

Light Metals 2014

**ELECTRODE TECHNOLOGY FOR
ALUMINUM PRODUCTION**

Cathode Materials and Wear

SESSION CHAIR
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Pacific Aluminium
Brisbane, Australia

ROOM TEMPERATURE CREEP BEHAVIOUR OF RAMMING PASTE BAKED AT DIFFERENT TEMPERATURES

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Keywords: Aluminium Electrolysis, Cold Ramming Paste, Creep, 3D Mechanical Characterization, Room Temperature

Abstract

To simulate the thermo-mechanical behaviour of ramming paste in aluminium electrolysis cells, experimental data are required to feed 3D constitutive models. Both axial and radial strain measurements are necessary to design constitutive laws and to identify the parameters. However, radial strains are difficult to obtain at high temperature due to limitations of measuring devices. Moreover, samples need to be sufficiently large to acquire significant radial strain amplitude. Hence, the creep behaviour of ramming paste was studied at room temperature so the radial behaviour could then be extrapolated for the high temperature case using the axial strain evolution as a function of the temperature. Mechanical properties of ramming paste, baked at temperatures ranging from 250 °C to 1000 °C, were measured at room temperature. Uniaxial creep tests were performed at three different stress levels for each baking temperature.

Introduction

The ramming paste, employed in the aluminium electrolysis cells, serves a critical purpose to the proper functioning of the cell. It must fill and seal voids between cathode blocks and between sidewall arrangement and cathode end lining, referred to as the joints and the peripheral seam. Poor conditions of these rammed zones may lead to infiltration of liquid bath and molten aluminium into the lining, often resulting in early pot failure [1]. Furthermore, ramming paste has to absorb the thermal expansion from the prebaked cathode blocks. The paste goes also through a series of chemical and physical changes during the preheating and start-up process. To ensure smooth operation and to increase the cell lifespan, the composition and properties of the chosen paste must be well known.

The behaviour of the ramming paste changes drastically as the temperature rises from ambient to operational temperature. It is initially soft and viscous, due to softeners added to the coal tar-based binder. These additives allow the paste to be rammed below the softening point of the coal tar pitch. Between 250 and 350 °C, volatilization starts as the paste simultaneously loses mass and swells due to a build-up of reaction gases. From 350 to 450 °C, the emanation rate increases until an inflexion point is reached. Volatilization rate is at its highest between 450 and 550 °C. Then, the ramming paste shrinkage, caused by the carbonization of the binder phase, begins while the mass loss reaches a plateau [2]. Dehydrogenation occurs until the solidification of the binder is finally completed and the ramming paste is fully baked. The various transformation stages of the paste are influenced by its composition, density, and the heating rate during baking but mostly by its final baking temperature.

Developing a constitutive model of the ramming paste to simulate its thermo-mechanical behaviour during the preheating of the cell is a complex task. The microstructural changes during baking affect its macroscopic mechanical behaviour. Moreover, prior to the complete baking of the rammed parts, the paste is compressed by the neighboring components of the cell due to their thermal dilation and thus, it experiences creep. Consequently, a representative model must take into account the visco-elastic behaviour of the paste, since creep of the ramming paste is an important phenomenon, especially at low baking temperatures [3]. In order to feed a three-dimensional creep model, experimental data including radial strain measurements are thus required.

Few experiments and observations related to the visco-elastic behaviour of the ramming paste have been performed, and very few are in the transverse direction. Orangi et al. [3] have investigated the ramming paste axial creep behaviour with tests carried out at both ambient and elevated temperatures. For samples baked at 200, 250, 500 and 1000 °C and tested at room temperature, it was shown that the duration of transient creep stage decreases by increasing the baking temperature. On the other hand, results revealed that the creep level is higher at elevated testing temperatures. From 200 to 450 °C, the rise in temperature softens the binder, which has a significant influence on the creep level. Similarly, to confirm the time-dependent behaviour of the ramming paste, D'Amours [4] performed a relaxation test (dual behaviour of creep) on a sample baked at 250 °C and tested at room temperature. In addition to stress, they also measured axial and radial strains. Under an axial loading of 50% of the compressive strength, substantial creep in the transverse direction was observed. This observation suggests that in order to develop a valuable creep model, more attention should be paid to the ramming paste radial behaviour.

To gain better knowledge on the mechanical properties of ramming paste and its visco-elastic behaviour, more experimental data are needed. Many compression tests were conducted to assess the effects of baking temperature on compressive strength, Young's modulus, Poisson's ratio, and damage coefficients. Additionally, to obtain new information on transverse behaviour of the ramming paste, uniaxial creep tests at room temperature under different stress levels were performed on samples baked at different temperatures. In order to acquire significant radial strain amplitude, the tests were carried on cylindrical samples twice as large as that specified by standard procedure ISO 17544:2004 [5]. To achieve large and evenly compacted samples, the ramming paste was compacted in multilayers. Employing this method, the green apparent density of the fabricated samples was obtained to be comparable to the average density of a representative assembly

of the peripheral seam [6, 7]. The obtained results give new insights on the mechanical properties of the ramming paste at room temperature, considered as the reference state.

Methodology

Sample fabrication

Four-inch cylindrical ramming paste samples were rammed in multilayer employing a procedure presented by St-Arnaud et al. [7]. This procedure, inspired from the ASTM D15570-09 standard [8], provides samples with dimensions of 101.6 mm (4 in) in diameter and about 203 mm (8 in) in height. The ramming paste is compacted in a split cylinder steel mold having the specified internal dimensions. The mold base plate was adapted to fit on the indexation plate of the apparatus employed, as illustrated in Figure 1. A mechanical rammer of 50.8 mm (2 in) diameter, operating in a circular pattern, falls repeatedly and freely through a distance of 457.2 mm (18 in) over the tamped surface. The 2.49 kg (5.5 lb) rammer covers the whole specimen surface in two turns. Eleven layers, of 275 g of cold ramming paste per layer, are poured one at a time after each round of compaction consisting of 14 impacts per layer. Finally, the last tamped layer is completely trimmed from the sample to remove the weakest part whose green apparent density is lower than the sample average. Samples apparent densities were then measured according to ASTM D5502-00 [9], using a precision balance (Sartorius CPA16001S) and a caliper (Mitutoyo CD-12" PSX).



Figure 1. Apparatus used for ramming paste compaction: Proctor Mechanical Rammer

Sample baking and preparation

The green ramming paste specimens were baked at 7 different baking temperatures: 250, 350, 460, 500, 560, 750 and 1000 °C. As specified in the ISO 20202:2004 standard [10], the heating rate was set at 35 °C/h between room temperature and 500 °C, and subsequently at 100 °C/h between 500 and 1000 °C. To avoid

oxidation, samples were placed in a steel box containing 4 specimens all covered with coke. The measured average green and baked apparent densities for each baking temperature are presented in Table I.

Table I. Green and baked apparent densities of the samples used for mechanical characterization

Baking temperature (°C)	Green apparent density		Baked apparent density	
	Average (g/cm ³)	Standard deviation (g/cm ³)	Average (g/cm ³)	Standard deviation (g/cm ³)
250	1.608	0.004	1.560	0.003
350	1.600	0.006	1.488	0.005
460	1.601	0.005	1.433	0.002
500	1.598	0.003	1.427	0.003
560	1.606	0.004	1.432	0.003
750	1.602	0.004	1.434	0.003
1000	1.606	0.003	1.434	0.002

Once baked, samples were cut and machined to ensure parallelism between both end surfaces. Samples baked below 500 °C were also cut but they were provided with sulfur capping, due to poor surface finish from machining. A surface preparation with epoxy (M-Bond adhesive resin, Type AE, Vishay Micro-Measurement) was performed on specimens baked at 560, 750 and 1000 °C to apply strain gages on even and smooth surfaces (Vishay Micro-Measurements, N2A-06-10CBE-350). Extensometers (MTS 632.11F-90) were used for the strain measurements of the 350, 460 and 500 °C samples.

Compression tests

All compression tests were carried out at room temperature using a MTS 311 load frame equipped with a 250 kN load cell. To evaluate the Young's modulus and Poisson's ratio, tests were carried out under a load corresponding to nearly 20% of the compressive strength (elastic domain). For damage tests, the cyclic loading was increased by 2 MPa per load step for the 560, 750 and 1000 °C cases, and by 1 MPa per load step for the others. All samples were then loaded until rupture occurred. The loading rate was set to 0.15 MPa/s as indicated in the ISO 18515:2007 standard [11].

Creep tests

Creep tests were carried in a closed chamber at a carefully controlled temperature of 25 °C, for three different baking temperatures and stress levels. Chamber temperature was controlled using a forced air convection system using heaters and fans to significantly reduce the temperature variations within the enclosure. This system was necessary to eliminate temperature variations caused by the laboratory temperature control system. Nonetheless, thermocouples were placed nearby every tested sample to keep track of the slight temperature changes in the chamber. A reference sample was also placed in the enclosure for data corrections. The custom-made test bench employs compressed air to apply the load via the air actuator. A load cell of 889.6 kN (200 000 lbf) is located at the bottom of the bench, upon which is placed a steel plate to stack steel spacers (adjustment for height) and the samples. As shown in Figure 2, four samples mounted in column, were tested simultaneously for every stress level. To avoid the bending of the columns, close attention was paid to their proper alignment. The baking temperatures chosen to

evaluate the visco-elastic behaviour of the ramming paste and respective stress levels are indicated in Table II. They were chosen in order to evaluate the effect of carbonization on the creep level.

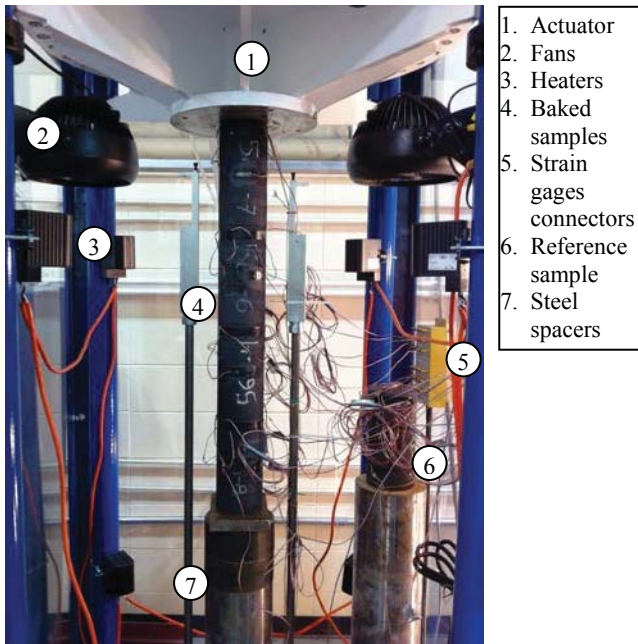


Figure 2. Layout of the samples during the creep tests

Table II. Applied loads for creep tests at different baking temperatures

Baking temperature (°C)	Stress applied (MPa)
560	3, 4, 6
750	4, 6, 8
1000	4, 6, 8

Results and discussion

Mass loss

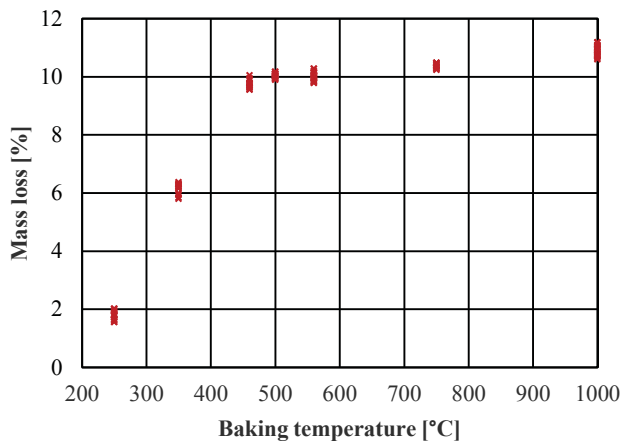


Figure 3. Percentage of mass loss of all the baked samples

The results shown for the mass loss of the baked samples, in Figure 3, are consistent with the thermogravimetric tests conducted on ramming paste for different heating rates by Tremblay et al. [12], and Bouchard [2]. The mass loss is slightly higher in the present case, which could be related to the difference in the initial mass or binder content and composition. At first, the evolution is fairly linear from 250 to 460 °C, while volatilization of reaction gases such as methane and low molecular weight polycyclic aromatic hydrocarbons (PAH) occurs. Afterward, mass loss reaches a plateau, around 500 °C as expected. As the carbonization progresses around 560 °C, the dehydrogenation and emanation of PAH with high molecular weight takes place until the samples are fully baked. At the same time, the mass loss slowly increases at a constant rate. Even if the mass is decreasing during this period, the density is still marginally increasing between 500 and 750 °C since shrinkage occurs.

Compressive strength

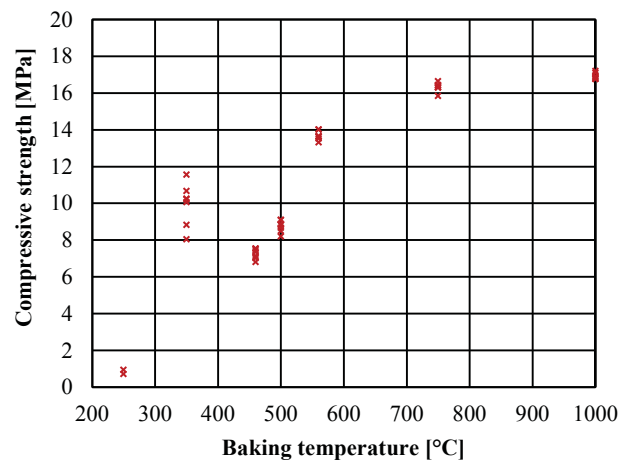


Figure 4. Compressive strength as a function of baked temperature

The compressive strength of the ramming paste depends definitely on the baking temperature, as seen in Figure 4, and can be explained by a combination of different factors. The first factor obviously is the mass loss. In addition, the carbonization, thereby changing the microstructure of the binding matrix, affects the samples. As shown, the mechanical strength increases considerably, from approximately 7 to 14 MPa, when baking temperature increases from 450 to 560 °C. Meanwhile, the mass loss difference is very low at this temperature range, which coincides with the beginning of carbonization. The cause of variations within the 350 °C data is however unclear. At lower baking temperatures, unfinished reactions or uneven swelling could be involved. Also, the greater remaining amount of coal tar pitch within the specimens below 460 °C might increase compressive strength marginally as pitch is harder at room temperature. This would explain the difference obtained for values at 350 °C compared to the subsequent baking temperatures, prior to carbonization. At 250 °C, although the baked densities are the highest, few reactions have occurred and the paste remains close to its green appearance, which explains its poor compressive strength.

Young's modulus

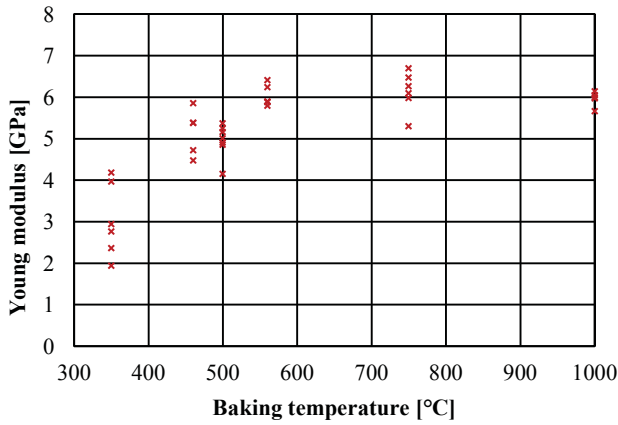


Figure 5. Young's modulus as a function of baked temperature

The evolution of the Young's modulus of the ramming paste with baking temperatures is presented in Figure 5. A minimum of four samples for each temperature were tested to assess the behaviour of the elastic part. As the compression tests were conducted at room temperature, the remaining coal tar pitch might have an influence on the Young's modulus for baking temperatures below 500 °C. As shown, some values for 460 °C are somewhat higher than those at 500 °C. The variations within each set of data could be attributed to the location of the measuring devices. Misaligned strain gages or extensometers on a specimen would also lead to such disparities. For baking temperatures above 500 °C, the development of porosity during the carbonization process might affect the values as well. It would explain the lower Young's modulus measured for 1000 °C compared to 750 °C.

Damage coefficients

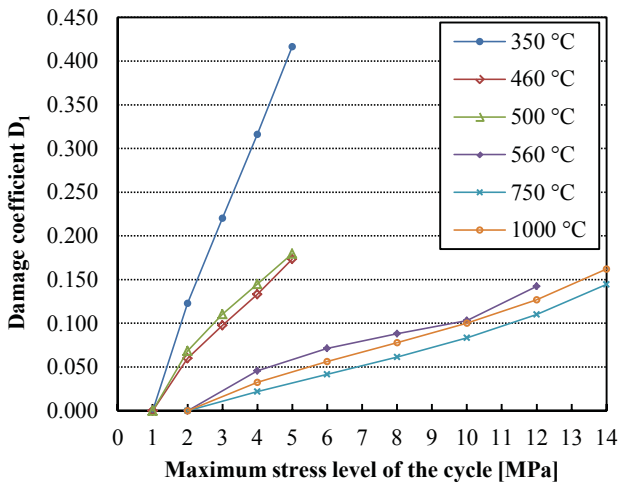


Figure 6. Evolution of the axial damage coefficients as a function of the maximum applied stress of a cycle for different baking temperatures

The axial damage coefficients have been calculated by applying a cyclic loading. The load steps were of 2 MPa (for samples baked at 560, 750 and 1000 °C) or 1 MPa for the more fragile samples

(baked at 350, 460 and 500 °C), as presented in Figure 6. Each step is repeated three times and the average slope of the second and third cycles are used to estimate the damage. The coefficients are calculated using equation 1:

$$D_1 = 1 - \sqrt{\frac{E_d}{E}} \quad (1)$$

where E is the undamaged static Young's modulus and E_d is the damaged value. E_d represents the degradation due to the damage induced in the material [13]. As shown, the degradation of the ramming paste is proportional to the applied stress. The observed damage is fairly linear. For a baking temperature of 350 °C, the damage coefficients increase rapidly, even at low stress levels. Samples baked at 460 and 500 °C are very similar and exhibit a lower degradation rate. Lastly, the 560, 750 and 1000 °C cases show comparable damage coefficients with the lowest values, compared to the stress level applied.

Poisson's ratio

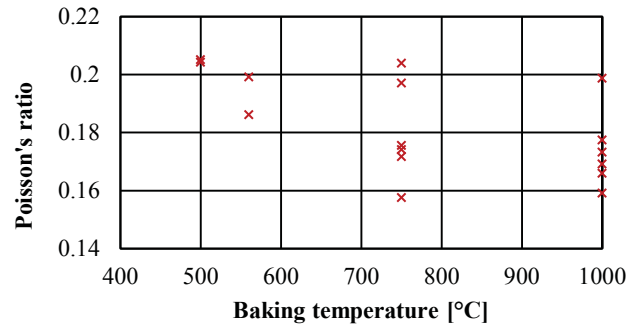


Figure 7. Poisson's ratio as a function of the baking temperature

The Poisson's ratio (Figure 7) was measured during the compression tests on baked samples provided with strain gages. Conversely to the Young's modulus values, the Poisson's ratio initially at nearly 0.5 for unbaked ramming paste decreases hastily by rising the baking temperature. During the latter process of baking, the data obtained for temperature above 500 °C show that the Poisson's ratio tends to stabilize around 0.17.

Creep tests

A typical creep curve at constant temperature is shown in Figure 8, which defines different regions of the curve.

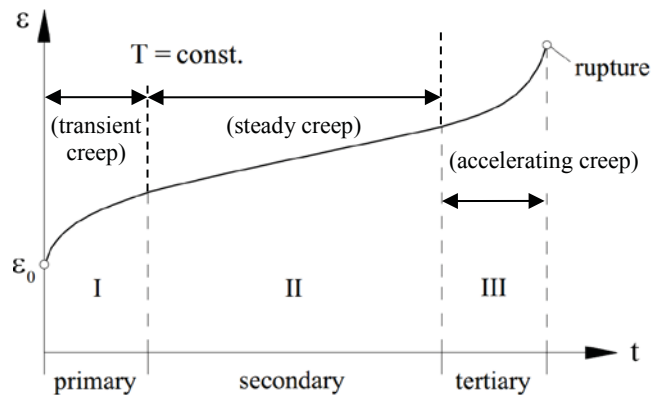


Figure 8. Typical creep curve at constant temperature [14]

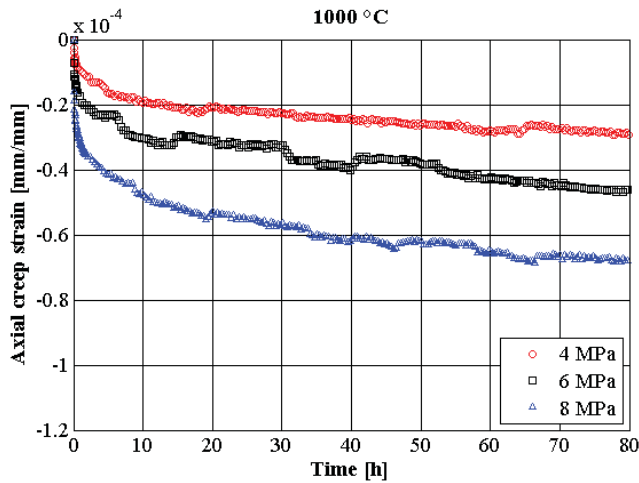


Figure 9. Axial creep strain for samples baked at 1000 °C

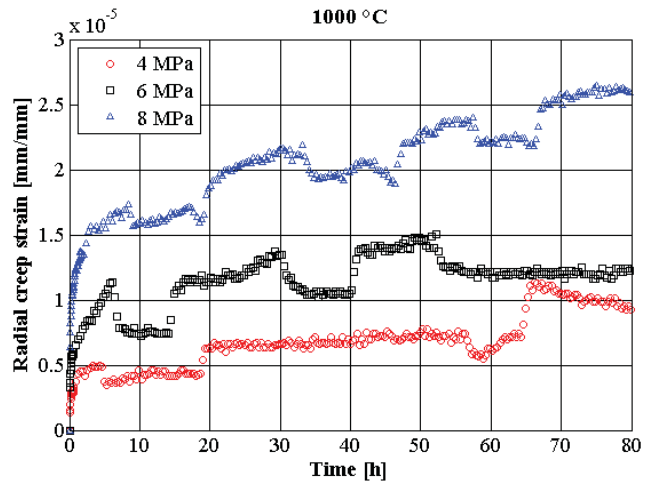


Figure 12. Radial creep strain for samples baked at 1000 °C

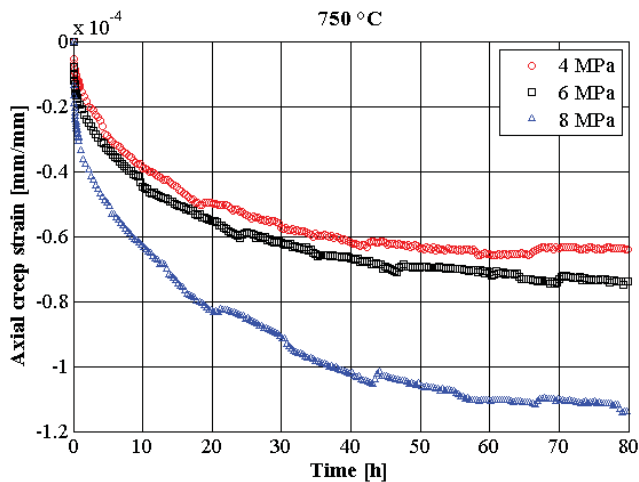


Figure 10. Axial creep strain for samples baked at 750 °C

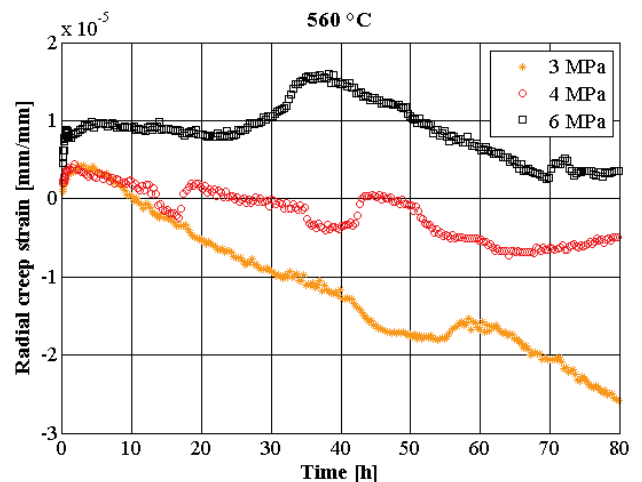


Figure 13. Radial creep strain for samples baked at 750 °C

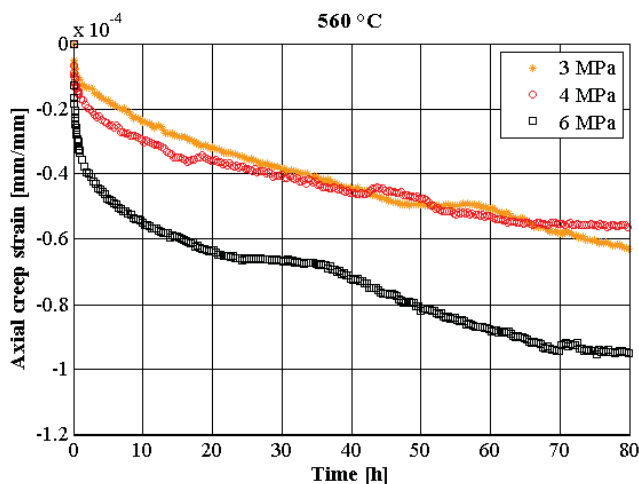


Figure 11. Axial creep strain for samples baked at 560 °C

Figures 9-13 show the axial and radial creep behaviours of the samples tested at room temperature and under a constant load. The results correspond to the axial and radial strain averages given by the strain gages on the whole column (four samples). The elastic part was removed. No data corrections were applied for temperature. The control sample temperature, given by its thermocouple, differed from those of the specimens in the column. Thus, corrections for temperature would induce more noise in the recorded signals. Even if the temperature variations within the test bench enclosure were significantly reduced by the temperature control system, the environmental conditions affected the data, mostly for the measured radial creep strain. The results presented in Figure 13 shows how difficult it is to observe the transverse creep while the measured strains are small, mainly at low stress levels. In addition to testing temperature, other factors such as the preparation method (epoxy), the column alignment, the strain gage positioning, may also influence the data. More investigation is needed to identify the main source of decreasing radial creep strains observed within the data for the baking temperatures of 560 and 750 °C.

Although the radial creep strains obtained for the 1000 °C case are low and slight temperature variations occurred (Figure 12), the

data are consistent with what is expected by increasing the stress level. At 4 MPa, the strain rate decreases very quickly and the steady creep (Region II) is reached first. At 6 MPa, the strain rate is much higher at the beginning and takes more time to stabilize. Finally, at 8 MPa, the highest radial creep strain was measured and the transient creep part (Region I) observed is the longest. The strain rate is also higher in the secondary creep region.

The results obtained for axial creep strain show the same behaviour (Figures 9, 10 and 11). As the applied stress increases, damage become more important and the creep strain grows. This phenomenon might explain the drastic rise shown on the 560 and 750 °C data, at respectively 6 and 8 MPa. On the other hand, the baking temperature also influences the creep level. Comparing the curves for 6 MPa at all temperatures, the 560 °C case exhibits the highest axial creep strain after 80h (-95 $\mu\epsilon$), then 750 °C (-74 $\mu\epsilon$) and the 1000 °C case has the lowest (-47 $\mu\epsilon$). Hence, the carbonization occurring above 500 °C has a significant importance on the creep level of ramming paste for a constant applied stress.

Conclusion

Compression tests were carried out in order to assess the mechanical behaviour of the ramming paste at ambient temperature, considered as the reference state. The specimens were consolidated employing a new compaction method to obtain larger size samples [7], which were necessary to acquire significant radial strain amplitude. They were then baked at different temperatures ranging between 250 and 1000 °C. The results showed the strong correlation between the baking temperature and the mechanical properties. The compressive strength and the Young's modulus increase considerably with an increase in baking temperature. Most changes within the ramming paste occur early during the heating process, i.e. prior to the beginning of the coal tar based binder's carbonization. Damage tests were also carried out to assess the evolution of the axial damage coefficients for different stress levels and baking temperatures. It was shown that the axial damage is important, even at low stress levels, for samples baked at 500 °C and below. Poisson's ratio was measured as well for samples baked at 500 °C or higher. The values obtained varied around 0.20 for the 500 °C sample and 0.17 for the fully baked samples.

In order to feed a three-dimensional creep model, creep tests were performed at room temperature on samples baked at 560, 750 and 1000 °C, at three stress levels. The radial creep strains were influenced mainly by temperature fluctuations within the creep test bench enclosure. Only the 1000 °C samples showed the expected behaviour. From the axial creep strain results, it is concluded that increasing the stress level extends the primary creep, increases the strain rate and step up the final creep strain measured after 80 hours. It was found that baking temperature has also a significant importance on the creep level. Comparing for the same applied stress, samples baked at 560 °C exhibit the highest axial creep strains at the end of the test while the lowest were given for 1000 °C.

Acknowledgements

The authors gratefully acknowledge the financial support provided by Alcoa Inc. and the Natural Sciences and Engineering Research Council of Canada (NSERC). A part of the research

presented in this paper was financed by the Fonds de Recherche du Québec-Nature et Technologies (FRQNT) by the intermediary of the Aluminium Research Centre – REGAL. Particular thankfulness is dedicated to Hugues Ferland, from the REGAL group at Université Laval, for his technical support. Also, authors wish to express their gratitude to Gregory Espagnet, trainee with the REGAL group, for his help with the experimental procedure.

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