Thermomechanical Characterization of the Carbon Anode During Baking

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Abstract

Aluminum electrolysis cell performance is highly related to the quality of carbon anodes. In this regard, anode baking is one of the most important steps in the anode manufacturing process in which green anodes undergo a pyrolysis to reach the desired properties. The understanding of the phenomena occurring during this process is essential in order to predict the final anode properties. This prediction could be achieved with the establishment of a three-dimensional thermo-chemo-mechanical baking model based on porous media. This model includes several parameters that must be identified in laboratory. This work is focused on the experimental characterization of the mechanical behavior as a function of the baking level. In order to limit the influence of raw material properties variation, laboratory scale carbon anode samples with constant recipe and homogeneous density were fabricated and used to generate the required database. The main mechanical properties measured were the Young modulus and the compressive strength. The rupture modes related to each baking level were also identified.

Keywords: Baking process, carbon anode, mechanical properties, high temperature test, rupture mode.

1. Introduction

Aluminium is commercially extracted from alumina in electrolysis cells through the Hall-Héroult process. The performance of a cell is strongly related to the carbon electrodes required to perform the electrolysis. The electrode group includes the cell lining and carbon anodes. The later ones are key elements in this process as they ensure transportation of electrical current in the cell and act as an electrochemical reducer in the aluminium production process according to the following global reaction:

$$2Al_2O_3 + 3C_{(s)} \rightarrow 4Al_{(l)} + 3CO_{2(g)}$$

Carbon anodes are typically made of calcined petroleum coke (65 wt.%), coal tar pitch (15 wt.%) and recycled butts (20 wt.%) mixed all together at around 170 °C to form the anode paste [1]. This paste is then compacted or vibrocompacted to form green anode blocks (dimensions vary according to cell technology). The anode blocks are then generally baked in pits of ring type furnace in the range of 1100 °C - 1200 °C [2].

In the baking process, the final properties of baked anode vary. This could be explained by the structure of the furnace which is composed of pits in which the green anodes are stacked on top

of each other. Thus, the positions of the anodes block are different which leads to a different baking history for each block.

The baking phase is characterized by chemical mechanisms in which the anode paste passes through different states affecting its final properties. As mentioned by D'Amours [3], these properties are mainly influenced by the chemical composition of the pitch and its phase changes. At about 100 °C, the pitch becomes soft and its viscosity decreases. Between 150 °C and 250 °C, the viscosity of the pitch increases improving the cohesion between aggregates because of the volatilization of part of its oil. Then, beyond 250 °C, the release of condensable volatiles takes place until 500 °C. By condensation and polymerization, the pitch transforms to a semi-coke at around 450 °C following by its carbonisation at more than 550 °C giving a solid material in its final microstructure. In this topic, several studies were carried out on carbonaceous materials based on the mixture coke/pitch to study the evolution of their mechanical properties at high temperature. D'Amours [3] tested the compressive strength and Young's modulus for partially and fully baked ramming paste samples. It was found that by increasing baking level from 175 °C to 400 °C, the compressive strength and the Young's modulus increase quickly until 250 °C and then stabilizes at 400 °C with a small decrease in Young's modulus beyond 700 °C. Similarly, Orangi [4] tested partially baked ramming paste samples at 200 °C and 250 °C. For tests carried out at 160 °C and 200 °C, the compressive strength increases simultaneously with the baking level. Also, the Young modulus increases from 200 °C to 350 °C and then gradually decreases. In regards to carbon anodes, Kallel et al. [5] measured its mechanical properties at baked levels ranging from room temperature up to 1200 °C and at different test temperatures. The results obtained showed that the compressive strength and the Young's modulus are characterized by low values between 120 °C and 400 °C. Furthermore, a transition was observed at 300 °C represented by a peak, but no explanation of this phase was mentioned [5]. In another study, Racine et al. [6] measured the Young's modulus of the anodes for test temperatures between 25 °C and 950 °C. They concluded that the Young's modulus remains almost stable regardless of the test temperatures.

In this work, laboratory scale carbon anode with fixed recipe and homogenous apparent density were fabricated. Mechnical tests were carried out at different test temperatures and baking levels. Results obtained will be part of an experimental database that will allow to feed a numerical baking model based on porous media. This model will serve to predict the final anode properties and comparing the numerical simulations results with those experimental ones.

2. Materials and Method

2.1. Samples

The raw materials used in this work were provided by Deschambault aluminium smelting plant (Alcoa, Canada). The anode recipe used consists of calcined coke (83.8 wt.%) and coal tar pitch (16.2 wt.%). The choice to make laboratory scale carbon anodes instead of industrial anodes is made for the use of a controlled recipe (Table 1) limited to petroleum coke, coal tar pitch and free of recycled butts to eliminate the effect of their variations on the mechanical properties of the anode. Also, the large coke aggregates (> 8 mesh) had not been used in the recipe to avoid the scale effect due to the ratio size of aggregates/sample size. And finally to make samples with a homogeneous apparent density.

The coke was preheated at 178 °C for at least 4 hours, followed by the addition of the pitch with an additional preheating of 30 minutes. Then, these materials were mixed at the same temperature for 10 minutes to obtain the anode paste. Finally, the anode paste was compacted at 168 °C by the mechanical proctor (Figure 1) [7]. The green anode samples had an approximate diameter and length of respectively 100 mm and 250 mm. The green apparent density was in the

range 1.55 g/cc and 1.58 g/cc [7]. Cylindrical cores of dimensions 50 x 100 mm (Figure 2, a) were cut and surfaced to ensure parallelism between their ends meeting the requirements of ASTM standard C39/C39M [8] and to be able to use the hydraulic press. Then, these cores were placed in an inconel box (Figure 2, b) and covered with coke breeze to prevent the oxidation reaction by the air [9]. Thereafter, this box was inserted into a Pyradia laboratory furnace (Figure 2, c) to bake the samples at specific temperatures as follows: 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, 700 °C and 1100 °C. The heating program used was as follows: the cycle started from room temperature up to 150 °C with a heating rate of 60 °C/h, then between 150 °C and 650 °C a heating rate of 20 °C/h and from 650 °C up to 1100 °C a heating rate of 50 °C/h. Once the desired baking level was reached, a soaking time of 20 hours was applied [9]. At the end of the program, the oven was switched off to cool the samples.

Table 1. Size distribution of coke particles and pitch in the anode paste [7].

Fraction of particles (US mesh)		**Mass (%)**	**Mass (g)**
Coke	-4 +8	22	242
	-8 +14	10	110
	-14 +30	11.5	126.5
	-30 +50	12.7	139.7
	-50 +100	8.8	96.8
	-100 +200	10.8	118.8
	<200 mesh	24.2	264
Total coke mass (g)		100	1100
Pitch		16.2	178.2

Figure 1. Compaction system (Proctor apparatus).

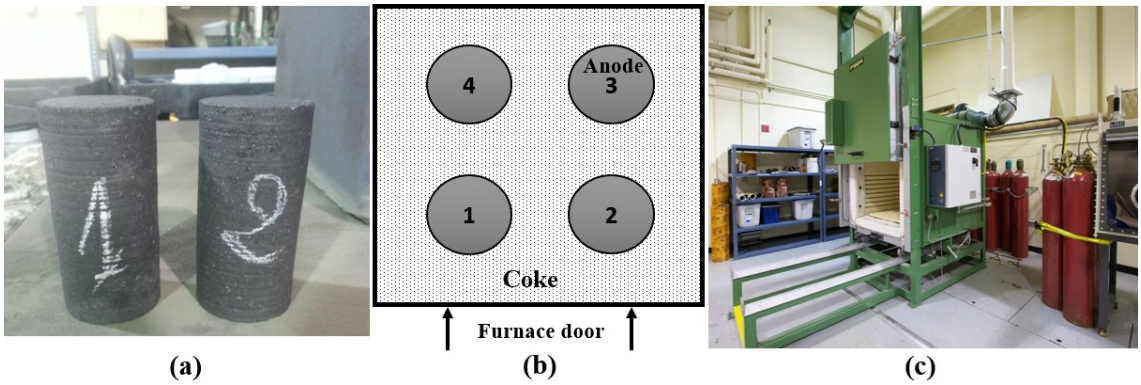

Figure 2. (a): Green anode samples ; (b): Samples position in the inconel box ; (c): Anode baking furnace.

2.2. Experimental Setup

The uniaxial compression tests at room and high temperatures were carried out using an hydraulic MTS 810 press (Figure 3) with a maximum loading capacity of 250 kN. A three zones split-tube furnace (LAB-TEMP^{TM}) is mounted on the press and can reach and maintain temperatures up to 1200 °C. The test chamber within the furnace was purged with argon to minimize mass losses related to oxidation of samples for test temperatures above 400 °C. A linear encoder (Heidenhain ND 280) was used to measure axial deformation during the test.

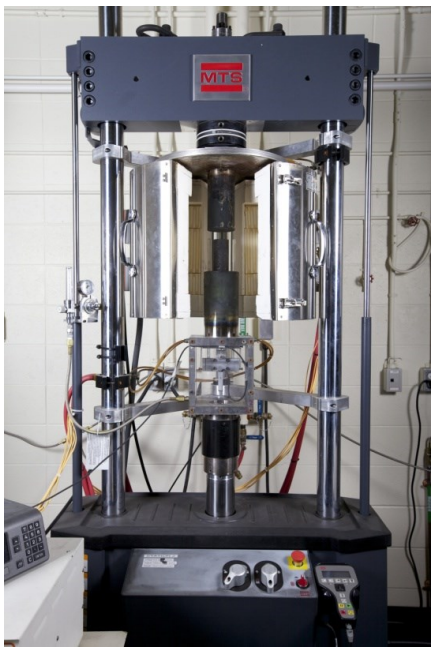

Figure 3. Compression test apparatus.

2.3. Experimental Procedure

As the samples undergo cooling after their baking, it was necessary to resume their baking levels during the mechanical tests. For this, test temperatures were chosen in order to avoid excessive release of volatiles during the tests. Table 2 shows test temperatures and corresponding anodes baking levels.

A heating rate of 10 °C/min was applied and maintained at the desired test temperature for a period of two hours so that the temperature be homogeneous in the sample. Initially, the test started with loading until rupture to determine the compressive strength. For the Young's modulus tests, three loading/unloading cycles were applied in accordance with the ASTM standard C469/469M-10 [10]. The first cycle served to close the internal pores of the sample. The slopes of the 2nd and 3rd loadings are averaged to obtain the Young's modulus taking into account the thermal expansion of sample during the test. These tests are repeated at least three times for each test temperature. Each point in the graphs is the average of 3 tests. The graphs were constructed based on points representing the average of 3 tests for each baking level.

Table 2. Test temperature vs anode baking level.

Test temperature (°C)	Sample baking level (°C)
25	25
175	200
275	300
400	400
450	500
600	600
700	700
1000	1100

3. Results and Discussion

3.1. Samples Baking Data

During their baking at different levels, the samples undergo dimensional variations and mass loss. Table 3 summarizes the results obtained before and after each baking level. Low mass losses were obtained at 200 °C and 300 °C compared to other high temperatures. This will be explained in the following sections.

Table 3. Samples dimensional variations and their mass loss corresponding to each baking level.

Baking level (°C)	Samples before baking			Samples after baking			Mass loss (%)
	$Ø_m$ (mm)	L_m (mm)	m (g)	$Ø_m$ (mm)	L_m (mm)	m (g)	
25	50.5	99.5	325.7	-	-	-	-
200	50.3	100.9	312.1	50.4	100.9	311.8	0.1
300	50.5	101.1	317.4	50.6	101	314.4	0.95
400	50.5	101.3	326.6	50.4	101.1	307	6.03
500	50.5	98.7	310.3	50.5	98.5	298.6	3.8
600	50.4	98.5	316.9	50.4	98.4	302.5	4.54
700	50.2	100.5	310.5	50.2	100.4	297.3	4.25
1100	50.5	98.1	306.7	50	97.9	293.3	4.4

3.2. Compression Test

A typical Young's modulus test curve as a function of strain is demonstrated in figure 4. The evolution of mechanical properties measured by MTS press as a function of baking level is presented respectively in figures 5 and 6. It can be seen that for baking levels between 200 °C and 400 °C, the compressive strength as well as the Young's modulus were lower compared to the room temperature where the pitch was solid. This could be explained that in this interval the pitch softened and the anode paste started to acquire a viscoelastic behavior. At 300 °C, the values increased seen that the polymerization of the pitch took place with a low volatilization (Table 3). However, a decrease in compressive strength and Young's modulus was found at 400 °C, which could be explained by the passage of pitch through a transition phase causing a mass loss in the anode of 6.03 % (≈ 37.2 wt.% of pitch) as mentioned in Table 3. Therefore, the consolidation between the coke particles was incomplete. Then, the mechanical properties increased progressively up to 600 °C, which can lead to the partial pitch carbonization, i.e. a semi-solid coke phase [11]. Until complete baking, the values of the compressive strength began to stabilize, and those of Young's modulus showed a plateau. This is due to the fact that the pitch was completely pyrolyzed (Table 3) and the anode crystalline structure became more stable. The final compressive strength obtained was about 63 MPa and the Young's modulus was about 2.7 GPa. Similar behaviors of compressive strength and Young's modulus for temperatures ranging from 200 °C to 1200 °C was found by Kallel et al. [5], with a compressive strength value of about 70 MPa at 1200 °C.

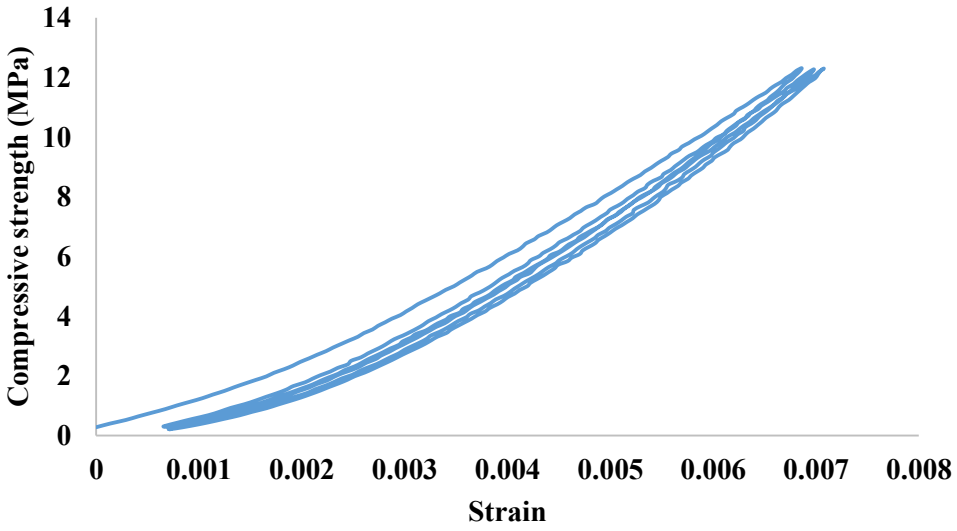

Figure 4. Typical curve of Young's modulus test at 1000 ° C.

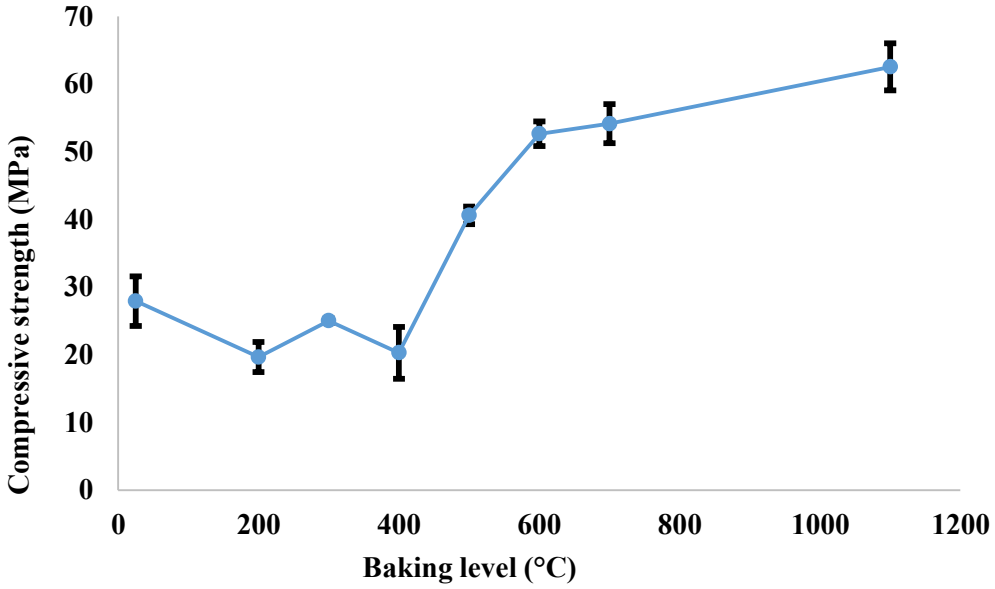

Figure 5. Compressive strength as a function of baking level.

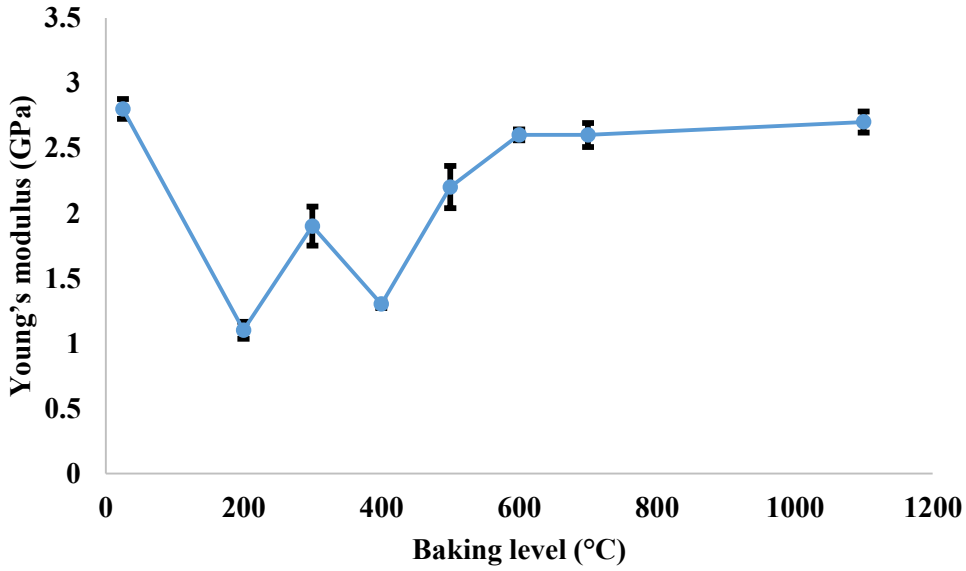

Figure 6. Young's modulus as a function of baking level.

3.3. Mass Loss Due to Mechanical Tests

The mass of the anode samples was measured before and after the high temperature tests where the oxidation of the sample could be significant. The mass losses in percentage for each test temperature are summarized in Table 4. Comparing these results with those of mass losses due to baking levels, it was found that there was a slight recovery of devolatilization mechanisms in the tests as the volatiles are not released completely during baking. Low mass losses were noted at 275 °C and 1000 °C temperatures where respectively the release of the volatiles begins and ends during baking. At 400 °C, the mass loss of the test is too low compared to that of baking where a large amount of condensables was released. From 450 °C up to 700 °C, the mass losses increase progressively because this interval is characterized by the release of condensable and non-condensable volatiles trapped in the samples. Generally, all results obtained showed that the

mass loss was less than 1 % with low degradation on the extern surface of the sample. This indicated that the mass loss due to the compression test was negligible, and confirmed that the test conditions were favorable.

Table 4. Mass loss due to test temperature.

Test temperature (°C)	% of mass loss
175	0.099
275	0.034
400	0.065
450	0.138
600	0.203
700	0.274
1000	0.068

3.4. Failure Modes

The rupture modes were identified using ASTM standard C39/C39M [8] for each baking level. At room temperature, a fragile rupture was observed (figure 7) and represented by mode 1 [8]. This mode was described by the formation of a cone at one end, vertical cracking through the plugs, and no cone formed at the other end. This could be explained by the fact that at room temprature, the pitch is a fragile material which gave this behavior to the green anode. Then, between 200 °C and 400 °C, a ductile rupture was obtained (figure 8) and described by mode 2 [8]. It was characterized by vertical columnar cracking between the two ends and no cone was formed. This behavior may be due to the pitch phase change which gives to the carbon anode a more viscoelastic behavior. Above 500 °C and until complete baking, a fragile rupture was obtained (figure 9) represented by mode 1 [8]. This could be explained that at about 450 °C begins the transformation of the binder matrix from a viscoelastic behaviour to a quasi-fragile one [11-12]. Thereafter, the condensable volatiles were released up to 550 °C [13]. Then, the post-coking process begins at 600 °C, in which the pitch releases its heavy volatiles represented by hydrogen and methane up to 900 °C [11-12]. Until complete baking, the matrix consolidation and the stabilization of the crystalline structure were completed.

Figure 7. Fragile rupture obtained at room temperature.

Figure 8. Ductile rupture obtained at 200 °C, 300 °C and 400 °C.

Figure 9. Fragile rupture obtained at 500 °C, 600 °C, 700 °C and 1100 °C.

4. Conclusions

In this paper, the mechanical properties of the carbon anode were identified using the uniaxial compression test at high temperature. Anode samples were fabricated, prepared and then partially baked at different temperatures up to 1100 °C. Test temperatures were selected while remaining close to the baking levels so as not to generate additional release of volatiles which could affect the results to be obtained. The results obtained were in agreement with the literature [5]; and showed that the compressive strength and the Young's modulus had low values between 200 °C and 400 °C, an interval where the anode paste had a viscoelastic behavior conferring to the anode a ductile rupture. Thus, the mass loss that the anode had undergone during the compression test was less than 1 %. In addition, a fragile rupture was observed for the room temperature and between 500 °C and 1100 °C, where in the former the pitch was solid and in the latter the binder matrix was completely consolidated with the coke aggregates. These results confirm that the rupture mode is unaffected by the apparent density, but just by the baking level of the anode paste.

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