Effects of Charcoal Addition on the Final Properties of Carbon Anodes

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Abstract

Wood Charcoal is an attractive alternative to petroleum coke in production of carbon anodes for the aluminum smelting process. Calcined petroleum coke is the major component in the anode recipe and its consumption results in a direct greenhouse gases (GHG) footprint for the industry. Charcoal, on the other hand, is considered as a green and abundant source of sulfur-free carbon with a massive worldwide production of more than 50 Mt per annum. Pre-treated charcoal was used to substitute up to 10 % of coke in the anode recipe in an attempt to investigate the effect of this substitution on final anode properties. The results showed deterioration in the anode properties by increasing the charcoal content. However, by adjusting the anode recipe this negative effect can be considerably mitigated, e.g. increasing the pitch content was found to be helpful to improve the physical properties of the anodes containing charcoal.

Keywords: Anodes; charcoal; petroleum coke; specific electrical resistivity; mechanical properties.

1. Introduction

All modern smelters use the Hall–Héroult process to electrolytically reduce the alumina dissolved in molten cryolite. In this process, carbon anodes are used to conduct high amperage direct electrical current necessary for smelting from the busbar to the electrolyte. Oxygen from alumina is discharged electrolytically and reacts immediately with the carbon anodes, producing gaseous carbon dioxide (CO_2) [1]. Calcined petroleum coke (CPC) is the major component in the anode recipe. Due to the changes in the oil refining industry [2], most coke supplies do not comply with anode specifications, which are essentially based on the upper limit of sulfur and heavy metal content, the density, the molecular structure, as well as the mechanical properties.

Being an abundant source of sulfur-free carbon [3], wood charcoal seems, at first glance, to be an attractive alternative for petroleum coke. Substitution of petroleum coke by charcoal in the anode recipe would reduce the fossil CO_2 emissions. Furthermore, the very low content of vanadium (V) and sulfur (S) in charcoal could allow the use of petroleum coke with higher S and V, thus decreasing the raw material cost. However, charcoal is characterized by its amorphous carbon structure and high concentration of inorganic minerals (Ca, Na). These undesirable properties result in a material with high reactivity to air and CO_2 in addition to low real and bulk density. Charcoal was investigated as raw material for anode production [4], the results showed significant deterioration in mechanical, electrical and reactivity of the anodes containing charcoal.

Hussein *et al.* [5] tried to improve the properties of raw charcoal via acid washing and heat treatment techniques. Heat treatment at elevated temperatures (1300 °C or higher) converted its carbon structure into a more ordered one. The calcined charcoal was found to have higher real density and lower specific surface area. In addition, performing an acid washing resulted in a significant depletion in its inorganic mineral content. A combination between acid leaching and calcination reduced both air and CO_2 reactivities of charcoal. Its air and CO_2 reaction profiles became comparable to those of the calcined petroleum coke. Substituting a portion up to 10 % of coke with pre-treated charcoal in the anode recipe did not show any negative effect on air and CO_2 reactivities of the baked anodes [5].

This work attempts to explore the effects of using the pre-treated charcoal as a raw material on the final anode properties. To fulfill the objective, wood charcoal was washed using 1 mol L^{-1} of hydrochloric acid (HCl) then calcined at the same temperature as the green petroleum coke is calcined, e.g. 1300 °C. Anode samples were made by substituting portion of coke fine fraction by the pre-treated charcoal. Mechanical and electrical properties of these anodes were measured and compared to those of reference anode entirely made of calcined coke and coal tar pitch. As the composition of the anode recipe was changed the by charcoal addition, the new anode recipe should be optimized. This can be done by changing the particle size distribution and/ or by changing pitch/coke mass ratio. During mixing process, pitch must coat the dry aggregate surface and be able to fill the pores. In this context, the effect of increasing the pitch content in the anode recipe on the electrical and mechanical properties was studied.

2. Materials and methods

2.1. Materials

Industrial calcined petroleum coke provided by Alcoa Inc. was crushed and classified into different size fraction as in Table 1. Commercially available maple wood charcoal was used as the charcoal source. The charcoal was first ball milled and sieved. Particle size of -400 mesh (-0.037mm) was selected for acid washing pre-treatment. The milled charcoal powder was soaked in 1 mol L^{-1} HCl (1 g charcoal per 100 ml HCl) in a round bottom flask, kept in an electrically heated sand bath. The process was performed at 65 °C for 3 h under continuous stirring. The mixture was then filtered and washed with hot distilled water. The recovered charcoal was then dried overnight at 100 °C. The acid-washed sample was calcined at 1300 °C in a tubular furnace under continuous argon flow. Chemical composition of the pre-treated charcoal and coke is presented in Table 2.

Table 1. Size distribution of coke particles

Particle size (US No)	-4 +8	-8 +14	-14 +30	-30 +50	-50 +100	-100 +200	-200 +400	-400
Particle size (mm)	-4.75 +2.36	-2.36 +1.40	-1.40 +0.600	-0.600 +0.300	-0.300 +0.150	-0.150 +0.075	-0.075 +0.038	-0.038
Wt.%	21.8	10	11.5	12.6	9	10.6	14.5	10

4. Conclusions

Using pre-treated charcoal in the anode recipe resulted in a general deterioration in the anode properties. Increasing the charcoal content led to decrease in density, conductivity and strength of the produced anode. This behavior was attributed to the relatively large surface area and low density of the charcoal particles. However, increasing the pitch content was found to be helpful to improve the wetting of charcoal resulting in a significant improvement in the physical properties of the anodes containing 10% charcoal. The best baked anode in this study (22% pitch and 10% charcoal) showed a density of 3% lower than that of the reference anode, an electrical resistivity of 18% higher, and similar mechanical properties.

5. References

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