Graphite Foil Barrier Material for Reduction Cells with Improved Service Temperature

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Abstract

Graphite foil could be used as a barrier material in lining of the reduction cells because of non-wetting by aluminum melt. Graphite foil is used as barrier in the lining of the industrial reduction cells [1]. However, there are two limitations in the application of the graphite foil in the lining: service temperature of graphite foil is limited and permeability of graphite foil to molten cryolite is not zero. The oxidation of the graphite foil starts at rather low temperature, and this fact implies some restriction on the design of reduction cell lining. The oxidation resistance of the graphite foil is determined by the specific surface area (the surface area of the graphite foil with density of 1 000 kg/m^3 is ~25 m^2/g) and by concentration of oxygen containing groups [2]. Surface oxygen containing groups decrease the activation energy of the oxidation for graphite matrix. The way to increase the oxidation resistance of the graphite foil barrier material is to eliminate the oxygen containing groups by special treatment. Another approach is to decrease the surface area by the impregnation of the graphite foil with inorganic substances, followed by thermal treatment resulting in formation of protection vitreous layers on the surface of graphite foil.

Keywords: Graphite foil, Reduction cell, Barrier material, Cryolite, Oxidation resistance.

1. Introduction

The refractory lining of the reduction cell is made from alumina-silica fireclay materials. This lining is a sort of a barrier between the molten bath, molten aluminum and the heat insulation materials in the bottom of the reduction cell [3]. From the point of view of chemistry, aluminosilicate refractory is not the best material to be in the contact with molten cryolite and aluminum at high temperatures [4]. Yet we can suppose, that due to economic reasons there will not be serious changes in the chemical composition of the refractory layer of the reduction cell.

Al_2O_3-SiO_2 refractories react with cryolite and sodium, that penetrate through carbon cathode blocks. The reactions of cryolite and sodium with refractory layer of the cathode may have negative consequences for the service of the reduction cells [3, 4]. The thermal conductivity of reacted refractory and heat insulation cathode materials increases, that may change the thermal balance and performance of the reduction cells. The volume of the major part of reactions of cryolite with alumina-silica compounds increases, that may cause bottom “heaving” of the carbon cathode blocks, the strains and cracking of cathode blocks. The world tendency to increase the amperage and current density in reduction cells does not stop [5]. The cryolite and sodium penetration through the carbon cathode blocks to refractory layer in modern high amperage cells is more intensive. Another trend in aluminum industry is recycling of the refractory lining of reduction cells [6], that might be very difficult if the refractory layer is infiltrated with cryolite.

Graphite foil, or compressed thermally expanded graphite (TEG), is a promising material to prevent the leakage of molten aluminum and cryolite into the refractory lining. Proshkin [1, 7, 8]

reported, that the graphite foil stops aluminium and due to ultrafine pore structure diminishes the flow of the bath. Laboratory tests had shown absolute non-wetting of the foil by molten aluminum. The dry autopsies had shown, that the barrier graphite foil stops the leakage of aluminum melt into the refractory layer.

However, there are two limitations in the application of the graphite foil in the lining: service temperature of graphite foil is limited and permeability of graphite foil to molten cryolite is not zero. The oxidation of the graphite foil starts at rather low temperature, and this fact implies some restriction on the design of reduction cell lining.

The objective of the research was to investigate the oxidation resistance of the graphite foil and to estimate the possibilities for some increase of the service temperature of the graphite foil in the lining of the reduction cell.

2. Materials and the Method of Investigation

2.1 Materials

The starting material was natural flake graphite GT-1 (ash contents 0.2-0.5 %, grain size < 0.315 mm) with true (XRD) density 2.256 g/cm^3. The natural graphite was soaked in 40 % sodium hydroxide solution. Exfoliated graphite (EG) was prepared by the shock thermal treatment of expandable graphite by carrying it in air flow through tube furnace heated to 900 °C.

The obtained exfoliated graphite had BET specific surface area 56-58 m^2/g, true (XRD) density 2.256 g/cm^3 (measured on exfoliated graphite) and bulk density 0.0024 g/cm^3. Graphite foil (GF) was prepared by pressing the exfoliated graphite into compacts with a bulk density from 0.5 g/cm^3 to 1.8 g/cm^3. The thickness of the foil was 0.7 mm.

2.2 Method of Investigation

The bulk (geometrical) density of GF was calculated as the ratio of GF mass to its volume. The bulk (geometrical) density was used as reference characteristic.

The specific surface area of the samples was measured by adsorption of nitrogen on MicroActive ASAP 2020 Plus 2.00 (Micromeritics Instrument Corp.).

The X-ray diffraction analysis was performed at Rigaku Ultima IV diffractometer (CuKα, λ = 1.5418 Å, 0.2 °/minute). Structures were analyzed at scanning electron microscope Tescan MIRA-3 with energy dispersive spectrometer (EDS) X-MAX150 Oxford instruments. The images were made in SE and BSE detector.

The true density was calculated according to the standard procedure, from XRD diffraction measurements of exfoliated graphite – the raw material to produce graphite foil.

The oxidation tests were performed by two methods. One kind of oxidation test was performed on 50 x 50 x 0.7 mm sheets of foil. All weighed pieces of foil were placed in the furnace and then were taken out after a certain time and were weighed again. The weight loss was calculated as using the Equation (1).

$$\frac{\Delta m}{m} = \frac{m_{initial} - m_{oxidized}}{m_{initial}} \quad (1)$$

5. References

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