Characterizing Pilot Anodes Made with CTP and Bio-Pitch using µCT

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Abstract

Replacing the fossil-based binder phase in pre-baked anodes with materials originating from wood pyrolysis products is suggested as a CO_2-neutral alternative to the currently used coal tar pitch (CTP). Recent work shows that bio-pitches (BPs) upgraded from bio-oils (or similar pyrolysis products) have good wetting towards calcined petroleum coke (CPC), and despite the relatively low coking value and the high reactivity of the bio-pitches, pilot-anodes with physical and electrochemical properties comparable to those made from CTP have been produced. The pilot anodes with bio-pitch have a higher shrinkage upon baking than anodes made from CTP, presumed to be due to the higher baking loss and better wetting between the coke and the BP. In this study the anode structure, including this shrinkage, is characterized using micro X-ray computed tomography (µCT). One pilot anode made from BP and one pilot anode made from CTP were scanned using µCT, baked, and then re-scanned using µCT after baking. The pre- and post-baking datasets are aligned in the image analysis software, allowing a direct comparison of the pre- and post-baking state.

Keywords: CO_2-neutral aluminium production, Bio-pitch, Pilot anodes, µCT.

1. Introduction

Calcined petroleum coke (CPC), recycled anode butts and coal tar pitch (CTP) are traditionally used in pre-baked anodes for aluminium production. To potentially reduce the carbon footprint in aluminium production, the fossil-based materials are suggested to be replaced by biocarbon options. Replacing the CPC with biocarbon seems difficult, and current research shows that only small amounts of biocarbon filler can be introduced in the anodes [1-3]. Replacing the CTP appears to be a better option to produce greener aluminium through biocarbon addition and may additionally reduce the toxic polycyclic aromatic hydrocarbon (PAH) emissions during the baking process.

Bio-pitch (BP) can be produced from bio-oils or other liquid products from pyrolysis of biomass (woods) [4]. Important parameters to evaluate and compare to those of CTP include coking value (CV), softening point (SP) and wetting behaviour when interacting with CTP. Typical BPs have lower CV and SP than traditional materials, but these properties can be somewhat controlled by changing the production parameters (temperature, heating rate, holding time and, pressure, in the case of vacuum pyrolysis) [5]. Lower SP may result in less energy consumption during mixing of anode paste, but low CV is traditionally associated with a more porous anode. Additionally, BPs have been found to not graphitize well, retaining an amorphous structure. An amorphous carbon typically exhibits higher electrical resistivity in the binder phase [6].

Despite the initial beliefs that anodes made from BPs with low CV will result in poor anodes, pilot anodes with CTP and BP have been produced with comparable physical [6] and electrochemical [7] properties. This has been theorized to be caused by the superior wetting properties of the BP towards CPC, compared to CTP. Studies [5] have shown good wetting behaviour during mixing, and a significantly larger shrink is observed for pilot anodes made from BPs (5 % vs 2.5 % in [6]). In theory, this may result in shorter distance between the coke particles, which will mitigate the larger loss of binder phase upon baking and the lower graphitization degree of this material.

In this study, the imaging technique of micro X-ray computed tomography (µCT) has been used to characterize several pilot anodes made from CTP and BP to get a better understanding of the wetting between binder and filler during production of green anodes, of possible shrinkage mechanisms during baking, and their effect on general quality of pilot anodes. The main advantage of µCT imaging is that it is non-destructive and gives data for the full sample volume. This allows for comparison of the same sample before and after some treatment; in this case baking at 1100 ºC.

2. Experimental

2.1 Pilot Anodes

For this study, BP was produced by the same procedure as described in [6], using atmospheric pressure, a heating rate of 0.5 °C/min up to 180 °C, and a soaking time of 1 hour. This treatment on the same bio-oil has previously been showed to result in a bio-pitch with a SP in the range of 85-90 °C and a CV of almost 35 %. Two series of pilot anodes were produced for the present study, using either the described BP or a CTP with a Mettler SP of 100 °C and CV of 62 %. Calcined petroleum coke with specific fractions (see more details in [6]) were mixed with 15.2 wt % binder at 178 °C for 10 min to form an anode paste, which were then formed as cylinders by pressing at 60 MPa. The CPC and CTP used in the work are materials currently used in the aluminium industry.

Twelve anodes were made at Laval University (6 CTP and 6 BP). Six anodes (3 CTP and 3 BP) were baked directly after pressing. The baking cycle consists of increasing the temperature to 150 °C (60 °C/h), then to 650 °C (20 °C/h), and finally to 1100 °C (50 °C/h), and this temperature was maintained for 20 h. Additionally, the six green anodes (3 CTP and 3 BP) were first investigated with µCT before one of each (BP-4 and CTP-4) was baked with a similar cycle at SINTEF Industry (almost a year after pressing). Despite the identical baking cycle settings, the major differences between the process at Laval and SINTEF are the size of crucible, height, packing density and type of packing coke, anode-anode distance in the crucible, and type and size of furnace. The size of the baking crucible used at SINTEF was 160 mm diameter and 150 mm height. The two anode samples were placed with approximately 30 mm distance between, and the crucible was then filled to the top by packing coke sized 0-5 mm.

2.2 µCT

Due to instrumental availability issues and time constraints, three different µCT labs with similar instruments had to be used in this work. They are all 225 kV tungsten reflection target instruments (cone beam volume CT) delivered by Nikon, but with different manipulator distances and panel sizes. The parameters were adjusted to give matching voxel sizes. Different scans were done at different scan volumes, to cover the samples at different sizes and resolution. The smaller volumes provide more details, but only cover the middle part of the sample in the height direction. The images were exported as 16-bit TIFF and processed in the public domain software ImageJ [8]

Since the anode density is in the lower end of what is common for industrial anodes, the effect of higher binder levels could be investigated in future work. There is usually a trade-off between higher binder level and higher permeability, as too much binder will cause the anode to expand during baking. Since the baking loss is higher for bio-pitch, the optimum binder level value can be higher for bio-pitch than for coal tar pitch.

Obviously, the density of the packing coke bed must be improved to avoid gas-burn, compared to what was done in this single baking experiment at SINTEF. Time and budget constrain did not allow for a second baking experiment.

It is possible to get a higher resolution scan of the full anode sample height using helical scanning mode, which is available in the new Pore Imaging Laboratory. This was not attempted in this work, as it requires some further optimization of scanning parameters beyond what has been done in our initial testing. Helical scanning is challenging with carbon materials due to their low attenuation contrast.

5. Conclusions

In this work, pilot anodes made with coal tar pitch and bio-pitch were investigated by µCT before and after baking. The resulting images are of high quality, demonstrating the method's usefulness when wanting to investigate the internal structure of anodes in a non-destructive way. In fact, images from the entire anode can be extracted from the dataset. Cracks are observed for both types of anodes in the vicinity of the isotropic/high sulfur grains, although a reduction of this cracking is observed after baking (more so for the BP anodes than the CTP anodes). It is suggested that the reason for the observed cracks is caused by the low flexibility of these types of coke grains, in combination with the method used to produce the anodes (pressing). Otherwise, baking gives only a small change to anode structure (loss of binder), and no significant macro-scale effects are visible. Overall, our µCT-based investigation suggests that the anode samples made of CTP and Bio-pitch have very similar microstructures, which agrees with their similar physical and electrochemical properties reported earlier.

Acknowledgements

This research was funded by Research Council of Norway grant number 294679 (BioCarbUp).
The authors would like to acknowledge the use of the Pore Imaging Laboratory (NO3.7d) at SINTEF Industry; research infrastructure under ECCSEL ERIC (The European Research Infrastructure for CO2 Capture, Utilisation, Transport and Storage). The Research Council of Norway is acknowledged for the support to the CT scan facilities of the Center of Excellence PoreLab, project number 262644; at the Department of Geoscience and Petroleum, NTNU, Trondheim, Norway. The authors would also like to acknowledge the use of the laboratory of the X-ray Physics Group at NTNU, part of the National Infrastructure NEXT, funded by NTNU, the Norwegian Research Council, and European program INFRAIA (90659800).

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