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STRUCTURAL CHARACTERISATION AND THERMOPHYSICAL PROPERTIES OF THE SIDE LEDGE IN HALL-HÉROULT CELLS

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Abstract

In the modern Hall-Héroult cells, a frozen bath layer – the side ledge – protects the sidewalls from the very corrosive liquid bath. This frozen bath layer has a significant impact on the heat balance of the cells as well as on the bath chemistry. For this reason, the geometry, the structure, the distribution of the chemical composition and certain physical properties of the side ledge must be studied. Those characteristics are important to the development of a mathematical model for the Hall-Héroult cells. Despite of all the research efforts invested, only a few results are available in the published literature. This paper presents a few results and observations, obtained by the analysis of side ledge samples, extracted from post-mortem cells. The results show a very inhomogeneous structure and a strong dependence of the thermo-physical properties on material structure and temperature.

Introduction

The side walls of the Hall-Héroult cells must be protected by a frozen bath layer (side ledge) from the highly corrosive electrolyte. For this reason, some energy is sacrificed by increased lateral heat loss in order to extend the life period of the cells. As a good insulator and phase change material, the side ledge plays an important role in the heat balance and the thermal stabilisation of the cells. Furthermore, the composition of the side ledge is somewhat different, compared to the electrolytic bath [1]. Consequently, the change of the thickness of the side ledge can significantly modify the composition (and thus certain physical properties) of the bath itself.

In the light of the above mentioned facts, the knowledge of the chemical and physical properties of the side ledge (such as distribution of chemical composition, structure, thermo-physical properties etc.) is crucial to any reliable thermal model of the aluminum reduction cells.

Lots of publications discuss about the thermal behaviour of the side ledge [2-7] but only very few detailed information can be found about the structure, the chemical composition and the thermal conductivity in the public literature. The main component of the side ledge is the cryolite – the compound with the highest liquidus temperature in the system – especially when the ledge is formed slowly, close to the equilibrium state [1]. However, the inhomogeneous appearance suggests that the side ledge has a more complex chemical composition. In all cases, it remains somewhat different compared to the bath, which contains excess AlF_3, CaF_2, alumina, other additives, carbon powder and dissolved CO_2. Such a difference changes the composition of the liquid layer next to the solidified bath, compared to that of the bulk and thus it affects the liquidus temperature at the interface of the solid-liquid phases [8]. Consequently, the estimation of the heat transfer between the solid-liquid phases becomes more complicated and the determination of the thermal conductivity of the side ledge becomes even more important.

In the frame of a cooperative project between Rio Tinto Alcan and UQAC, side ledge samples were extracted from post-mortem industrial cells, shortly after the shutdown of the operations. After preparation and adequate storage, those samples were used to carry out different chemical, structural and thermo-physical analysis. During certain tests, the samples were reheated to high temperatures, in order to create conditions similar to those found in industrial cell during their operation. In the present paper, a few results of this complete study are presented.

Sample collection and preparation

Cylindrical shaped samples were cut from the cold side ledge of a typical industrial cell a few days after its shutdown, using special equipment designed for this purpose. Samples with rotational axis normal to the cell wall were taken at different positions of the cell, namely at longer side, shorter side and corner, both at the bath and the metal levels. At certain locations, the side ledge was too fragile or too thin to be sampled. No water was used to the cooling of the sample during cutting, in order to avoid the chemical transformation of the side ledge as well as prevent toxic gas emissions.

Samples (including their orientation) were identified and put in hermetically closed barrels, filled with argon gas and containing some desiccant at the bottom in order to avoid any reaction with moisture or oxygen. Several tests were carried on those side ledge samples, but in this paper only the X-ray, dilatometric and thermal conductivity studies will be discussed.

X-ray tomography study

Two cylindrical shaped samples with dimensions of few centimeters, taken at the bath and the metal level respectively were used for this study. Analyses were carried out in a SkyScan 1172 X-ray tomographe, able to receive samples with dimensions not exceeding 10cm. As the resolution of the instrument is constant, the smaller is the sample, the finer details can be observed.

Dilatometric study

The thermal dilatation of cylindrical shaped samples (100mm height with a diameter of 12.5mm) in the range of 25 – 600 °C were tested under argon atmosphere, using UNITHERM™ 1101 (Anter Corp.) dilatometer. The measurement of this property is necessary to obtain the variation of the density of the side ledge as the function of the temperature. Density data are used when thermal conductivity is computed from the thermal diffusivity data obtained with the flash method.

Measures of thermal conductivity

The variation of the thermal conductivity of side ledge with the temperature was measured with the laser flash [9] and monotone heating methods [10]. The first uses small disc shaped samples (∅ 12.5 mm, thickness 3mm) and thus can determine local thermal conductivity. It is more and more used for inhomogeneous materials after minor modifications [11]. The second technique measures the global value of the apparent thermal conductivity of samples with relatively big volumes (∅ 100 mm, height must be at least 100 mm). The monotone technique is convenient even for highly porous or granular materials.

The flash technique involves the illumination of a disc shaped sample at one side with a short, high energy laser flash and the measurement of the thermal response on the opposite side (figure 1). With good design and an appropriate light source, the amplitude of the thermal excursion can reach a few degrees Celsius. The surfaces of the samples must be painted black and matte in order to achieve an emissivity as high as possible, close to 1. Design must minimize the heat losses due to the direct contact with the sample holder. Heat loss by radiation and convection must be included in the evaluation of the thermal response curves (figure 1).

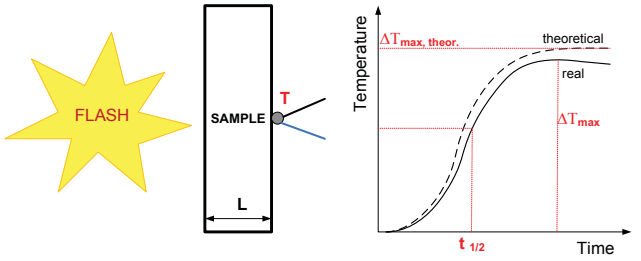


Figure 1. Principle of the laser flash method

In the present study, a FlashLineTH 5000 (Anter corp.) apparatus with infrared laser source and radiometric detector was used. The radiometer determined the average temperature of the rear surface. Measurements were carried out between 100 and 550 °C under argon atmosphere. Higher temperatures were avoided for security reasons. Namely, certain AlF_3 rich particles can melt even at 700 °C [12] that might damage the apparatus, especially the temperature detector. At least 3 samples were taken from every position and measurements were repeated 5 times at all temperature plateaus.

As a first approximation, the thermal diffusivity (α) can be determined simply from the sample thickness (L) and the time necessary to reach the half of the amplitude of variation of the temperature on the rear side of the sample ($t_{1/2}$). During the measurements we used the Clark and Taylor correction method to take into account the heat losses during the tests. To obtain the thermal conductivity (k), the density (ρ) and the heat capacity (C_p) must be known at the temperature of the test:

$$k = \alpha \rho C_P \qquad \text{equation 1}$$

The density can be determined by the dilatometer. The volumetric heat capacity ρCp can be obtained by the flash method itself, if a reference sample with known heat capacity is also used. The design of the apparatus and an identical surface coating must assure that the same amount of energy is absorbed by both the studied samples and the reference. Furthermore, their thermal conductivities must be in the same order of magnitude in order to minimize the error due to the heat loss.

The monotone heating (***MH***) method consists of a constant rate heating of the external surface of a cylindrical shaped sample with a relatively big volume and measuring, how the temperature in the middle of the sample follows it. The height of the sample must be at least three times bigger than its diameter. ***MH*** tests were carried out in an apparatus developed at GRIPS-UQAC [10], under argon atmosphere (figure 2). In order to compensate the end effect, a three-zone furnace is used. The studied sample was put in the central zone, while the top and bottom parts, containing sand were kept at the same temperature as the central zone using independently controlled heating elements. This solution – with the external isolation of the furnace – eliminates the axial heat flux and only the radial heat transfer is maintained. Temperatures at the center, the outer surface and in a certain radial position between them were measured with N-type thermocouples. The first two is necessary to measure the thermal diffusivity, while the third is necessary to obtain the heat capacity. The thermocouple at the outer surface also supplied the input signal for the controller.
As a limitation of this technique, the thermal conductivity can not be determined from the measured temperature curves:

- during the initial transition period under about 200 °C
- in all the temperature ranges where any energy producing or consuming transformation phenomenon takes place

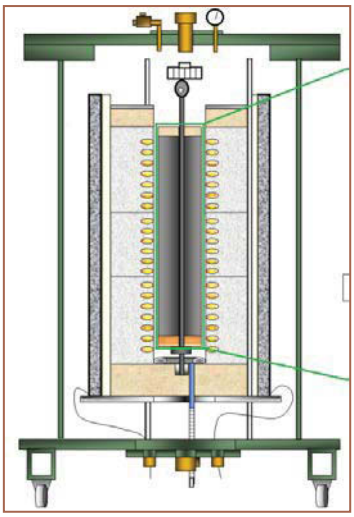


Figure 2. Schema of monotone heating apparatus

The optimal heating rate depends on the thermal conductivity of the sample and must be determined by preliminary tests. On one hand, a too slow rate results in very low temperature difference between the surface and the center that makes difficult the correct evaluation of the data. Furthermore, it increases the duration of the tests and the argon consumption. On the other hand, if too high heating rate is chosen, the elevated temperature gradient in the radial direction results in strongly varying thermal properties and once again, the analysis of the data becomes erroneous.

MH tests were carried out between 25 – 920 °C. Before all tests, the samples were heated up to 300 °C and cooled down to room temperature, in order to eliminate possible moisture content. In

some cases, the heating period was repeated three times with the same sample to verify hysteresis caused by the structural, crystalline and chemical transformations at high temperatures.

Results and discussion

X-ray tomography

The figures 3 and 4 show a few examples of the cross sections of the side ledge samples, taken from the bath and metal level respectively. As well known, the tomography reveals the cross sections of any sample after a treatment with image analyzing software of the X-ray apparatus itself. On the images, a whiter zone corresponds to the higher density material. Contrarily, the dark zones represent pores.

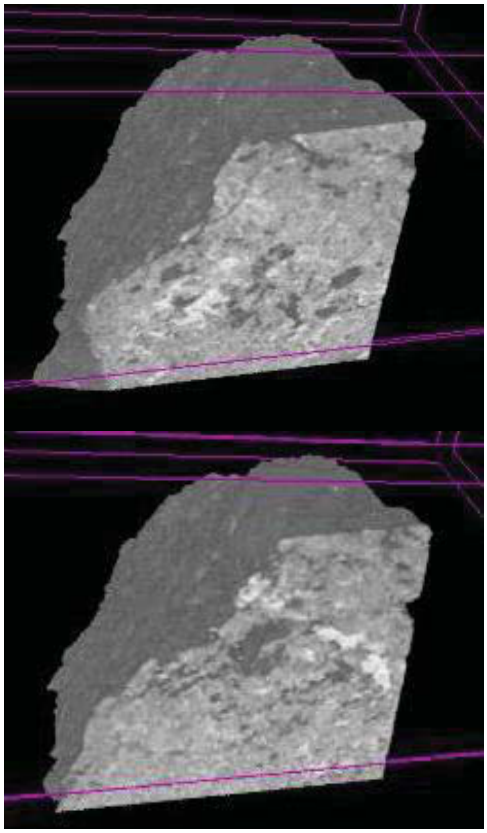


Figure 3. Examples of cross sections of side ledge sample taken from the bath level

The comparison of figures 3 and 4 reveals a significant difference between the structures of the side ledge taken at different height. Namely, the side ledge taken at the bath level seems to be very inhomogeneous, with lots of small pores and cracks, as well as with a few high density particles, mainly concentrated in the same zones. On the other hand, the structure of the side ledge originating from the metal level is much more homogenous with only a few cracks and “tunnels”. The two almost circular shaped holes on the figure 4 are the cross sections of two “tunnels”, joining farther in the sample. Those macroscopic voids and cracks were created very likely due to the shrinkage during the cooling down of the cell after shutdown. Such difference between the side ledges of different levels is in accordance with their different thermal behavior.

Figure 5 shows an example of the spatial and size distribution of the high density particles and dark zones (pores) in a thin layer of the side ledge sample taken at the bath level. Figures 5a and 5b were obtained from the same tomographic picture but using a different image treatment techniques. The blue lines in figure 5a were added later to indicate the approximate vertical boundaries of the sample. In certain cases, the high density particles have elongated, irregular column-like shapes that can indicate directional solidification. Both the high density particles and the pores have a big variety in size and shape.

No high density zones but only a few long ”channels” were found with this image treatment technique in the samples taken at the metal level (figure 6). The round-shaped dark zone at the top of figure 6 shows the contour of the examined sample.

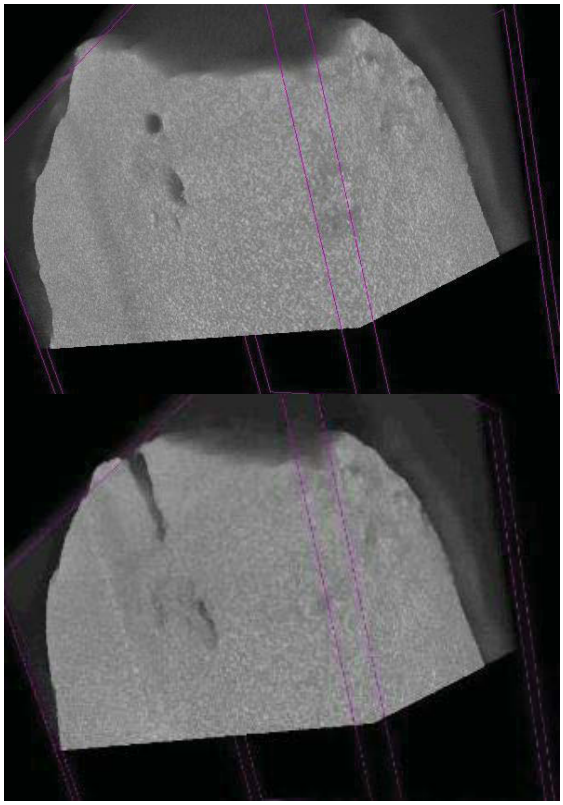
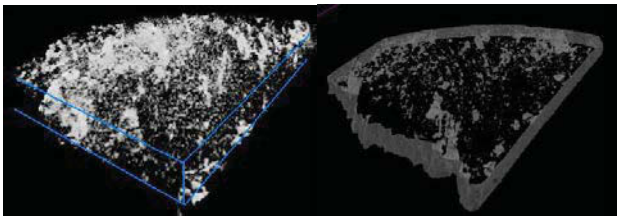


Figure 4. Examples of cross sections of side ledge sample taken at the metal level



a) b)

Figure 5. Three-dimensional image of the structure of a thin layer of the side ledge sample taken at the bath level, obtained with X-ray tomography; spatial and size distribution of a) the high density zones b) the pores

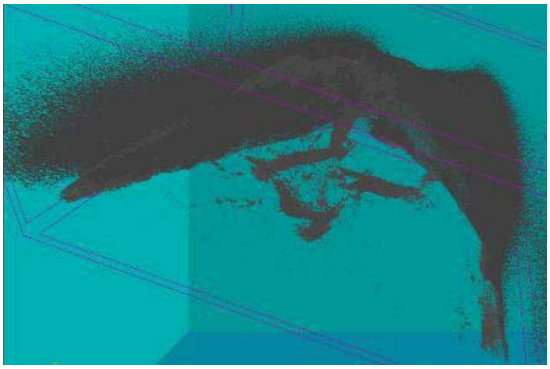


Figure 6. 3D image of the structure of the part of a side ledge sample taken at the metal level; distribution of the voids

Thermo-physical properties

In this section, only a few results are presented, using comparative thermal diffusivity data. Figure 7 compares thermal diffusivity data obtained with flash and monotone heating methods using side ledge samples taken at different positions around the cell wall, but in all cases at the bath level. The image within figure 7 shows the sample prepared for the monotone heating test. Two zones can be clearly distinguished, a dark one on the bottom-right side and a lighter colored one the top-left side. Thermocouples were inserted at the center and on both sides to measure simultaneously the thermal conductivity of those two different zones.

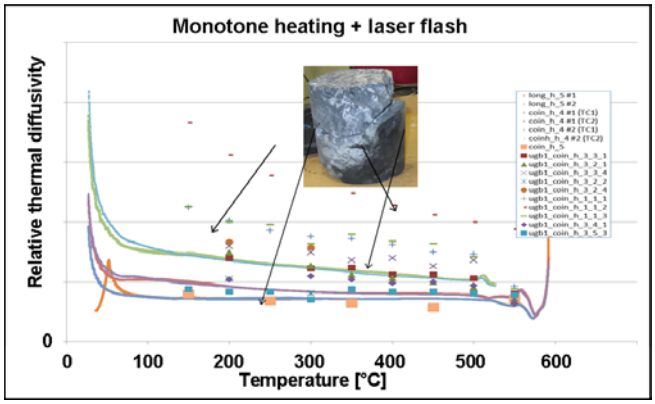


Figure 7. The variation of the thermal diffusivity of side ledge samples taken from difference positions at the bath level, obtained either with laser flash or monotone heating methods in the temperature range of 100 – 600 °C

The results show that the monotone technique – measuring the apparent heat conductivity on bigger samples – gives slightly lower values compared to the data obtained with the laser flash method. This is likely the result of the cumulative effect of the serially connected thermal resistances of a big number of consecutive pores and voids between the particles in the direction of heat flow.

The darker zone – situating generally closer to the cell wall and containing a bigger amount of carbon – seems to conduct better the heat, compared to lighter one. This tendency was confirmed with both techniques applied in this work. On the other hand, the thermal diffusivity data obtained with the lighter colored fraction of the side ledge from the bath level varies only slightly along the perimeter of the cell.

The thermal diffusivity seems to decrease slowly with the temperature in the range of 150-600 °C. The variation is a slightly stronger for the darker zone samples.

Figure 8 shows the variation of the relative thermal diffusivity of dark and light colored samples (took in all cases at the bath level) with the temperature in a larger temperature range. The downward peaks around 580 and 800 °C are related to endothermic phase transitions [11]. In those ranges, the real value of the thermal diffusivity can be estimated only by interpolation of the data. The difference between the thermal diffusivities of the dark and light colored zones diminishes when the solidus temperature is approached.

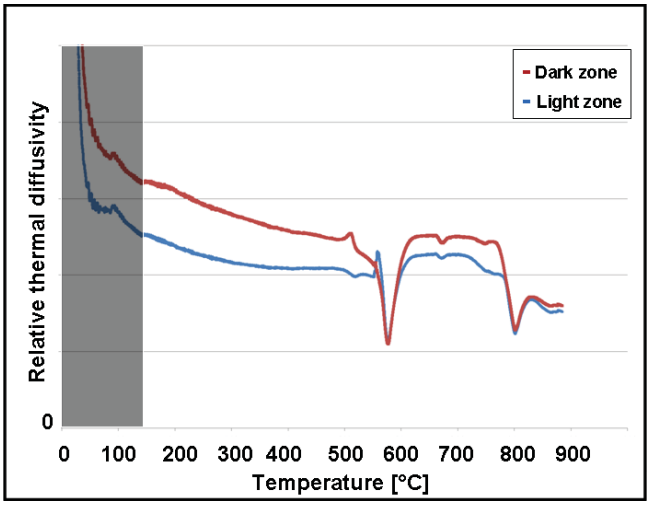


Figure 8. Evolution of the thermal diffusivity with the temperature in the range of 100 – 900 °C obtained with dark and light colored samples taken at the bath level

Conclusions

Post-mortem side ledge samples were taken from different horizontal positions and heights in real, industrial aluminum electrolysis cells a few days after the shutdown. A complete analysis of those samples revealed among others that:

- The structure of side ledge at the bath and metal levels is quite different. The first is very inhomogeneous and contains high density particles as well as a big amount of isolated voids with great variety of size and shape. The side ledge at the metal level is more compact and homogenous. It contains no high density particles and only a few interconnected cracks and ”channels” can be identified. Some of them are formed probably by thermal shrinkage during the cooling down of the cell after the shutdown and thus they do not exist in operating cells.
- The thermal diffusivity (and the thermal conductivity) decrease slightly with temperature. They vary only slightly with the perimetral position at the bath level. The darker zones – situated generally closer to the cell wall and containing a bigger concentration of carbon – conduct better the heat, compared to other regions.

Acknowledgment

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