Formulation without Ultrafine Coke Particles: A Way to Increase the Features of the Carbon Anode

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Abstract

Carbon anode properties (reactivity and electrical resistivity) may affect the anode lifetime in the Hall-Héroult cell. In order to extend the anode lifetime a number of solutions have been proposed. Some of them include the appropriate choice of the raw materials (coke, anthracite, etc.), the optimization of the manufacturing process and the adjustment of the anode formulation. In this work, removing the ultrafines fraction from the coke was proposed, aiming at reducing the air and CO_2 reactivity of the anode. Dry sieving of the fine fraction with 37, 45 and 53 µm sieves allowed removing the finest particles from the coke recipe. The replacement of the ultrafines by a same amount of larger particles within the fine fraction and by some adjustments such as the pitch content, revealed the effects of ultrafine removal on the gas reactivity and electrical resistivity of anodes. A decrease of the apparent density and an augmentation of the electrical resistivity of the modified recipe were noticed, whereas the dusting during the reactivity tests was reduced.

Keywords: ultrafine coke particles, apparent density, air and CO_2 reactivity, electrical resistivity, dusting phenomenon.

1 Introduction

Primary aluminum is produced by reduction of alumina (Al_2O_3) in an electrolysis cell at 960 °C according to the Hall-Héroult process (Equation 1). The cell is made of carbon anodes, carbon cathode and molten cryolite as electrolyte. The anode is composed of calcined petroleum coke (with different particle sizes), recycled anodes (butts) and coal-tar-pitch.

$$2\ Al_2O_3\ (diss) + 3\ C\ (anode) \rightarrow 4\ Al\ (l, m) + 3\ CO_2\ (g) \qquad (1)$$

According to the stoichiometric reduction reaction of alumina, 334 kg of carbon is theoretically required to produce one ton of aluminum. However, the real consumption of carbon (in electrolysis cell at an industrial scale) is about 415 kg per ton of aluminum [1]. This overconsumption of carbon is essentially due to the reversibility of the reduction reaction, as well as the anode gasification with air, Eq. (2a, 2b) and CO_2, Eq. (3) [2-5].

$$C\ (anode) + O_2\ (g) \rightarrow CO_2\ (g) \quad (2a)$$

$$2\ C\ (anode) + O_2\ (g) \rightarrow 2\ CO\ (g) \quad (2b)$$

$$C\ (anode) + CO_2\ (g) \rightarrow 2\ CO\ (g) \quad (3)$$

An empirical model was proposed by Fisher *et al.* [6] to reveal the importance of the anode properties on its overconsumption in the electrolysis pots; Purity, Structure and Porosity model (PSP). No mathematical formula has been assigned to this model as of this date. Several studies have been published to determine precisely the essential anode features affecting the carbon overconsumption caused by the three abovementioned chemical reactions (Eq. 2a, 2b and 3). A number of parameters were identified as important factors affecting the anode overconsumption such as the level of impurities [7-10], the graphitization level (related to the final temperature and the soaking time during baking) [2, 11-14], the anode porosity, the apparent density and the pore size distribution [4, 15-18]. Some of these features could be adjusted by modifying of the anode manufacturing steps such as the vibration time or the soaking time during baking [2, 3, 19]. In the same way, anode formulation could be modified to optimize the anode quality and to decrease its overconsumption.

The anode formulation could be adjusted with the variation of the pitch content [20-24], the fraction of butts [5, 25-27] and the particle size distribution of coke [28-34]. The size distribution of coke is roughly divided in coarse (+ 74 µm) and fine fractions. The fine fraction of coke particles is important to increase the vibrated bulk density (VBD) [35-37], to improve the compaction behavior of the anode paste [23, 28, 38], thus increasing the apparent density and the mechanical properties of anode [28, 33, 34] and decreasing its air and CO_2 reactivity [30] as well as its electrical resistivity.

In the industrial practice, the fineness of coke particles is determined by the Blaine Number (BN). The BN is related to the external surface area of the particles, and consequently to the particle size distribution. A high BN of a coke recipe indicates that it contains higher fraction of fine particles. A high BN (superior to 4000) could significantly increase the air and CO_2 reactivity as well as the pitch demand. This would result in an augmentation of the total anode cost [34]. Therefore, a balance must be respected to determine the optimal fineness of the coke particles. On the one hand, the apparent density of anode increases and its porosity and permeability decreases with a high BN, resulting in a decrease of air and CO_2 reactivity. On the other hand, a higher fineness generates a high surface area of coke particles, increasing the reactivity of coke particles and dusting [39, 40].

The aim of this work is to reveal the effect of ultrafine fraction of the coke recipe on the anode properties; i.e. air reactivity, dusting and electrical resistivity. Considering the review about the fineness of coke in the anode formulation, a new particle size distribution is proposed. The fine fraction of the coke recipe was modified by removing the ultrafine particles and replacing them with the coke in the range of upper limit of fine fractions. Several adjustments were carried out in order to maintain the paste properties such as the weight substitution of sub-fraction by an equivalent amount of the “truncated fraction”.

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