kg mass of aluminum was cast to electrode of 40 mm diameter and 80 cm length and the slag was prefused at 250°C in an 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 750°C. The electrode was immerged to obtain ingot of 70 mm diameter and 20–25 cm length under a voltage of 12 V, a current of 700 A and a descending speed of 53 mm min$^{-1}$, as shown Fig. 2. After remelting, a part of the bottom of the ingot was cut due to the instability during the starting process. Finally, aluminum samples for chemical composition analysis, metallographic observation and mechanical properties testing were taken from the ingots, and the sludge was collected for X-ray diffraction (XRD) analysis.

The chemical compositions of the aluminum sample were analysed with an ICP-AES machine (ICP, Iris Advantagte 1000). The physical properties of slag were measured with comprehensive measuring instrument of melt’s physical
properties (RTW-10). 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). Furthermore, the sludge were analysed using an Energy Dispersive Spectroscopy (EDX) attached to the Analytical Transmission Electron Microscope (TEM, JEM-2010). Tensile properties were tested at room temperature by Zwick/Roell test machine. Each value of the tensile properties reported was the average of four tests at the same condition. The sizes of the specimens for mechanical properties testing were shown in Fig. 3.

3. Results and Discussion

Table 1 shows the contents of main impurity in the commercial purity aluminum before and after electroslag refining. The Fe concentration of the aluminum sample is obviously reduced after electroslag refining, and the concentration decreases to about 0.30% from 0.48 mass% before electroslag refining. The result indicates that the rate of Fe reduction is more than 35% through electroslag refining.

Figure 4 shows the microstructure of the aluminum sample before and after electroslag refining. In contrast, the needle shaped FeAl$_3$ phase at grain boundaries obviously becomes less and thinner after electroslag refining, as shown in Fig. 4(a)–(c).

Table 2 presents the mechanical properties of the aluminum samples before and after electroslag refining. Comparison has been made with the commercial aluminum samples before and after electroslag refining. The result shows that the mechanical properties of the samples after electroslag refining have a minor improvement in the elastic modulus, yield strength and ultimate strength. However, the tensile elongation of the sample after electroslag refining is 33% higher than the sample before electroslag refining. The increased tensile elongation and the minor improvement in the elastic modulus, yield strengths and ultimate strength may be attributed to reduction of iron.3,5) After electroslag refining, the Fe content of the aluminum sample decreases to 0.30% from 0.48 mass% and the needle like FeAl$_3$ binary phase at grain boundaries becomes less and thinner. The probability of cracks initiation on these brittle Fe-rich phases decreases distinctly under stress. Therefore, the mechanical properties of commercial aluminum were improved after electroslag refining.

The XRD pattern of the collected sludge is shown in Fig. 5. The elpasolite (K$_2$NaAlF$_6$) phase, inorganic compound Fe$_2$P and Al$_2$O$_3$ were found in the sludge. The elpasolite phase was a resultant of AlF$_6^{3-}$ combined with Na$^{+}$ and K$^+$, because Na$_3$AlF$_6$, KCl, NaCl were resolved into Na$^+$, AlF$_6^{3-}$, K$^+$ and Cl$^-$ in the molten slag. Al$_2$O$_3$ was the common phase in the Al melt, which was captured by the molten slag. The Fe$_2$P phase may form as a result of chemical reaction between the Al droplets and the molten slag, and subsequently be captured by the molten slag during the electroslag refining process. Furthermore, the collected sludge was examined by TEM. The TEM image and EDS spectra of the collected sludge were shown in Fig. 6. TEM analysis revealed similar results as shown in Fig. 5. K$_2$NaAlF$_6$, Al$_2$O$_3$ and Fe$_2$P were also found in the sludge, as shown Fig. 6(a). The black dough-like phase is K$_2$NaAlF$_6$, as shown Fig. 6(b), and the transparent film-like phase is
Al$_2$O$_3$, as shown Fig. 6(c). The black particle is Fe$_2$P phase, as shown Fig. 6(d). In the electroslag refining process, the temperature of molten slag is 750°C lower than the melting point of Fe$_2$P (1370°C). Therefore, the formed particulate Fe$_2$P can be captured by molten slag and was finally removed with the sludge, which accounts for the reason why the electroslag refining can reduce the Fe content in the aluminum.

The Al-Fe-P system was thermodynamically assessed using the FactSage software, so as to explain the reaction mechanism between melt and molten slag. Figure 7 shows the calculated isothermal section of Al-Fe-P system at 750°C. In the Al-Fe-P system, there is no Fe-rich phases formed except the normal Al$_{13}$Fe$_4$ (also denoted as FeAl$_3$)$_{17}$ solid solution in the Al-rich corner, whereas iron phosphide compounds, such as FeP$_2$, FeP and Fe$_2$P, form in the P-rich corner. Based on the thermodynamic calculations, the addition of P-containing flux or phosphides is not possible for iron removal in the aluminum melt, because it is difficult to obtain an enough high [P] activity according to the phase diagrams. However, if an local enrichment of [P] can obtained, the iron phosphide compounds can precipitate from the melt, as can been seen from the P corner of the phase diagram. In the electroslag refining process, the molten flux is

\[\text{Table 1 The contents of main impurity in the commercial purity aluminum before and after ESR (mass%).}\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Si</th>
<th>Cu</th>
<th>Ga</th>
<th>Mg</th>
<th>Zn</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before ESR</td>
<td>0.4805</td>
<td>0.0402</td>
<td>0.0016</td>
<td>0.0128</td>
<td>0.0017</td>
<td>0.0023</td>
<td>0.0176</td>
<td>0.0090</td>
</tr>
<tr>
<td>Top after ESR</td>
<td>0.2954</td>
<td>0.0355</td>
<td>0.0026</td>
<td>0.0132</td>
<td>0.0012</td>
<td>0.0032</td>
<td>0.0157</td>
<td>0.0102</td>
</tr>
<tr>
<td>Middle after ESR</td>
<td>0.3026</td>
<td>0.0365</td>
<td>0.0027</td>
<td>0.0130</td>
<td>0.0011</td>
<td>0.0033</td>
<td>0.0159</td>
<td>0.0092</td>
</tr>
<tr>
<td>Bottom after ESR</td>
<td>0.3012</td>
<td>0.0389</td>
<td>0.0024</td>
<td>0.0125</td>
<td>0.0015</td>
<td>0.0029</td>
<td>0.0160</td>
<td>0.0078</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic modulus, $E$/GPa</th>
<th>Yield strength, $YS_{0.2}$/MPa</th>
<th>Ultimate strength, $UTS$/MPa</th>
<th>Tensile elongation, $EL/%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before ESR</td>
<td>36</td>
<td>20</td>
<td>51</td>
<td>27</td>
</tr>
<tr>
<td>After ESR</td>
<td>39</td>
<td>23</td>
<td>56</td>
<td>36</td>
</tr>
</tbody>
</table>

Fig. 4 The microstructure of the aluminum sample: (a) Before ESR (b) top after ESR (c) bottom after ESR.

Table 2 The mechanical properties of the aluminum samples before and after ESR.
used as a refining medium. Because 10 mass% AlP was added into the flux, an local enrichment of [P] was formed in the molten flux. When the molten droplets formed at the tip of the electrode fell through the molten slag bath, the chemical reaction between the Al droplets and the molten slag took place in the P-rich condition. The iron phosphide compound Fe₂P formed spontaneously and subsequently was captured by the molten slag in the electroslag refining process.

Therefore, thermodynamic phase diagram calculation theoretically supports the presence of Fe₂P.

Moreover, refining takes place because of the reaction between the metal and the molten slag in three stages: during formation of a droplet on the electrode tip, as the detached droplet falls through the slag, and after the molten metal had collected in a pool at the top of the ingot. The reaction interface between melt and slag is multiplied many times in these three stages.¹⁴ Meanwhile, the remelting current interacts with its induced magnetism to create the electromagnetic force.¹⁸ The electromagnetic force formed in the electroslag refining process has a function of stirring to the molten slag. The reaction balance between melt and slag is broken continuously and the reaction interface between melt and slag is renewed continuously. Therefore, the reaction between melt and flux is promoted greatly in the electroslag refining process.

4. Conclusion

Electroslag refining using KCl-NaCl-Na₃AlF₆ flux containing P can decrease the iron content in commercial purity aluminum from 0.48% to 0.30 mass% (more than a 35% reduction in Fe content). The mechanical properties of commercial purity aluminum were improved after electroslag refining, especially in tensile elongation increased by 33%. The main reason for iron reduction in commercial purity aluminum is the formation of Fe₂P, which is confirmed by XRD and TEM analysis of the sludge. The thermodynamic phase diagram calculation for Al-Fe-P system accounts for the formation of Fe₂P theoretically in the electroslag refining process.
Acknowledgement

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REFERENCES