CHARACTERIZATION OF ANODE BUTT MATERIAL USING X-RAY COMPUTED TOMOGRAPHY SCANNING

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Introduction

The Hall-Héroult process, where alumina is reduced by carbon to produce aluminum, is currently the largest user of premium carbon products worldwide consuming over 11 million tons in form of carbon anodes annually [1]. To improve the economics of the process, anode butts, the unused parts of the anode remaining from operation in the reducing pot, are crushed and used as filler in the production of new anodes. About 20% of the anode is recycled butt material that accounts for over 300,000 tons annually [2]. The lower part has been in contact with the hot electrolyte experiencing temperatures in the range of 930 to 980°C. The lower part of the anode may also have been consumed by CO_2 burn, where typically the binder coke is attacked selectively. CO_2 burn may also affect the side of the anode. Further, the top part of the anode may reach temperatures of 350 to 600°C depending on the protective cover of electrolyte material, and air burn may also take place. Hence, the butt chemistry may differ significantly from that of petroleum coke, where the lower part of the butt may be altered due to the interaction with the cryolite as well as the modification of the surface chemistry due to the burn-off from CO_2. The top part of the butt could be highly oxidized during the air burning, while the middle part of the butt may not be affected by any of the above.

This work examines the spatial distribution of physical properties such as densities and porosities of anode butts as a function of their position in the reducing pot. X-Ray Computed Tomography (X-Ray CT) was used to non-destructively study the overall structure of an anode butt.

Experimental

The experiments conducted using industrial anode butts, Butt-2 and -4, collected from different plants. The bath temperature was about 960°C and the pots were operated at 4.6 volts and 100,000 to 350,000 amps. The height of a new anode was 58 centimeters prior to setting in the pot and this height reduced to 18 centimeters when the butt was removed after approximately 24 days of service. Butt-2 contained recycled anode butts in the formulation of the original anode and had experienced standard operating conditions in the pot as well as a preparation for recycling. Butt-4 was a butt from an anode that originally did not contain any recycled anode-butt material. Table 1 summarizes the conditions of these two anode butts.

Table 1. Characteristics of selected anode butts.

Anode butt code	Characteristics
Butt-2	-About 24 days of operation in the pot -Included recycled butts in the formulation of original anode
Butt-4	-About 24 days of operation in the pot. -No recycled butts in the formulation of original anode

The samples used in this study were cored from the center of the butts (core #5) and had approximately 51 millimeters O.D. These samples were first scanned with the X-Ray CT scanner using a large focal spot source at 200 kV. Samples shorter than 150 millimeters were scanned parallel to the axial axis of the sample with a resolution of about 400 microns. Samples longer than 150 millimeters were scanned perpendicular to the axial axis with a resolution of about 300 microns. The samples were later sliced perpendicular to the axial axis into sections approximately 5 millimeters thick. The diameter and thickness of each slice were measured to the nearest 0.01 millimeter by a Caliper. The weight of each slice was measured to the nearest 0.0001 gram. The apparent density (ρ_{app}) was calculated by the ratio of mass and volume. Each slice was later cracked into smaller pieces approximately 1-3 grams. About 5-6 grams of sample were weighed to the nearest 0.0001 gram and the absolute volume was performed by a Helium substitution using the Quantachrome Multipcynometer. The absolute density (ρ_{abs}) was calculated by the ratio of mass and volume. The specific pore volume (v_p) was calculated by

$$v_p = \frac{1}{\rho_{app}} - \frac{1}{\rho_{abs}} \qquad (1)$$

X-Ray CT is a non-destructive method for obtaining three-dimensional attenuations of an object. The attenuation maps depend on bulk density and apparent atomic number of the material. With proper calibration the distribution of parameters such as density, porosity, and composition can be acquired.

Results and Discussion

An axial CT sliced of a 140 millimeter (Butt-2) drilled sample is shown in Figure 1(a). The variation in density and rough heterogeneities are seen throughout the sample. A brighter color at the electrolytic end shows a higher density of the carbon material compared to a darker color at the rest of the core. This indicates a densification of the structure of the carbon that has been in contact with the electrolytic bath. A slightly lighter color at the airburn end of the anode butt shows a higher density of the carbon material that has experienced the air burn-off. The black spots indicate that various sizes of pores are distributed throughout the butt sample. The differences of pore distribution are clearly seen in the three CT slices—airburn end, middle and electrolytic end, as shown in Figure 2(a). The airburn side (left) shows high porosity (dark spots) which the electrolytic end (right) shows high density and low porosity.

The CT observation is confirmed by the measurement of apparent and absolute densities and the calculation of the specific pore volumes. Figures 1(b) and 1(c) show the absolute and apparent densities, respectively, as a function of distance from the airburn side of Butt-2. The absolute density of Butt-2 increases from about 1.995 g/cm^3 in the center to 2.030 g/cm^3 on both airburn and electrolytic surfaces, while the apparent density decreases from about 1.580 g/cm^3 in the center to about 1.300 g/cm^3 on both surfaces. The specific pore volume calculated by Equation (1) is shown in Figure 1(d) where the center of the core exhibits the lowest value of about 0.140 cm^3/g and this value increases to about 0.260 cm^3/g on both surfaces. The results obtained in this study were similar to those obtained by Cutshall and Bullough [4] who observed a decrease in apparent density and an increase in porosity from the center of the core to the electrolytic surface. The high density sites associated with the large porosity at both ends indicates the connection of these properties to the reactions occurred at the airburn and the electrolytic ends.

Both Butt-2 and -4 give similar results in terms of physical properties throughout the cores, where both anode butts exhibit a major change in densities and pore volume at a distance about 20 millimeters from both airburn and electrolytic ends. The absolute density, apparent density and specific pore volume of Butt-4 are shown in Figures 2(b), 2(c) and 2(d), respectively. However, Butt-4 shows slightly lower apparent and absolute densities than Butt-2 since Butt-4 did not contain recycled butt material. There are two observations from the slightly different properties between Butt-2 and -4 at the airburn and catalytic ends. The first observation is a higher impact of the reactions at the airburn side of Butt-4 than that of Butt-2. This is shown by a very low apparent density and a fairly high specific pore volume of the airburn side (Figures 2(c) and 2(d)). These results indicate a higher reactivity with air of the anode butt near the airburn side of Butt-4 than that of Butt-2. Another observation is the properties of both samples at the electrolytic end. Butt-4 seems to have less impact of the reactions at the electrolytic end than Butt-2 as shown in the apparent density (Figures 1(c) and 2(c) for Butt-2 and -4, respectively) and specific pore volume (Figures 1(d) and 2(d) for Butt-2 and -4, respectively). These results indicate that Butt-4 has a lower reactivity with CO_2 than Butt-2, which originally contained recycled butt material. The observation discussed here confirmed previous results that sodium content greatly promotes CO_2 reactivity and may be assigned to variations in anode consumption rates [4, 5].

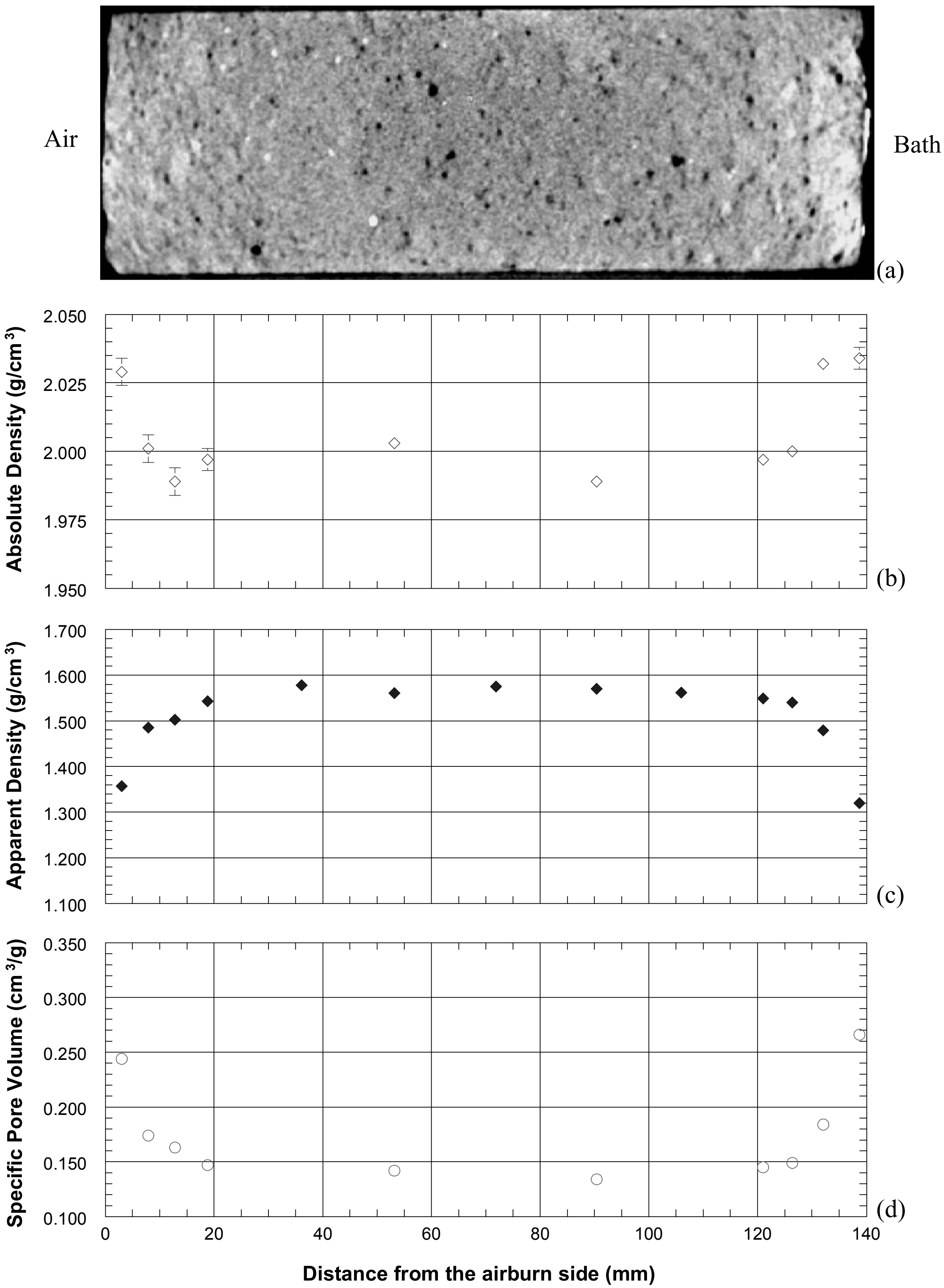

Figure 1. (a) Axial scanning of the X-Ray CT with the same intensity color maps, (b) absolute density (◇), (c) apparent density (◆), and (d) specific pore volume (○) of the Anode butt-2 Core #5 at different distance from the airburn side.

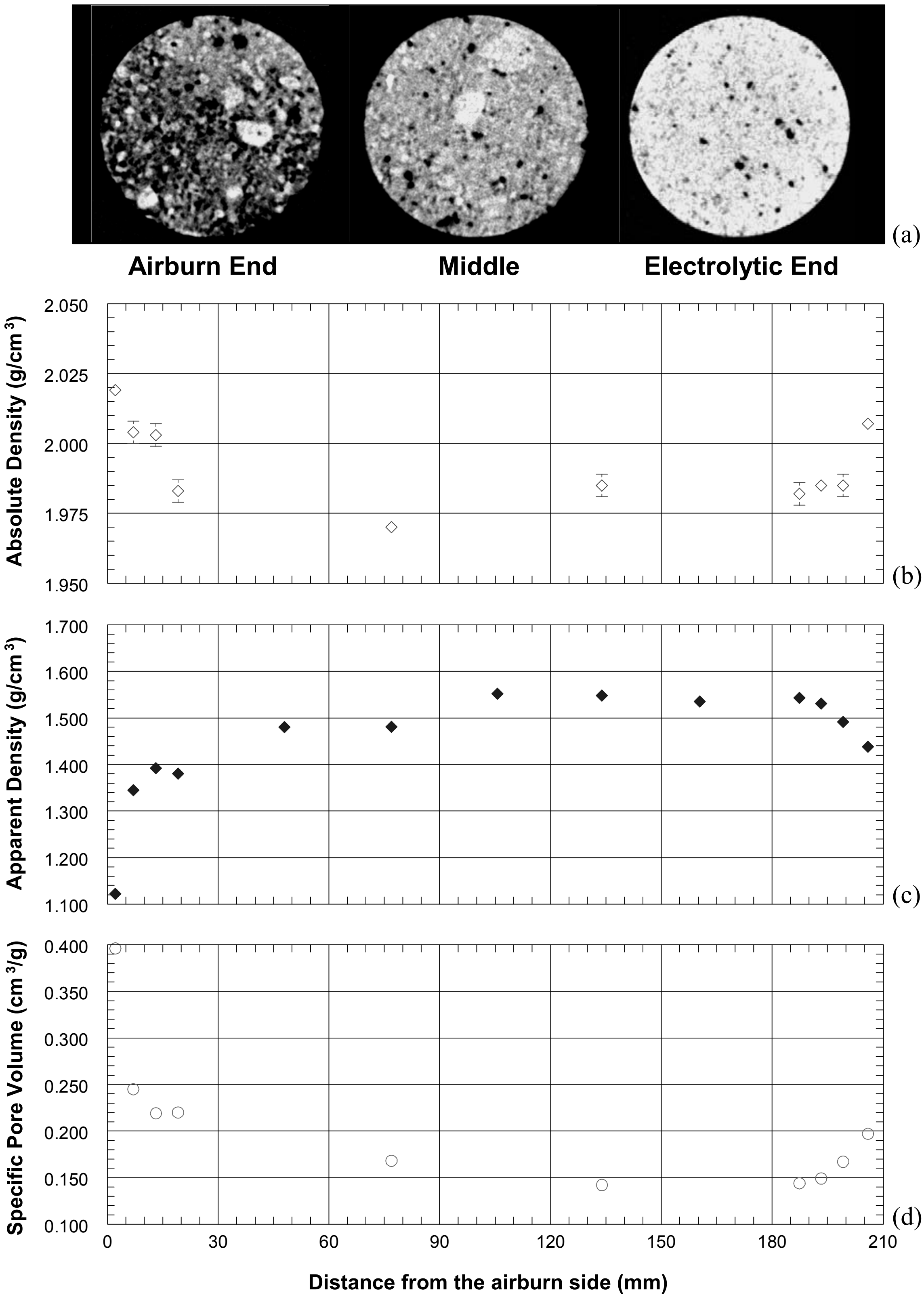

Figure 2. (a) Radial scanning of the X-Ray CT with the same intensity color maps, (b) absolute density (◇), (c) apparent density (◆), and (d) specific pore volume (○) of the Anode butt-4 Core #5 at different distance from the airburn side.

Conclusions

Two industrial anode butts, with and without recycled butt material (Butt-2 and Butt-4, respectively) were studied. Non-destructive X-Ray imaging was used to quantify the spatial distribution of density and porosity in the sample. Apparent and absolute densities were measured and the specific pore volumes were calculated as a function of the distance from the airburn side. The results from the X-Ray CT and the densities and pore volume measurement showed a decrease in apparent density, and an increase in absolute density and specific pore volume from the center of the core to the surfaces. The anode butt that did not contain recycled butt material in the original formulation showed a higher reactivity with air at the airburn side while it had lower reactivity with CO_2 at the electrolytic side. These results have confirmed that sodium content greatly promotes air, and, in particular, CO_2 reactivity of the anode butts.

References

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