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 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 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 which is dipped into the liquid bath from the top of the cell. A perpendicular oriented graphitic material (\(L = 200 \text{ mm}, \Theta = 30 \text{ mm}\)) was used as cathode sample, its properties namely listed in Table 1. The immersion depth in order to eliminate boundary effects. Figure 4 illustrates the wear results.

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. 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.

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 \(\text{Al}_4\text{C}_3\) inside the bath [3]. The driving force for the \(\text{Al}_4\text{C}_3\) formation can be expressed through the following reaction:

\[
4\text{Al}^{3+} + 3\text{C} + 12\text{e}^- \rightarrow \text{Al}_4\text{C}_3
\]

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

\[
\text{Al}_4\text{C}_3 (s) + 5\text{AlF}_3 (l) + 9\text{NaF} (l) \rightarrow 3\text{Na}_3\text{Al}_3\text{CF}_8 (l)
\]

The limited solubility in the bath makes the \(\text{Al}_4\text{C}_3\) 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 (\(L = 200 \text{ mm}, \Theta = 30 \text{ mm}\)) was used as cathode sample, its properties namely listed in Table 1. The immersion depth in order to eliminate boundary effects. Figure 4 illustrates the wear results.

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:

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