Research paper

Effects of heat treatment and acid washing on properties and reactivity of charcoal

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ABSTRACT

Due to its highly amorphous carbon structure and abundant minerals content, as received charcoal possesses several undesirable characteristics such as low density and electrical conductivity in addition to its extremely high air and CO_2 reactivities. These disadvantages are the most challenging obstacle for using this material as an alternative for petroleum coke in anode manufacturing processes. In this work, heat treatment under inert conditions was found to be a useful method to improve the molecular structure of charcoal, during this process continuous growth of the more ordered carbon structure at the expense of the amorphous forms was detected using XRD and Raman spectroscopy. Consequently, an improvement in the physical properties and the reactivity of charcoal occurred. In addition, acid washing was employed to eliminate the inorganic minerals of the charcoal. It was found that combination between acid washing and heat treatment produced charcoal having lower reactivity and better physical properties. The burning behavior of the pretreated charcoal samples was found to be comparable to that of calcined petroleum coke. Accordingly, using the pretreated charcoal to substitute up to 10% of coke in the anode recipe did not show a negative effect on the anode's reactivity to both air and CO_2.

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1. Introduction

Wood Charcoal is an attractive alternative to petroleum coke in production of carbon anode 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 [1]. 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 [2]. Using charcoal in anode production is however a big challenge since it does not meet the specifications required for anode making. Charcoal is characterized by its low density and high electrical resistivity in addition to its extremely high air and CO_2 reactivities [1]. Any solution for these issues allowing substitution of petroleum coke by charcoal may thus be of great economical and environmental interest for aluminum industry.

The anode is made by mixing petroleum coke with coal tar pitch to form a paste, which is then consolidated and baked. It is then cooled, connected to the electrical busbars, and suspended in the electrolyte at high temperatures ranging between 900 and 970 °C. The anode is consumed in the electrolyte thus supplying part of the energy required for the reduction of alumina. The lifetime of an anode in the electrolyte is around 25 days. Typically to produce one kg aluminum, 0.41 kg of carbon is required, generating about 1.5 kg CO_2 [3].

The price of anode-grade petroleum coke is continuously escalating while its quality is incessantly degrading. Less than 20% of petroleum coke production meets anode specifications. These specifications are essentially based on their upper limit of sulfur, heavy metal contents (specially Vanadium), density, molecular structure as well as mechanical properties (e.g. Hardgrove Grindability Index (HGI)). Reflecting changes in the refinery industry [4], coke supplies are becoming higher in sulfur and heavy metals content with higher isotropic structure. In addition, the spectacular increase in aluminum production volume and almost constant level

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of production for petroleum coke imbalances the supply and demand equilibrium resulting in its escalating price.

An attempt to investigate the possibility of using charcoal as a substituent of petroleum coke in anodes for aluminum production was done by Monsen et al. [1]. The results showed deterioration in both air and CO_2 reactivities of the anode samples contain charcoal. The porous structure together with high alkali and alkaline earth metal contents (e.g. Na, K and Ca) make charcoal extremely reactive with respect to air and CO_2. They finally concluded that addition of charcoal to the anode recipe had deleterious effect on the final anode properties.

Raw charcoal has amorphous carbon structure consisting of short and distorted aromatic layers. Heat treatment (HT) under inert conditions is a useful method to improve its molecular structure. During this process continuous growth of the more ordered carbon structure at the expense of the amorphous forms was proven using X-ray diffraction (XRD) [5–7] and Raman spectroscopy [8]. As the carbon structure of charcoal is continuously improved by increasing the heat treatment temperature, remarkable changes in its physical properties occur, e.g. as real density (as measured by Helium Pycnometry) and specific surface area (as measured by N_2 or CO_2 adsorption-BET). Considerable increase in real density of charcoal occurs as the HT temperature is increased [6,7]. A maximum real density of 2.0 g cm^{-3} was reached at 1000 °C. Upon heating the cellulose carbon up to 1300 °C, a significant reduction in its surface area was observed. This behavior could be explained by the conversion of open micropores to closed micropores as a result of the structural ordering at elevated temperature [5].

Reactivity of carbonaceous materials can be reduced by increasing HT temperature. This is attributed to the structural ordering during heat treatment. As HT temperature is increased, the concentration of the more ordered and condensed carbon increases at the expense of the amorphous phase. Due to the structural ordering, the concentration of edge carbon atoms (high reactive form of carbon atoms) decreases, resulting in lesser amount of active sites and thus lowering the reactivity to oxidative gases [9]. In addition, surface area of the carbonaceous materials decreases by increasing the HT temperature, contributing in a reduction of its reactivity [10].

Charcoal is also known to contain a range of inorganic minerals such as phosphorus, potassium, sodium, calcium, magnesium and silicon [11]. Indeed, inorganic impurities increase charcoal reactivity to air and CO_2 at high temperature due to their catalytic effects [12,13]. A process of demineralization of charcoal by washing with a chemical solution was proposed to reduce its content of inorganic minerals [14]. The samples which were washed by mineral acids showed lower reactivity [15].

2. Material and methods

2.1. Methodology

This work attempts to explore the effect of heat treatment and acid washing on the reactivity of charcoal with the aim to elaborate alternative and appealing materials that approach the specifications required for anode manufacturing. At high temperature the structure of charcoal could be ordered to some extent. The acid washing may remove the inorganic impurities, which are documented to act as catalysts for carbon oxidation reactions. Overall, it is expected that combined heat treatment and acid washing will result in charcoal with better properties and lower air and CO_2 reactivities.

To fulfill the objective, wood charcoal samples were washed using different concentrations of HCl to determine the optimum leaching conditions. Afterwards, the acid-washed samples were calcined at a temperature similar to that for the green petroleum coke, i.e., 1300 °C. Anode samples were made by substituting a portion of the coke fine fraction by the thus-prepared charcoal. The pretreated charcoal as well as the resulting anode samples were characterized using helium density measurements, surface area analysis, XRD, XRF and Thermogravimetric analyses (TGA) in order to assess their potential application in anode manufacturing.

2.2. Raw materials

Commercially available Maple wood charcoal was used as the charcoal source and industrial calcined petroleum coke (CPC), provided by Alcoa Inc., was used as the reference. Ash content and metallic elemental composition of the wood charcoal and petroleum coke are shown in Table 1. In order to destroy its very porous structure, charcoal pieces were ground in a ball mill then sieved to separate the fraction with a particle size of less than −400 mesh (<0.037 mm). CPC was also crushed and classified into different size fractions and the fraction with a particle size of less than 400 mesh (<0.037 mm) was selected.

2.3. Heat treatment

Raw charcoal (10 g) was loaded in a ceramic boat, placed in a tubular furnace and heated at a constant heating rate of 10 K min^{-1} to the target heat treatment temperature, and then kept at this temperature for 4 h. The furnace was then switched off and the sample was kept in the furnace to cool down to room temperature. During the heat treatment process argon was delivered into the mullite tube at a flow rate of 1.0 dm^3 min^{-1}, thereby ensuring that the whole process, including heating-up and cooling-down steps, is performed in an inert environment. A wide range of heat treatment temperatures, covering between 600 and 1400 °C, was used following the same procedure.

2.4. Acid washing

Raw charcoal was washed with various hydrochloric acid (HCl) concentrations (0.01, 0.1 and 1 mol dm^{-3}). For each run, a sample of 10 g was soaked in a volume of 100 cm^3 of acid in a round bottom flask at 65 °C for 3 h under continuous stirring. The mixture was then filtered using a filter paper and washed with hot deionized water until no chlorine was detected in the filtrate using $AgNO_3$ as an indicator. The recovered charcoal was then dried overnight at 100 °C. Hereafter, the raw charcoal, charcoals washed using 0.01, 0.1 and 1 mol dm^{-3} HCl are named as RC, HL0.01, HL0.1 and HL1, respectively.

2.5. Combination between acid washing and heat treatment processes

The acid-washed samples were calcined at 1300 °C in order to investigate the simultaneous effect of both acid washing and HT. That temperature was selected to be the same as that used industrially to calcine the green petroleum coke. Hereafter, charcoal washed using 0.01, 0.1 and 1 mol dm^{-3} HCl and then calcined at 1300 °C are named as HL0.01.C, HL0.1.C and HL1.C, respectively.

2.6. Laboratory pilot scale anode preparation

Laboratory scale anodes were prepared using petroleum coke with specific size fractions, as listed in Table 2, and coal tar pitch. The reference anode was made completely of petroleum coke. Different coke fractions were individually weighed and mixed with