

NEW OBSERVATIONS IN CREEP BEHAVIOUR OF RAMMING PASTE IN ALUMINIUM ELECTROLYSIS CELL

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Abstract

Creep of ramming paste was studied from ambient to operational temperature in order to characterize its mechanical behaviour as used in the peripheral joint of aluminium electrolysis cells. Two types of uniaxial creep test over a specified stress level were performed on two inch samples: tests at room temperature for samples baked at different temperatures and test at temperatures close to the sample baking temperature. It is concluded that at certain baking temperatures and given stress level, three types of creep, called primary, secondary and tertiary, take place successively. In addition, at lower baking temperatures (200 °C), the creep level is larger in comparison with creep at higher baking temperatures. Also, for specified baking temperature, creep strain obtained by high temperature testing is larger than creep strain obtained by room temperature testing. These results give new insights on the ramming paste behaviour in aluminium electrolysis cell.

Introduction

Previous research

In the aluminium electrolysis process, ramming paste undergoes various transformations from ambient to the operational temperature. At first, at lower temperatures (dependent on percentage of aggregates and binder in composition, green density, heating rate, etc.) it swells due to trapped gas, binder vapours and products of pyrolysis within the paste and simultaneously it loses mass due to escaping the trapped gas and volatiles. Later it shrinks because of carbonization of binder, which is accompanied by volatilization, dehydrogenation and structural changes. To make ramming paste rammable at room temperature, softeners are added to the binder. The softeners vaporize at temperatures lower than the solidification temperature of the binder. Ramming paste may mechanically be compressed by thermal expansion of cathode blocks, the steel shell and other components with which it is in contact. Hence, mechanical loads are one source of creep before ramming paste is fully baked.

D'Amours [1] has carried out relaxation tests on ramming paste at room temperature. The cylindrical samples were baked at 250 °C then loaded axially up to about 50% of their uniaxial compressive strength at a speed of 4 mm/min. Subsequently, the apparatus was mechanically locked so that the total axial strain remains constant during the test. The obtained curve for axial stress is illustrated in figure 1. After rapid compression, the stress has reduced by 12% in one hour. As seen in this figure, stress relaxation in the long-term period is steady. After 90 hours, the stress has dropped by

19%. The reason of relaxation is that the sample is not fully baked and is ductile when the load is applied.

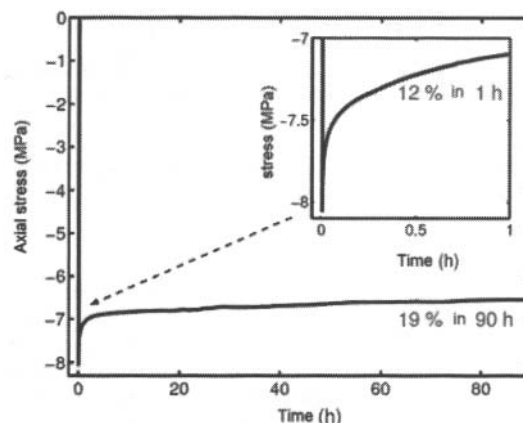


Figure 1. Total axial stress measured during relaxation test [1].

The results of simulated relaxation test (dual behaviour of creep) by Richard [2] have shown that the visco-plastic behaviour of the ramming paste is an important phenomenon. In this test by applying strain, stress (load) was measured. The materials used for simulation and the tests were carbon (C), ramming paste (P), concrete (B), dense brick (BRO) and insulated brick (BIL) (figure 2). The role of dense bricks was to transfer the applied load by beam to other materials. The three components of carbon, ramming paste and concrete were equipped with thermocouples. After isolating the assembly, except than carbon block at centre, the heat (24-933.4°C) was applied by an oven. Mainly, the heat was absorbed by carbon at the centre and diffused horizontally in the ramming paste and other elements through their interfaces (figure 2).

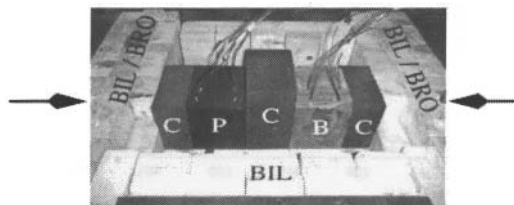


Figure 2. Set-up of simulated creep test [2].

The results of load evolution during relaxation simulation test by Richard [2], using D'Amours' constitutive model [3] for ramming paste, have been compared with the experimental results in figure

3. The result obtained by experiments doesn't have good agreement with viscoelastoplastic simulation results (TC-VEP2) at the time of 500 to 1900 min. A strong increase in net load at the beginning of the ramming paste baking is observed because D'Amours has considered that the chemical strain fully assigned to the stress during swelling.

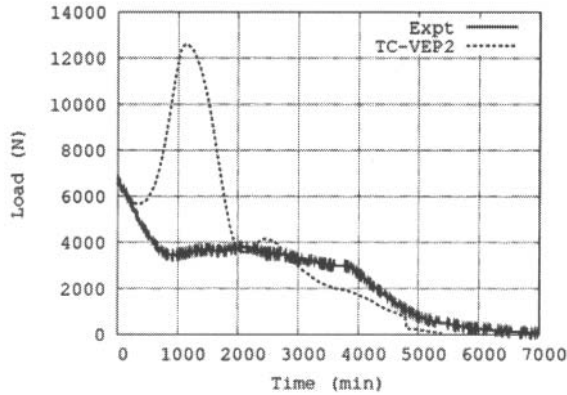


Figure 3. Load evolution during the validation test, with viscous aspects [2].

Binder viscosity

Viscosity of binder plays an important role in creep behaviour of ramming paste during preheating period of aluminium electrolysis cell. As we know, binder of cold ramming paste is constituted of coal tar pitch and softeners. Softening point of binder is around 50 °C. During the carbonization of coal tar pitch, the viscosity decreases at 200-360 °C and reaches its minimum at 360-400 °C and then increases at 400-450 °C (figure 4). The decrease of viscosity of pitch after its melting may be attributed to the solubilisation of benzene insoluble (BI) in addition to increase of thermal movement of pitch with increasing temperature. The viscosity increase above 400°C can be explained by the growth of a high molecular weight mesophase [4].

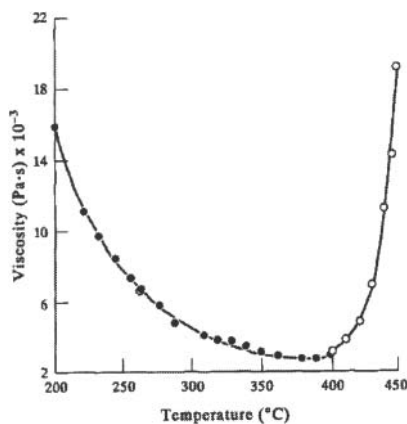


Figure 4. Viscosity of coal tar pitch during carbonization, heating rate: 3°C/min (200-400°C) and 0.5 °C/min (400-450°C), [4].

Creep stages

A typical creep curve for metals, polymers, and porous materials such as ceramic is represented in figure 5. The temperature at which materials begin to creep depends on their melting point [5]. In the case of ramming paste, this temperature depends on the melting point of binder.

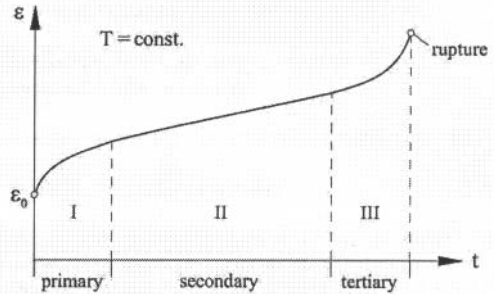


Figure 5. Typical creep curve for materials [5].

The hypothesis used for ramming paste creep is that the response of the specimen loaded by σ_0 at time t_0 can be divided into an elastic part and creep part:

$$\varepsilon_{total} = \frac{\sigma_0}{E(T)} + \varepsilon_c \quad (1)$$

, where $E(T)$ is the modulus of elasticity, T is the temperature and ε_c is the creep strain including viscous strain (ε_v) and damage strain (ε_d); hence creep strain is expressed as equation 2.:

$$\begin{aligned} \varepsilon_c &= f(\varepsilon_v, \varepsilon_d) \\ &= \varepsilon_{total} - \frac{\sigma_0}{E(T)} \end{aligned} \quad (2)$$

In primary stage of creep, the strain rate decreases, it is constant in secondary stage and strain rate increases in tertiary stage. These three stages are called transient creep, steady creep and accelerating creep respectively which rupture happens in tertiary stage of creep [5].

In the present paper, creep of ramming paste is investigated for the samples baked at 200 °C to 1000 °C. The applied load is considered as a percentage of compressive strength of the sample at specified temperature. The tests were performed at room temperature and elevated temperature close to the temperature at which the samples were baked.

Preliminaries

Sample fabrication

Two inch cylindrical samples of ramming paste were compacted on both sides using methodology presented by Orangi et al. [6]. A split cylinder steel mould with internal diameter of 5.08 cm (2 in.) was used to make the samples. The assembly of this mould is illustrated in figure 6. It is consisted of lower plate, upper plate, rammer and split cylinder. The weight of the steel rammer used for compaction was 1189 g. To fabricate the cylindrical samples two inch by four inch, 330 g of the paste material was poured in the mould and compacted by Hilti hammer for two seconds (figure 7).

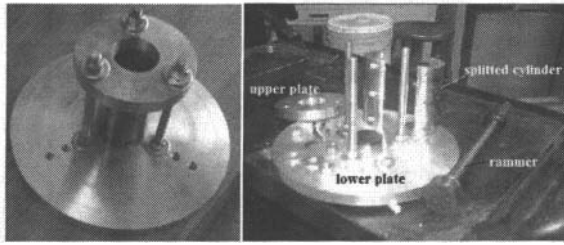


Figure 6. Split steel mould used for fabrication of ramming paste samples.

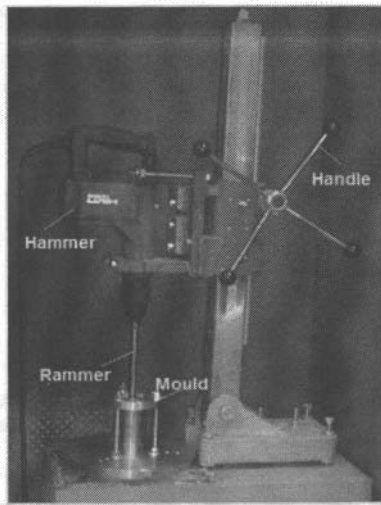


Figure 7. Hilti hammer used for compaction of cold ramming paste [6].

Sample baking and preparation

Green samples were placed in alumina crucibles and covered with coke. The samples were heated using the heating programme as specified in standard ISO 20202 to final baking temperatures of 200, 250, 500 and 1000 °C. In order to prepare the baked samples for creep tests, they were cleaned and machined. The green density and baked density of the samples used for creep test are presented in table 1 and table 2. The apparent density was calculated as the ratio of mass to the apparent volume measured using the procedure specified in standard ASTM D 5502-00.

Table 1. Green and baked densities of samples used for creep test at room temperature.

Baking temperature (°C)	Green density (g/cm ³)	Baked density (g/cm ³)
200	1.570	1.514
250	1.598	1.500
500	1.619	1.449
1000	1.636	1.440

Table 2. Green and baked densities of samples used for creep test at elevated temperatures.

Baking temperature (°C)	Green density (g/cm ³)	Baked density (g/cm ³)
200	1.572	1.516
250	1.579	1.511

Tests

Room temperature

Room temperature tests were carried out on the samples baked at 200, 250, 500 and 1000 °C. The load applied to the samples was approximately 20% of compressive strength of the samples at room temperature (table 3), except for the sample baked at 250 °C which was loaded to less than 40% of its compressive strength. The loading rate was chosen 0.15 MPa/sec for all samples [ISO 18515]. One sample was used to measure the compressive strength at each baking temperature.

Table 3. The load applied for performing creep test at room temperature.

Baking temperature (°C)	Compressive strength (MPa)	σ_0 (MPa)
200	6.622	1.3
250	15.973	6.0
500	11.394	2.2
1000	10.362	2.0

High temperature

The samples baked at 200 and 250 °C were tested at 160 and 200 °C respectively. The load applied to the sample baked at 250 °C was 40% of its compressive strength at 200 °C and for the sample baked at 200 °C was chosen 0.097 MPa. The loading rate was also 0.15 MPa/sec for these tests. The applied stress in creep test at elevated temperature is seen in table 4. The apparatus used for both types of test, room and high temperature, is shown in figure 8. The MTS press, equipped with furnace, displacement and load measurement system and argon valve, is used to measure the compressive strength and to do the creep test of two inch samples.

Table 4. Applied load for creep test at high temperature.

Baking temperature (°C)	Test temperature (°C)	σ_0 (MPa)
200	160	< 0.097 (refer to high temperature tests section)
250	200	3.74

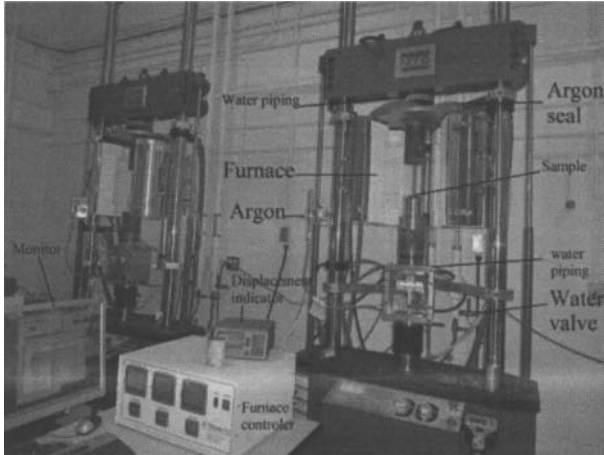


Figure 8. The apparatus of creep test at room and elevated temperatures for two inch sample.

Results

Room temperature tests

Let consider that ϵ_e is the elastic strain:

$$\frac{\sigma_0}{E(T)} = \epsilon_e \quad (3)$$

The equation (2) is written as equation (4):

$$\epsilon_c = \epsilon_{total} - \epsilon_e \quad (4)$$

Thus, the total strain obtained by creep test is the sum of elastic strain and creep strain. Elastic strain was determined by the strain that is related to the certain time. This certain time is the time that applied stress is fixed.

The creep strain of baked sample at 200°C and tested at room temperature has been plotted in figure 9. During 5 hours of creep test, three types of creep are visible in this diagram, transient creep (primary creep), steady creep (secondary creep) and accelerating creep (tertiary creep). As seen in figure 10, strain rate is high at first but decreases in primary stage and approximately is constant in secondary stage and increases in tertiary stage.

The result of the room temperature test for sample baked at 250 °C is shown in figure 11. During 12 hours with load of 6MPa, it seems that transient creep stage has not finished yet. Comparing creep behaviour of samples baked at 200 °C and at 250 °C shows that creep strain of the first is very much larger than the second. This is related to the binder viscosity that is higher for the sample baked at 250 °C. Also, there could be a large change in viscosity associated with vaporization of pitch species at 243 °C [6]. After four hours, there is an increase in creep strain 1.725 to 1.755 which would be related to thermal variation of laboratory.

Creep strain obtained for the sample baked at 500 °C and tested at ambient temperature is illustrated in figure 12. Primary and secondary creep has taken place successively during 4.5 hours. After 4.5 hours, fluctuations are observed in creep strain. The applied load and obtained displacement were checked in the recorded data. The applied load was constant during the test and the recorded displacement showed the similar variation as figure 12. The fluctuation in creep strain would be related to the thermal

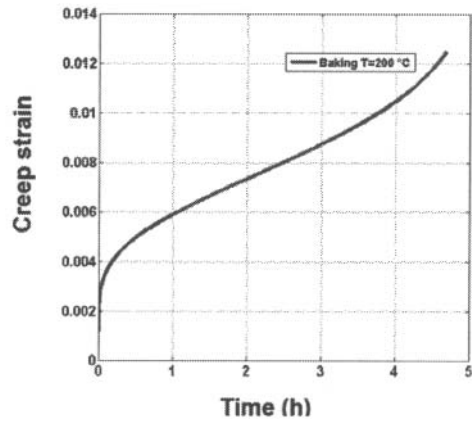


Figure 9. Creep strain of baked sample at 200 °C and tested at room temperature.

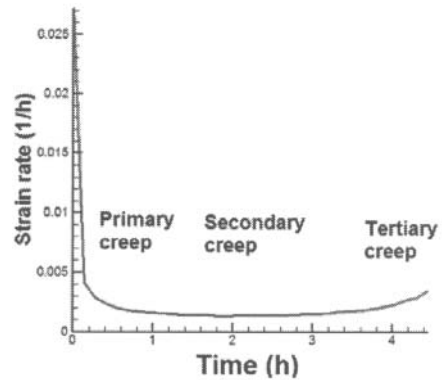


Figure 10. Strain rate of baked sample at 200 °C and tested at room temperature.

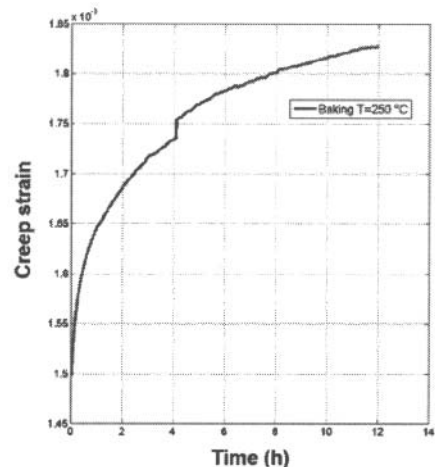


Figure 11. Creep strain of sample baked at 250 °C and tested at room temperature.

variation in the laboratory or to the disturbance by the external force applied to the quartz rods of the machine.

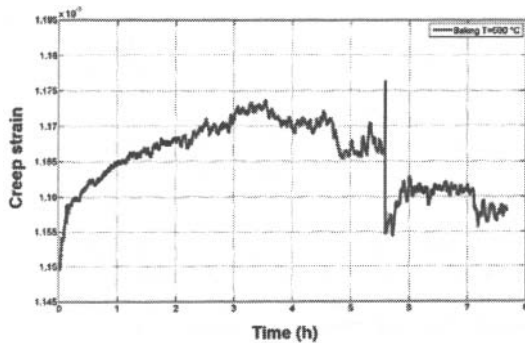


Figure 12. Creep strain of baked sample at 500°C and tested at room temperature.

The result of creep test at room temperature for the sample baked at 1000 °C is shown in figure 13. During 20 hours, two stages of creep, primary and secondary, have happened successively. After 20 hours, creep strain decreased. It seems that the third stage of creep has started.

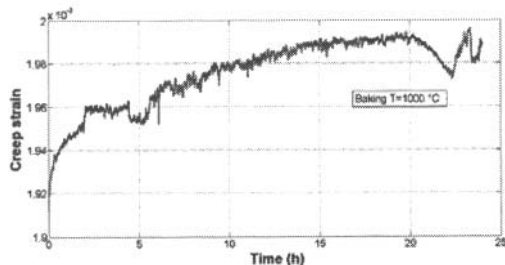


Figure 13. Creep strain of sample baked at 1000 °C and tested at room temperature.

As it is observed in figure 14, complex behaviours for different baking temperatures have been obtained for room temperature tests. Maximum logarithmic specific creep strain is reported for baking temperature of 200 °C and minimum one is related for 250 °C. The most important point is that the logarithmic specific creep strain for baking temperature of 1000 °C is lower than that of 200 °C and higher than 250 and 500 °C. This could be associated with baked density, binder viscosity or binder carbonization.

In figure 15, transient and part of steady creep zones resulted from room temperature test for different baking temperatures have been compared. In this graph, total strains obtained from room temperature test have been normalized to the applied stress. As seen, the duration of transient creep stage is the largest for baking temperature of 200 °C. Also, the duration of transient creep stage decreases by increasing baking temperature. Hence, creep level in transient zone at lower baking temperature is larger than that at higher baking temperature. For three baking temperatures of 250, 500 and 1000 °C, strain rate in steady zone is very much smaller than the strain rate at baking temperature of 200 °C. This would be related to the low binder viscosity at baking temperature of 200 °C.

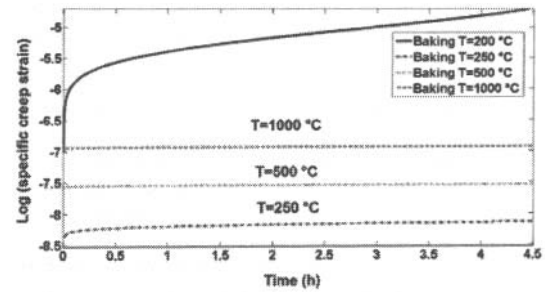


Figure 14. Logarithmic specific creep strain for ramming paste at different baking temperatures.

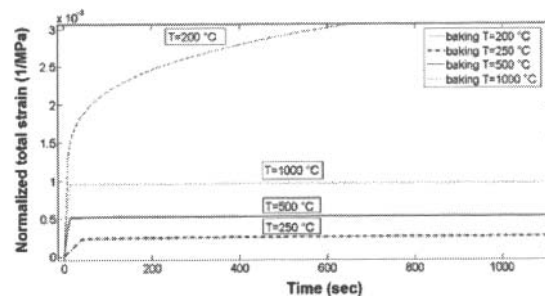


Figure 15. Part of viscoelastic zone for different baking temperatures.

High temperature tests

The creep test for sample baked at 200 °C and tested at 160 °C was not performed. Applying a preload of 0.097 MPa at this temperature for one hour, crushed the sample. The compressive strength at 160 °C for baked sample at 200 °C was lower than 0.097 MPa while the minimum value measured by the press was 0.097 MPa. To this end, compressive strength couldn't be determined and creep test wasn't carried out due to lack of compressive resistance. In figure 16, the crushed sample at 160 °C and then cooled are shown from left to right respectively. The sample has crushed from middle due to compressive load; this is similar to the rupture of green sample.

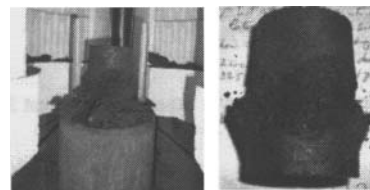


Figure 16. Crushing the baked sample at 200 °C under the load of 0.097 MPa at 160 °C, hot and cooled, left to right.

For the sample baked at 250 °C, high temperature creep test was performed at 200 °C. The press load in this test was set up to 3.74 MPa (40% of its compressive strength). At 200 °C, under this load, the sample has been crushed after 11 minutes (figure 17). It has been ruptured from external surface at 200 °C. This seems to be related to this reason that the external surface is weaker than central part of the sample. The weakness of external surface

would be related to this fact that the volume of gas escaping from external surface is higher than that in central part of the sample consequently porosity volume increases in external surface. This type of rupture (comparing with figure 16) would be contributed to the waking of wing cracks. When a crack is inclined to the (major compressive) loading direction, wing cracks will be developed. Tensile stress induced by the slip along the crack is the origin of wing cracks (figure 17.b). Behind the cracked external surface, inclined cracks were observed in the remaining part of the sample. This is what we call wing cracks [8].

Three stages of creep have happened successively in creep test at 200 °C for baked sample at 250 °C. The result of this test has been compared with room temperature one (figure 18). The press was set up for 6 MPa (40% of its compressive strength) at room temperature test. Comparing two curves of specific creep strain, one sees that creep at room temperature is relatively quite small. High level of creep at 200 °C is due to the lower viscosity of binder.

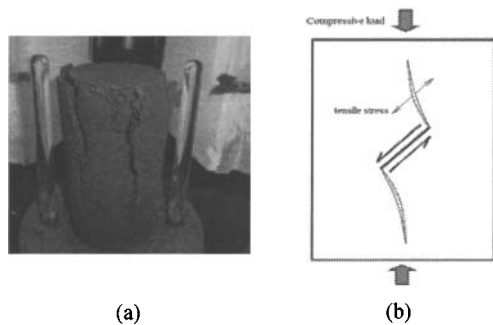


Figure 17. a) Crushed sample during the creep test at 200 °C for baking temperature of 250 °C, b) Schematic of typical wing crack propagation under compression.

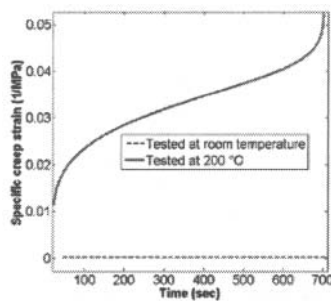


Figure 18. Specific creep strain for sample baked at 250 °C and tested at 25 and 200 °C.

Conclusion

Creep of ramming paste during baking process was studied and new results were obtained. For room temperature tests at various baking temperatures, complex creep behaviours were observed. At loading to 20% of compressive strength of the baked sample, it is difficult to draw firm conclusions about how baking temperature influences creep strain. For instance, increasing baking temperature from 200 to 250 °C has decreased the specific creep strain very much. However, specific creep strain of baked sample at 1000 °C is larger than that of baked sample at 250 °C and 500 °C. This may be associated with porosity percentage and

carbonization of binder pitch and binder viscosity. Finally, based on the results of creep test at elevated temperature for baked sample at 250 °C, one sees that creep level is higher than that in room temperature test that is related to viscosity of binder pitch. Also, creep level of baked sample at 200 °C and tested at 160 °C is too high. To avoid thermal variation during the test period in room temperature tests, the furnace will be set up to constant temperature.

As future work, high temperature creep test for samples baked at temperatures higher than 250°C will be performed. Also, the effect of porosity evolution on the creep behaviour of the ramming paste and creep of the ramming paste at temperature lower than 200 °C will be studied.

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