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Aging of carbon materials for aluminium electrolysis at alternating temperatures

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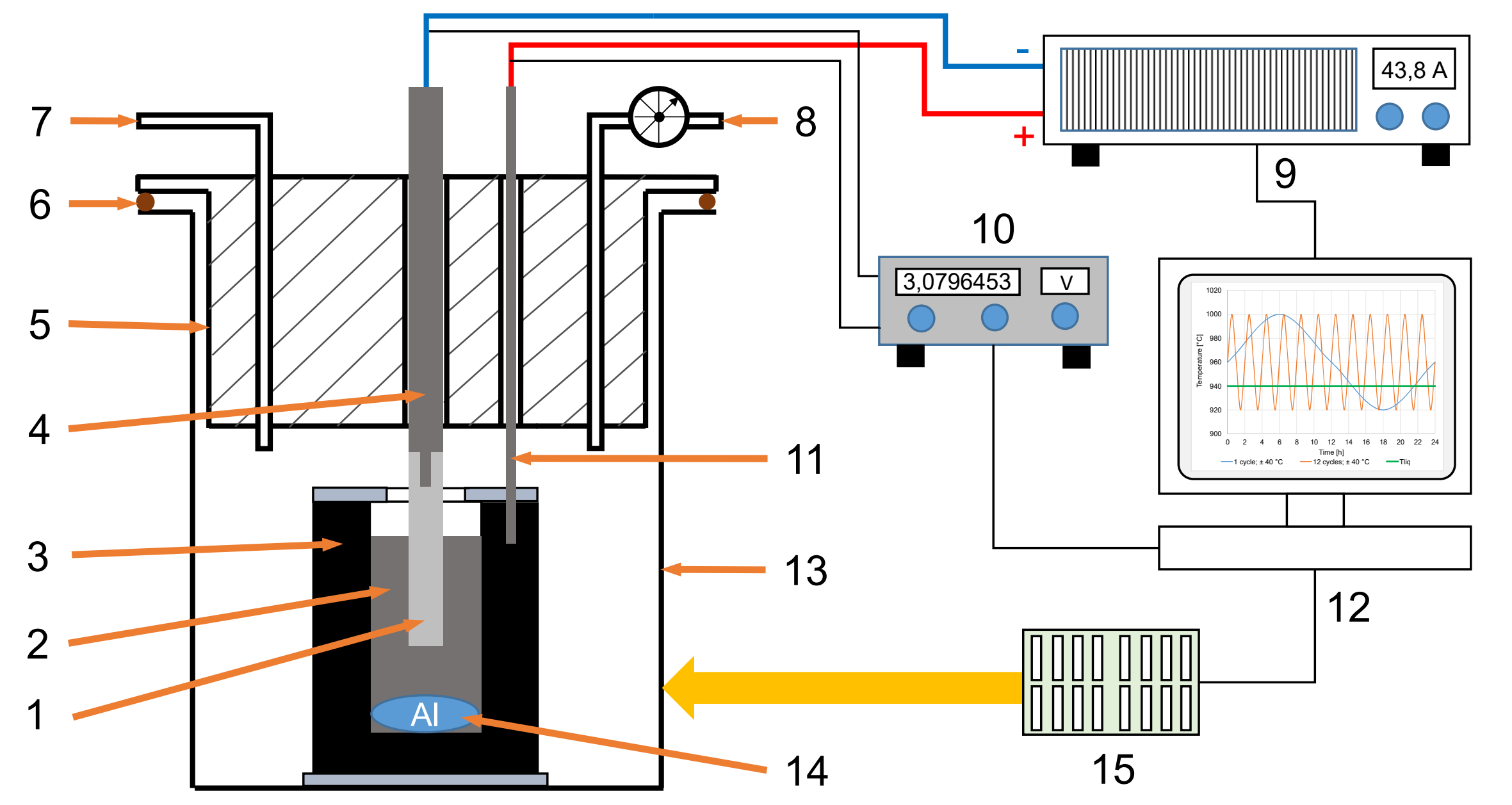
Motivation

For many years ongoing efforts have been made to optimize the manufacturing route for primary aluminium. Nowadays, the Hall-Héroult process is established as the worldwide standardized method to decompose alumina [1]. Global action to increase the amount of renewable energy has created new ideas in terms of industrial resources management. One of the latest developments in the aluminium industry has focused on the implementation of a controlled power modulation [2]. During operation the bottom lining of an electrolysis cell, usually called the cathode, is subject to a continuous wear process. Thus, the carbon cathode can be expected as a key component, determining the operational life span of a cell. While standard cells are basically designed for constant power supply, alternating power loads might boost this degradation process with respect to the alternating thermal loads. Regardless the latest cell design improvements, accelerated aging of the cathode material represents a high potential risk of a production shutdown. Since in situ measurements are costly and time-consuming, laboratory experiments are taken into account.

Experimental setup

A laboratory electrolysis cell was used for all experiments (Figure 1). A typical feature of this cell type is given by the arrangement of the electrodes in a reverse fashion. A graphite crucible serves as electrolyte container which is polarized anodically while a cathodically polarized cylindrical graphitic rod, the sample, which is dipped into the liquid bath from the top of the cell. A pool of pure aluminium is added to the bath initially. The cell is placed inside a muffle furnace under inert gas atmosphere and heated up to a temperature slightly above the liquidus temperature of the bath. A constant current was applied to the system as the resulting voltage was recorded by a high precision voltmeter.



1 Cathode
2 Electrolyte
3 Graphite crucible
4 Cathode connecting rod
5 Steel lid
6 Sealing cord
7 Inert gas inlet
8 Inert gas outlet with pressure gauge
9 Power supply
10 Voltmeter
11 Anode connecting rod
12 Workstation
13 Steel muffle
14 Aluminium reservoir
15 Temperature controller

Figure 1: Components of the laboratory electrolysis cell

Wear results

The diameters of the sample were determined before and after each experiment. Therefore the excessive solidified bath was removed from the surface of the sample. Horizontally fixed inside a dividing spindle, the diameters were measured at each millimeter in longitudinal direction with a laser micrometer (Figure 2). Figure 3 shows a typical wear profile.

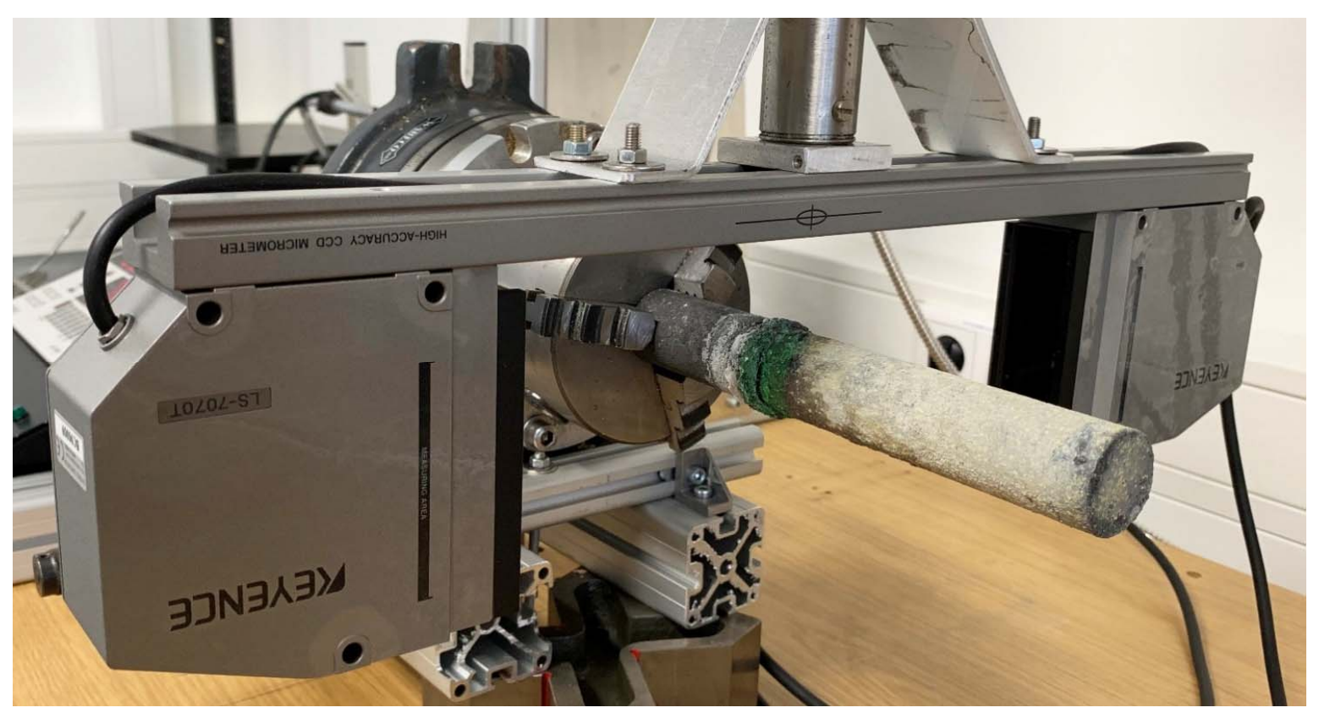


Figure 2: Wear measurement device

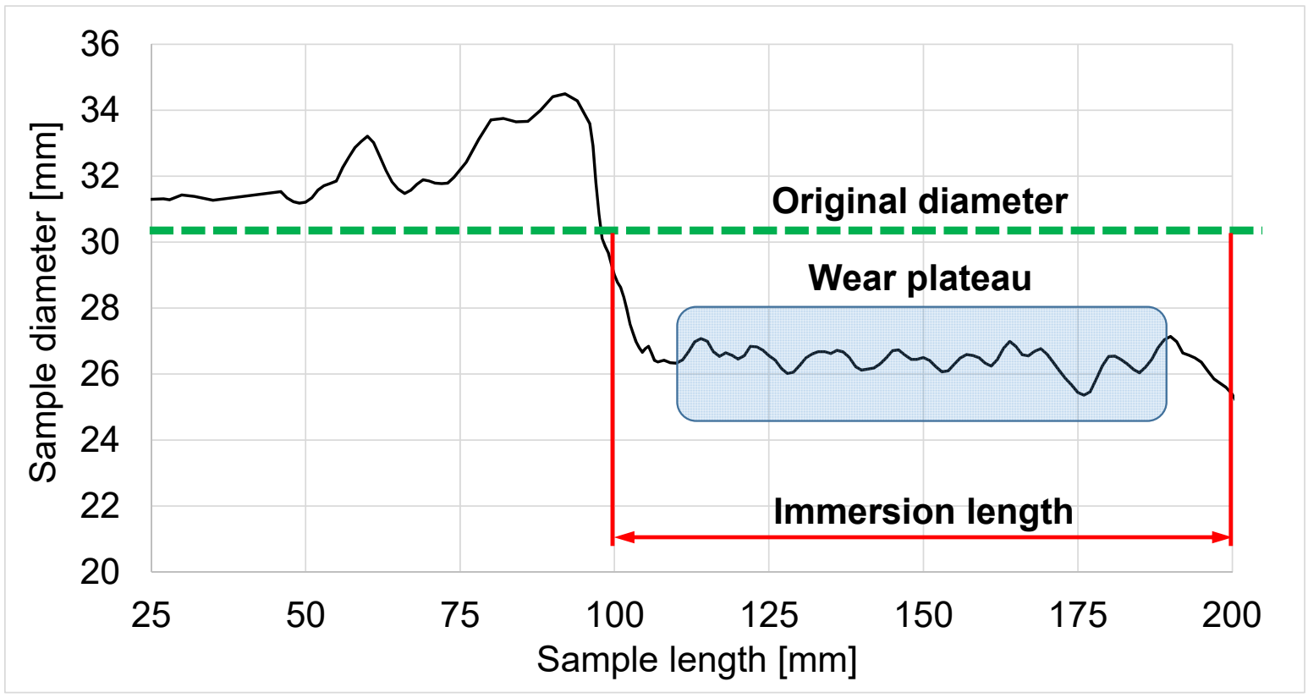


Figure 3: Surface profile

The average wear rates of the samples were calculated from the data, considering only the 80 mm long central region (Wear plateau) of the immersed length in order to eliminate boundary effects. Figure 4 illustrates the wear results.

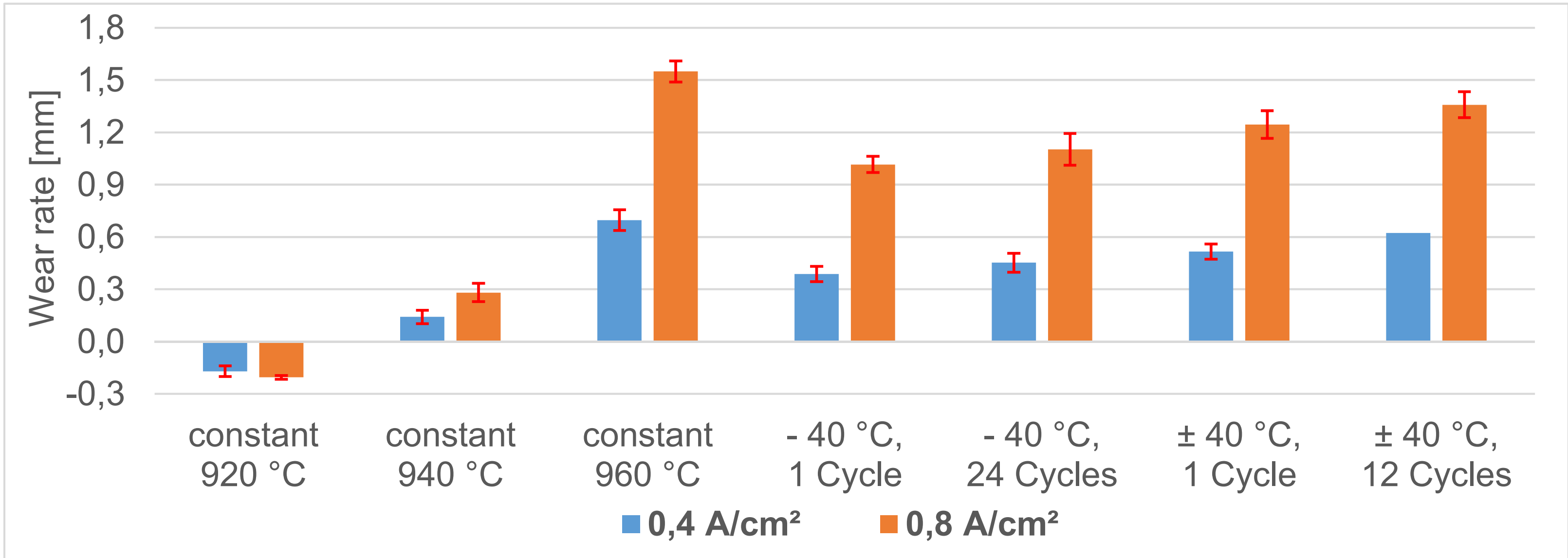


Figure 4: Overall wear results

Electrochemical wear

Nowadays, the most relevant wear mechanism is widely agreed to be electrochemical in nature, originating from the formation, the dissolution and transport of aluminium carbide Al_4C_3 inside the bath [3]. The driving force for the Al_4C_3 formation can be expressed through the following reaction:

$4\ Al^{3+} + 3\ C + 12\ e^- \rightarrow Al_4C_3$

The supply of Al^{3+} ions and their transport into the cathode increase with the current inside the system. The aluminium carbide formed at the bath layer-carbon interface can dissolve into the bath according to the reaction [3]:

$Al_4C_3\ (s) + 5\ AlF_3\ (l) + 9\ NaF\ (l) \rightarrow 3\ Na_3Al_3CF_8\ (l)$

The limited solubility in the bath makes the Al_4C_3 transport rely on the supply of unsaturated bath at the cathode surface in order to sustain the wear process.

Testing procedure

A perpendicular oriented graphitic material (L = 200 mm, Ø = 30 mm) was used as cathode sample, its properties namely listed in Table 1. The immersion depth of the specimen was 100 mm. The typical bath composition is given in Table 2.

Table 1: Cathode material properties

Apparent density [g/cm³]	Open porosity [%]	Compression strength [MPa]	Electrical resistivity [μΩ · m]
1,71	16	17,46	14,79

Table 2: Electrolyte composition

Component	Na_3AlF_6 (Cryolite)	Al_2O_3	AlF_3	CaF_2
Weight-%	75	10	10	5
Liquidus temperature [°C]	945			

All tests were carried out for a total time of 24 hours at different current densities. Reference samples were examined at 920, 940 and 960 °C under isothermal conditions. In comparison, cyclic thermal loads with different temperature amplitudes were applied to the specimens, representing alternating (960 ± 40 °C) and negative modulation (960 - 40 °C). Table 3 summarizes the selected experimental parameters.

Table 3: Thermal loading parameters

Temperature [°C]	920	940	960	960	960	960	960
Current density [A/cm²]	0,4 / 0,8	0,4 / 0,8	0,4 / 0,8	0,4 / 0,8	0,4 / 0,8	0,4 / 0,8	0,4 / 0,8
Temperature amplitude [°C]	-	-	-	± 40	- 40	± 40	- 40
Number of cycles	-	-	-	1	1	12	24
Heating / Cooling rate [°C / h]	-	-	-	6,67 / 6,67	3,33 / 3,33	90 / 90	90 / 90

Outcome and conclusions

The following outcomes can be derived from the present work:

- At higher current density the wear rate increases significantly
- Lower temperatures slow down the wear at isothermal conditions
- Symmetric thermal cycling of ± 40 around 960 °C provokes less wear in comparison to isothermal electrolysis at the same temperature
- Experiments with solely negative thermal modulation (below 960 °C) show a higher wear rate than during the isothermal tests at 940 °C
- Increase of cycle numbers boosts the wear rate.

When the bath temperature drops below the liquidus temperature partial solidification occurs at the cathode surface. It can be assumed that the layer of frozen electrolyte slows down the electrolysis process. Higher viscosity of the bath in cooperation with a reduced wettability of the carbon will result in a limited bath penetration. Additionally, impeded transport of aluminium carbide away from the cathode surface seem to restrict the wear process. Alternating temperatures however could accelerate the natural convection inside the cell.

References:

[1] J. Thonstad, P. Fellner, G. M. Haarberg, J. Hives, H. Kvande, and Sterten A., Aluminium-Electrolysis - Fundamentals of the Hall-Heroult Process, 3rd Edition. Aluminium-Verlag GmbH, Düsseldorf, 2001.
[2] R. Düssel, Entwicklung eines Regelungskonzepts für Aluminium-Elektrolysezellen unter Berücksichtigung einer variablen Stromstärke und eines regelbaren Wärmeverlusts, Wuppertal, (2016).
[3] M. Sørlie, H. A. Øye, Cathodes in Aluminium Electrolysis, 3rd ed., Aluminium-Verlag Marketing & Kommunikation GmbH, Germany, 2010.

Acknowledgement:
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