Evolution of Mechanical Properties of Carbon Anodes During Baking

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Abstract

To be considered as a good quality product, carbon anodes must not only have a low electrical resistivity, but also a high mechanical resistance to crack generation and propagation. To obtain such anodes, a good understanding of the evolution of their mechanical properties during baking is crucial. Traditional mechanical characterization approaches consist of baking anode samples at specific temperatures and performing the tests at either room temperature or slightly lower than that of the baking level. In the latter case, it is well-known that numerous chemical reactions take place during the tests which affect the results. In this paper, an innovative approach is proposed to ensure the reliability of mechanical properties measurements. The anode cores were taken from industrial green anodes removed directly from the production line of Aluminerie Alouette Inc. (AAI) and then baked to different temperatures in a laboratory furnace of the UQAC/AAI Chair. Compression tests initially performed using the Gleeble system showed that this system was not suitable for low temperature testing, at which the anode samples were in a semi-solid state. To overcome this problem, a new setup was installed on a classical CRIMS press which accurately measures the Young's modulus, compressive strength, and particularly, Poison's ratio.

Keywords: Carbon anodes; baking process; mechanical properties; high temperature mechanical property testing.

1. Introduction

Carbon anodes are used in aluminium smelters both as an electrical conductor and a carbon source for the electrolytic process. Their production process begins with the formation of a green anode, which is composed of solid petroleum coke particles, coal tar pitch and recycled materials [1]. The coke particles serve as an inert carbonaceous filler necessary for the electrolysis reaction while the pitch carbonizes and binds the coke particles to each other by adhesion to their surfaces and pores while filling the empty space between the particles, thus giving the mix mechanical strength. The components are mixed together in a mixer at around 180°C, transferred to a shaping mold and then vibrocompacted to densify the mixture. Finally, the green anodes are baked using a large refractory furnace up to a temperature of 1200°C, following an average heating rate of 11°C/h. During this operation, packing coke is used to provide structural support to the green anodes and protection from oxidation by air during baking. The baking carbonizes and solidifies the compressed mixture which then acquire the necessary properties to efficiently perform in an electrolytic industrial cell.

During the baking process, carbon anodes undergo various chemical transformations, which greatly influence the final product quality. The current literature on carbonaceous materials states that since the coke particles in the anode are already calcined, evolution of the anode properties through the process is mainly caused by the binder phase changes [2-4]. At 100°C, the viscosity of the pitch decreases, caused by the modification of the crystalline structure of the pitch from amorphous to liquid. This process continues up to the softening point, which begins in the temperature range of 120 to 150°C for the lightest constituents, and stops around 200 to 250°C for the heavier ones. Between 250 to 500°C, volatilization starts as the anode simultaneously loses mass and swells. The volatilization process comprises the distillation of the condensable gases and the release of low molecular weight condensable (tar) from pitch into simpler components like methane and hydrogen, which will further increase the viscosity of the binder [5]. Subsequently, between 400 and 500°C, the material tends to solidify through the binder's polymerization and polycondensation into a semi-coke. For temperatures higher than 550°C, the pitch enters its pyrolysis phase which further carbonizes the material, bringing the anode microstructure towards its final form [5]. During this process, the volatile generation produces pressure within the anode and leads to crack generation, affecting the final quality of the product [6].

Chemical reactions have a direct impact on the evolution of the mechanical properties during the baking process. A number of authors tested the mechanical properties of carbon-based materials over the years. However, certain phenomena must be better understood to ensure the proper comprehension of the anodic carbon paste behavior during baking. In order to get the necessary information which describes the evolution of the thermomechanical properties during this phase, a new methodology has been developed. Mechanical compression tests were performed at different selected testing temperatures to describe the evolution of Young's modulus, Poisson's ratio and compressive strength. In order to have the entire history of the evolution of the mechanical properties during the baking phase, the tests were carried out on green, partially baked, and fully baked carbon anode samples. In this paper, the influence of the baking level and testing temperature on the thermomechanical behaviour of the carbon anode paste is investigated. This work will later be used in a numerical model that simulate the mechanical behavior of the anode paste during its baking phase in an industrial furnace [7] and aim to improve anode quality through a better understanding of the baking process.

2. Previous works

A few works have been carried out on carbon-based materials over the years to describe the evolution of their mechanical properties. The traditional testing approach is based on room temperature tests as a way to identify the mechanical properties of the specific material. Andersen and Zhang [8] measured the compressive strength and Young's modulus of fully baked anode samples at room temperature and in the temperature range of 200°C to 400°C. Their results showed a strong dependence of these properties on the testing temperature. D'Amours [2] measured the Young's modulus, Poisson's ratio and compressive strength of the ramming paste at room temperature as a function of the baking level for partially baked anodes up to 1000°C. The author concluded that Poisson's ratio continuously decreases from 180°C up to 1000°C while the Young's modulus and compressive strength increase quickly starting around 250°C to 450°C, and then stabilizes with a slight decrease in Young's modulus after 800°C. The same conclusions were drawn by St-Arnaud et al. [9] who measured the compressive strength, Young's modulus and Poisson's ratio of ramming paste at room temperature on larger samples.

To better understand the temperature dependency of carbon-based material mechanical behavior, some authors also tested samples at higher temperatures. D'Amours [2] measured the Young's modulus and compressive strength of partially baked ramming paste samples tested at temperatures slightly below the baking temperature. Results showed a different trend compared

7. References

1. Kirstine Louise Hulse, Anode manufacture : Raw materials, formulation and processing parameters. 2000, Sierre, Suisse: R & D Carbon Ltd. 416.
2. Guillaume D'Amours, Développement de lois constitutives thermomécaniques pour les matériaux à base de carbone lors du préchauffage d'une cuve d'électrolyse, 2004, *Université Laval*, Québec, Canada.
3. Juraj Chmelar, Trygve Foosnaes, and Hrald A.Oye, Thermal dilation of green anodes during baking. *Light Metals,* 2006, 597-602.
4. Nicole Bouchard, Pyrolyse de divers brais utilisés dans la technologie söderberg et analyse des matières volatiles, 1998, *Université du Québec à Chicoutimi*, Chicoutimi, Canada.
5. Ying Lu, Effect of pitch properties on anode properties, 2016, *Université du Québec à Chicoutimi*, Chicoutimi, Canada.
6. Salah Amrani, Impact de la préparation des anodes crues et des conditions de cuisson sur la fissuration dans des anodes denses, 2015 *Université du Québec à Chicoutimi*, Chicoutimi, Canada.
7. P-L. Girard, et al., Numerical investigation of the load free permanent strain in carbon anode during baking process, in *Proceedings of 34th Internationa ICSOBA conference*. 2016: Québec, Canada.
8. D.H. Andersen and Z.L. Zhang, Fracture and physical properties of carbon anodes for the aluminum reduction cell. *Engineering Fracture Mechanics*, 2011. 78(17), 2998–3016.
9. Pierre-Olivier St-Arnaud, et al., Creep behaviour of ramming paste baked at different temperatures and tested at room temperature, in *TMS*. 2014. 1233-1238.
10. Sakineh Orangi, Time-dependant behaviour of ramming paste used in hall-héroult cell: Characterization and constitutive law 2014, *Université Laval*, Québec, Canada.
11. Dany Racine, et al., Innovative procedure for the characterisation of therno-mechanical propreties of carbon base materials using the gleeble® 3800 system. *Light metals,* 2015, 1169-1173.
12. ASTM International Standard test method for static modulus of elasticity and poisson's ratio of concrete in compression, in *ASTMC469/C469M – 10*. 2010: West Conshohocken, PA.