CREEP BEHAVIORS OF INDUSTRIAL GRAPHITIC AND GRAPHITIZED CATHODES DURING MODIFIED RAPOPORT TESTS

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Abstract

Creep is of importance for evaluating the materials deterioration and deformation of the cathodes in aluminum reduction cells. The purpose of this work is to obtain the creep data for various industrial cathode products. A modified Rapoport equipment was used for measuring the creep behaviors during aluminum electrolysis with CR=4.0 and at temperature of 965°C. Testing samples were taken from three typical industrial cathode blocks: semi-graphitic, full graphitic and graphitized carbon products and were characterized for their graphitized degree using XRD method. The values of d_{002} for all cathode samples were lowered after aluminum electrolysis, and the graphitized cathode showed a smaller creep deformation than those of semi-graphitic and full graphitic cathode samples. The results have demonstrated a correlation between the graphitization degree and the creep deformation using a consistent testing procedure, and the obtained data will be useful for better quality control in cathode manufacture and improvement in cell structure design.

Introduction

Numerous efforts have been made for several decades in improving the cathode properties for a long service life of aluminum reduction cells. The major deformations of the cathode during aluminum electrolysis are found in close relationship with thermal and sodium expansions [1-7]. Recently, creep deformation has received research attention due to its effect on materials deterioration of the cathodes. The creep phenomenon in various cathode carbons was observed using uniaxial compression tests with free lateral strains in laboratory aluminum electrolysis [8,9]. Similar creep behaviors with TiB_2/carbon composite cathode materials were investigated in a modified Rapoport apparatus, where the addition of TiB_2 in the carbons showed an improved resistance to the creep deformation [10].

The creep data can not only be useful in cell structure design and cathode construction due to its effect on the cathode deformation, but can also be applied as a quantitative indication for evaluating the materials deterioration and their service life under operating environment.

In this work, the creep behaviors of the cathode carbons during aluminum electrolysis have been investigated against varying degrees of graphitization. All cathode samples were uniformly taken from various industrial cathode blocks that were produced using different technologies; and the electrolysis performances were carried out under operating conditions similar to the industrial environment. The aim of this work is to obtain technical data using a consistent procedure to be used for better quality control in cathode manufacture and improvement in cell structure design.

Experimental

Creep Measurement in a Modified Rapoport System

Figure 1 shows the modified Rapoport system used for the measurements of creep strain during aluminum electrolysis. The testing sample rested on a machined Alsint support and acted as the cathode during electrolysis, while the graphite crucible was the anode. The graphite crucible was placed in a vertical resistance furnace and was fixed onto an anode rod. In the electrolysis process, a direct current was passed through the anode rod, the sidewall of the graphite crucible, molten electrolyte and the testing cathode sample to a negative end. The creep strain of the sample during tests was measured by a LVD transducer (range 10 mm, resolution 1 μm) located on the top of the furnace. The signals of the creep strain were logged once a minute into a computer connected to the LVD transducer.

The experiments were conducted in this furnace that was flushed with argon gas (99.99%) through the gas inlet and the gas outlet, and the temperature was controlled with a thermocouple in the crucible. The external load was provided by a constant pressure system, which could maintain the pressure at a given value for a period of time. During the testing, the applied pressure was increased each time in steps of 2 MPa.
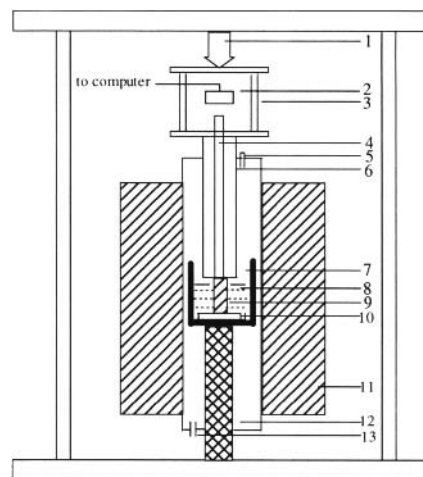

Figure 1. A modified Rapoport system for creep measurement: 1–Load; 2–LVD transducer; 3–Loading frame; 4–Measuring extension pin; 5–Gas outlet; 6–Loading extension rod; 7–Graphite crucible; 8–Cryolitic melt; 9–Testing cathode sample; 10-Alsint support; 11–Resistance furnace; 12–Anode rod; 13– Gas inlet

The experiments of aluminum electrolysis were performed with a current density of 0.5 A/cm^2 at the cathode and a cryolite ratio of 4.0. The cathode sample was 40 mm immersed in the melt and was subject to creep measurement after 2 h electrolysis.

Materials and Chemicals

All testing samples were machined to a cylindrical form for use as a cathode sample in laboratory aluminum electrolysis. Table I shows the density and the porosity of the testing samples taken from three different types of industrial cathode blocks of HC35, HC100 and SMH. As the heating treatment temperature for the carbons increased, the apparent density of the cathode products rose while the porosity lowered.

Table I. Density, Porosity and Heat Treatment Temperature of Various Industrial Cathode Samples

Sample	Materials	Apparent Density (g.m^{-3})	Apparent porosity (%)	Heat treatment temperature (°C)
HC35	Anthracitic+ graphite (35%)	1.57	14.04	1200
HC100	Graphite (100%)	1.64	18.12	1350
SMH	Fully graphitized	1.58	22.27	2850

The chemicals used were cryolite (industrial grade with a cryolite ratio of 2.0), and the additives of Al_2O_3, CaF_2, NaF (analytical reagent). All chemicals were dried at 400°C for 4 hours before testing in aluminum electrolysis. For each run, the total mass of the electrolyte was 160 g containing 5 % CaF_2 and 8 % Al_2O_3.

XRD Measurement for Interlayer Spacing in Carbons

For XRD measurement of interlayer spacing, the carbon specimen was cut from the cathode samples and ground to fine powders. The interlayer spacing (d_{002}) in cathode carbons could be calculated through the Bragg equation:

$$2d \sin\theta = \lambda \qquad (1)$$

$$d = \frac{\lambda}{2\sin\theta} \qquad (2)$$

where λ is the wavelength of X-ray, and θ is the incident beam angle that can be acquired by XRD data.

Figure 2 is a sample holder for XRD analysis, where the sample powders of the sieve fraction < 75 pm were spread on the central plane area using spray adhesive and sieving the sample powder regularly on the glue film to reach a random particle distribution. This treatment can ensure the operating error of XRD measurements less than 5% for various carbon materials [11].
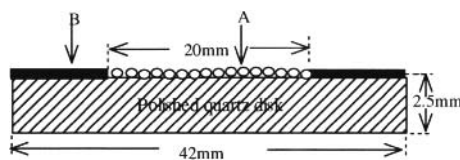

Figure 2. Schematic drawing of a sample holder for X-ray diffraction measurements of graphite carbon materials. A: Carbon powder sample at the glue film; B: Paper mask.

Results and Discussion

Creep Deformation Measurement of Various Cathode Materials

During aluminum electrolysis , metallic sodium is generated by the chemical reactions below

$$3NaF(l) + Al(l) = AlF_3(l) + 3Na(\text{in } C) \qquad (3)$$

$$Na(\text{in } Al) = Na(\text{in } C) \qquad (4)$$
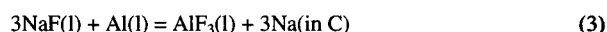
Previous studies showed that the creep of the carbons was related to the diffusion of this metallic sodium in the cathodes [9, 11].

Figure 3 show the creep strain curves vs. testing time for a graphitized cathode sample of SMH with the loading pressures of 2 MPa, 4 MPa and 6 MPa, respectively, at the temperature of 965°C and the cryolite ratio of 4.0. Here, the reason for using the high ratio of the cryolitic melt is to accelerate the rate process of the sodium diffusion in order to reduce the testing time. It is found that no matter which cathode material used, most of the creep curves can be divided into two stages. In the first stage or in the period of 10 min to 15 min from the starting time, the curve exhibits the feature of a typical transient creep that the creep rate (the curve slope) is high at first but soon decreases. This is followed by the secondary stage of a steady-state creep (relatively flat section of the curves), where the creep rate is small and the strain increases slowly with increased testing time, especially when the pressure is 6 MPa. No third stage, i.e., accelerating creep, is recorded which might result in a fracture in the testing samples.
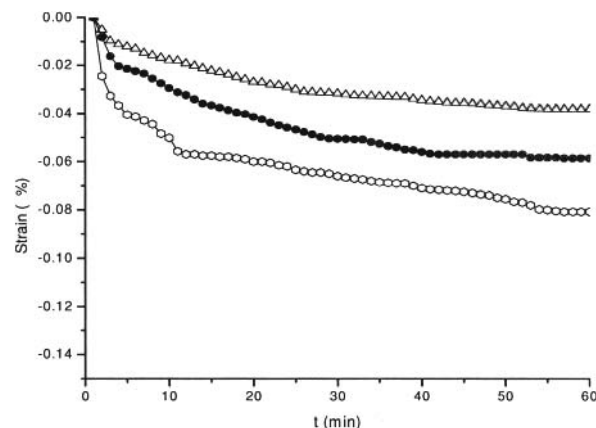

Figure 3. Creep strain curves with testing time for cathode sample SMH (loading pressure: 2 MPa, 4 MPa, and 6 MPa from top to bottom) during aluminum electrolysis with CR=4.0 and at 965°C

In Figures 4 5, there are creep strain curves vs. testing time for the semi-graphitic (HC35) and the fully graphitic (HC100) cathodes, respectively, with the loading pressures and electrolysis parameters the same as those used for the graphitized cathode sample of SMH. Among them, HC35 had the highest specific creep strain amplitude, followed by HC100; and both are higher than that of SMH. This phenomenon has a close relationship with the heat treatment temperature of the cathode samples. SMH had the highest heat treatment temperature, followed by HC100 and HC35. Therefore, the SMH sample showed the lowest specific creep strain amplitude. This is because that the higher heat treatment temperature will make a higher Femi level with less F1 layer structure within the graphite materials, resulting in fewer amounts of intercalation compounds between the graphite layers [12].
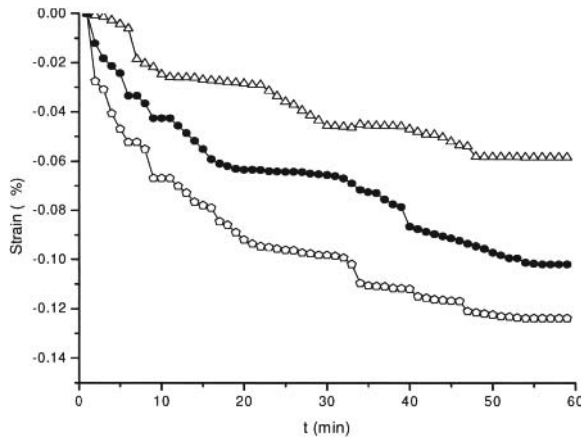

Figure 4. Creep strain curves vs. testing time for cathode sample HC100 (loading pressure: 2 MPa, 4 MPa, and 6 MPa from top to bottom) during aluminum electrolysis with CR=4.0 and at 965°C
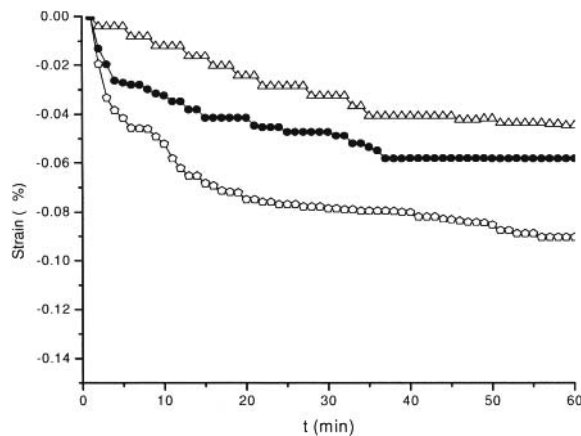

Figure 5. Creep strain curves vs. testing time for cathode sample HC35 (loading pressure: 2 MPa, 4 MPa, and 6 MPa from top to bottom) during aluminum electrolysis with CR=4.0 and at 965°C

The creep strain is highly dependent on the applied stress, temperature and testing time. The existing creep process may be expressed by defining a normalized reference time, $\tilde{t}_{ref}$, as shown in Equation (5):

$$\tilde{t}_{ref} = \frac{t_{0.5\varepsilon_{total}^c}}{t_{\varepsilon_{total}^c}} \qquad (5)$$

where $t_{\varepsilon_{total}^c}$ is time required to reach the steady state, which is the total creep strain, and $t_{0.5\varepsilon_{total}^c}$ is the time elapsed when 50% of the total creep strain is reached.

Table II gives the estimated normalized reference times for the carbon samples of HC35, HC100 and SMH under the external pressure of 2 MPa, 4 MPa, and 6 MPa. Here the creep deformation of carbon cathodes can be considered as time dependent and permanent at high temperatures. The axial strains are used to calculate these values. The estimations are based on the creep strains curves presented in Figures 3–5. For any pressure of the loading, the reference time for creep deformation of the HC35 is the longest, followed by HC100 and SMH. This order is quite similar to the one observed on those cathodes vs. the sodium penetration [2, 10], suggesting phenomenologically the same cause, that is, C-Na intercalation that results in the carbon structure deterioration including the creep. HC35 has the lowest degree in graphitization among the tested cathode carbons, leading to cleavage and slip of the basal planes (Van der Waals bonds) in the materials. Therefore, it requires the biggest $\tilde{t}_{ref}$ with the same pressure during aluminum electrolysis. More quantitative details about the creep deformation vs. service time for the cathode carbons under pressure are still under investigation.

Table II . Normalized Reference Time $\tilde{t}_{ref}$(min/min)(CR=4.0)

Pressure (MPa)	SMH	HC100	HC35
2	0.2143	0.4286	0.4583
4	0.1892	0.1942	0.2642
6	0.0926	0.1235	0.1702

XRD and Interlayer Spacing of Cathode Materials

After the experiment, a small piece of specimen with 4 mm thickness, cut from the bottom 10 mm of the cathode sample, was analyzed by XRD. This interlayer spacing can be an important parameter for characterization of cathode creep. For the purpose of comparison, a sample of high purity graphite (HPG) with consistent quality could serve as a reference standard material in our laboratory.

Figures 6 and 7 show the XRD analysis of the carbon cathodes before and after aluminum electrolysis, respectively. Whether before electrolysis or after electrolysis, the 2θ value of SMH at the characteristic peaks is the largest of the tested samples, followed by HPG and HC100, and finally HC35. The interlayer spacing (d) of SMH is the lowest according to Equation 2, which means smaller change in its graphite structure and stronger stability against the creep deformation. This implies that the interlayer

spacing values of cathode carbons obtained from the XRD data can serve as a characteristic parameter for evaluation of the cathode quality and its resistance to creep deformation.
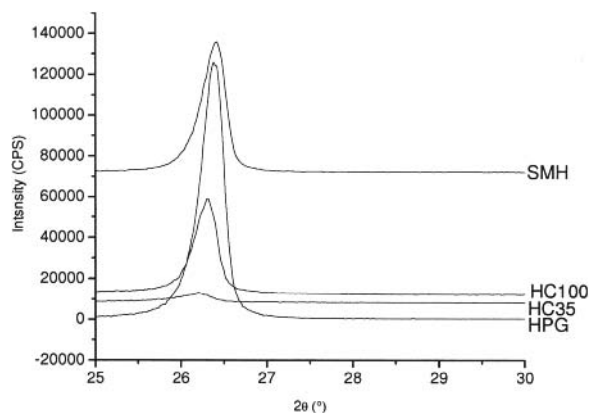

Figure 6. XRD analysis of the cathode samples without aluminum electrolysis at 25°C
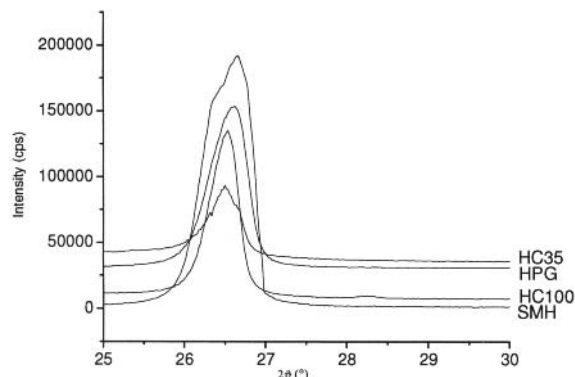

Figure 7. XRD analysis of the cathode samples after aluminum electrolysis at 965°C and CR=4.0

Table III   The Interlayer Spacing d_{002} (Å) in Cathode Carbons

Time	SMH	HC100	HC35	HPG
Before electrolysis	3.3730	3.3856	3.4010	3.3735
After electrolysis	3.3595	3.3683	3.3656	3.3570

For comparisons of micro-structural change related to the degree in graphitization for the cathode materials, the values of the interlayer spacing (d) for the tested samples are calculated, as presented in Table III.

For clarification and comparison, a chart of various changes of the interlayer spacing in the tested cathode carbons before and after aluminum electrolysis is presented in Figure 8. The creep behavior of the carbon or graphite materials is the result of a number of chemical and micro-mechanical processes, such as the motion of defects, diffusion in grain boundary, grain boundary

sliding, mass penetration in micro-pores, migration and re-crystallization, etc. It could be a time-consuming and labor-intensive work to make quantitative measurements on all those effects in practice. The summary of the obtained results in this investigation demonstrate a consistent method applicable in creep-related materials evaluation and structure design for reduction cathodes.
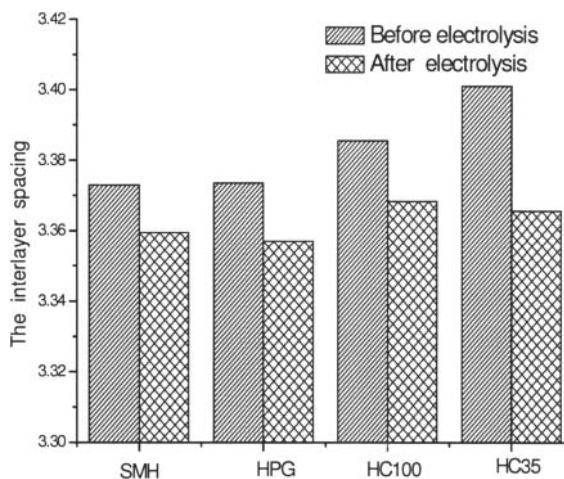

Figure 8. Chart summarizing changes in the interlayer spacing of the tested cathode carbons before and after aluminum electrolysis

Conclusions

1. Creep deformation of industrial cathode carbons with varying degrees of graphitization can be quantitatively differentiated using a modified Rapoport system under identical loading pressure, operating temperature and testing time, etc.

2. The creep strain of the tested cathode carbons is decreased with increased graphitization: SMH (fully graphitized) < HC100 (100% graphitic) < HC35 (35% graphitic), while the time span in the creep process is increased with lowered degree in graphitization.

3. A reduction in the interlayer spacing (d_{002}) of the cathode carbons after aluminum electrolysis is found with all types of tested cathodes that have exhibited a creep behavior, and the change in d_{002} values before/after aluminum electrolysis is closely correlated to the creep resistance of the cathode materials.

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