Evolution of Anode Porosity under Air Oxidation: The Unveiling of the Active Pore Size

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Abstract

Carbon anode, used in the aluminum electrolysis (Hall-Héroult process) is overconsumed by air oxidation. Several anode features may affect this overconsumption such as the impurity content, the graphitization level and the anode porosity (e.g. apparent density, porosity, pore size distribution). The two first parameters are basically related to the quality of the raw materials and the coke calcination conditions. The anode porosityis however affected by the anode manufacturing conditions, thus possible to be modified, to some extent, by adjusting the anode recipe and the processing parameters. This work aims at investigating the effect of anode porosityon its air reactivity. The porosity was characterized in several pore size ranges, measured by mercury porosimetry. Anode samples, in particle form, were then gasified at different levels under air at 525°C. The volume variation of each pore range versus carbon conversion was assessed and used to determine the size of the most active pores for air oxidation. Limitation of this pore size range could be used as an additional guideline, along with other targets such as high homogeneity and density, to set the optimum anode manufacturing parameters.

Keywords: Air reactivity; pore size distribution; active pore size; apparent density; gasification.

1 Introduction

Aluminum is produced by the reduction of alumina (Al_2O_3) in an electrolysis cell at 960°C according to the Hall-Héroult process. The cell is made of carbon anodes, carbon cathode and molten cryolite as electrolyte. The carbon anode is composed of calcined petroleum coke, used anodes (butts) and coal tar pitch. In the electrolysis cell, the anode top is exposed to the ambient air (despite a covering of crushed bath and alumina) and the temperature is comprised between 400 and 600 °C [1]. In this range, the oxygen of the air can react with the carbon anode, according to the Equations 2. Both reactions are undesirable since the carbon anode is consumed without producing metal. Between 8 and 30% of anode is consumed by the air oxidation (according to the anode quality and the cell conditions)[2].

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

Several studies have been published to reveal the essential parameters controlling the air oxidation. The air reactivity is correlated with different parameters i.e. the raw material properties such as the calcination level of coke [3-5], the level of anode impurities [6-9] and the air reactivity of the coke[10], or the manufacturing steps of the anode, for instance, the temperature and the soaking time during anode baking [11-15] and the anode recipe [16, 17]. Some studies also reported the effect of the operation conditions in the cell, i.e. the temperature of the anode top, the protection effect of alumina covering [1, 18] and the current density[19].

Most of these parameters are controlled by the quality of the raw materials. Edwards [20] detailed the deterioration of the coke quality and the new challenges of the aluminum smelters to keep a good quality of anodes. To decrease the air oxidation, the anode manufacturing steps could be considered to counterbalance the poor properties of raw materials. Tkac [21] proposed that some parameters such as the interaction of the pitch content, the mixing time of raw materials and the applied pressure during vibrocompation influence the air reactivity. These parameters could influence the anode oxidation because they may increase the anode porosity and favor air burning.

Suriyapraphadilok et al.[22]and Bird et al. [23] remarked that the interior of anode changed with the air gasification leading to pore volume variations. Turkdogan [24] proposed that the pores larger than a micron in carbon material control the air reactivity. For coke materials, the active pore range seems to be comprised between 0.5 and 15 µm [5]. In the same way, Tran et al. [25]found that the volume of the three pore size ranges (inferior to 2 nm, between 2 and 50 nm and superior to 50 nm) increased with the gasification percentage. Tordai [26] revealed that the anode air burning takes place preferentially in the pores comprised between 1 and 10 µm. Chevarin et al. [27] proposed that the air reactivity of industrial carbon anode could be controlled by the pores with a pore entrance radius of 1.5 and 12 µm. The porosity thus seems to have a significant effect on the air reactivity of anode material. However, the weight of each pore size during the anode gasification was not clearly quantified. In this work, the authors try to reveal the role of porosity and external surface of particles in gasification of carbon anodes.

2 Experimental procedure

2.1 Materials

Prebaked anodes at laboratory scale were prepared following atypical recipe used in the anode manufacturing process. The raw materials used in this work were provided by Deschambault aluminium smelting plant (Alcoa, Canada). The anode recipe comprised calcined coke (86.1 wt.%) and coal tar pitch (13.9 wt.%) (Table 1).Fractions of the coke particle are detailed in Table 2. The coke particles were preheated at 185 °C for 90 minutes admixed with the pitch. The blend was mixed at the same temperature for 10 minutes and then pressed at 150 °C during 3 minutes by applying a uniaxial pressure of 70 MPa [28-30]. This sample, called green anode, had a diameter of 50 mm and an approximate height of 100 mm. prior to baking in a muffle furnace, the green samples were placed in an Inconel® box and covered by coke particles in order to protect them against air oxidation. The heating program was as follows: from room temperature to 150 °C at a heating rate of 60 °C/h, then from 150 °C to 650 °C at a rate of 20 °C/h, and finally from 650 °C to 1100 °C at a rate of 50 °C/h. This was followed by a soaking time of 20 hours at 1100 °C. At the end of this cycle, the furnace was switched off and allowed to cool to room temperature. The anode samples were thereafter crushed using jaw and roll crushers and sieved through two different USA standard sieve trays, which were chosen in order to get a narrow particle size range of 4000 to 4380 µm(- 4 + 5 US Mesh). The particle size range

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6 References

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