Cathode Wear – Autopsy Findings Related to Degradation Mechanisms

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Abstract

Cathode wear has been an important issue for the primary aluminium industry owing to its crucial role in determining the service life of the electrolysis cells used in the production of the metal [1]. The increasing importance of understanding the mechanism(s) behind the wear of the carbon cathode in the industry over the past few years is connected to the industry's shift from less graphitized to highly graphitized cathode blocks to enhance productivity and improve energy efficiency [2]. The high electrical and thermal conductivity of the highly graphitized carbon cathode blocks allows for the industry to increase both production and energy efficiency through the design of larger pots as well as retrofitting older ones. A reduction in the service life of the electrolysis cells is, however, observed as the cathode blocks are shifted to more graphitized carbon. Observations of spent potlinings show a wear pattern characterized by the so-called W and WW wear patterns [3].

This paper discusses the mechanism(s) behind cathode wear based on autopsy of spent potlinings conducted at different aluminium smelting plants operating at different amperages and different carbon cathode materials.

Keywords: Cathode wear, cathode autopsy, wear mechanisms.

1. Experimental

Autopsies of spent potlinings lined with different carbon cathode types and operated at different amperages were conducted to understand the mechanisms of cathode wear. The cathode surface of six spent potlinings were observed and characterized by employing photography, manual wear pattern measurements, and 3D laser interferometry. Carbon cathode and bath samples collected from the spent potlinings were also characterized by X-ray diffraction (XRD), optical and scanning electron microscopy (SEM-EDX) as well as X-ray computed tomography (CT).

2. Results and Discussion

The results obtained from the autopsies show the same macro trends similar to what have been reported by others [1, 4 - 6]. The highest wear was observed to be located close to the ends of the cathode blocks while the centre channel areas showed the least wear. Apart from the general W or WW wear patterns that are commonly observed, this work focused more on the micro wear pattern resembling what is called wide shallow pitting corrosion in metals.

Figure **42** shows pictures of the cathode surface with pitting corrosion in one of the potholes located towards the outer ends of a cathode block.

Figure 42. Pitting on the cathode surface of a spent potlining.
Left picture includes part of the 5 cm diameter drill used to take core samples.
Right picture shows more details of the micro wear pattern.

Typical for all cells were that the pitting cavities were larger in areas with high wear, i.e., more coarse cavities towards the cathode block sides and gradually smaller towards the centre of the cells where the overall wear was lower. The average size of the pitting observed on the cathode surface (Figure 1) was measured to be approximately 7 mm.

CT images were used the reveal the microstructure within the cathode block as well as to determine the average aggregate coke grain size, which was found to be in the range of less than 3 mm. Both the SEM and the CT results showed that the wear along the carbon-electrolyte interface indicated an even wear of the coke aggregates and the binder matrix with no indication of aggregate detachment.

X-ray diffraction analysis was used to study differences between regular bath samples above the metal pad with bath samples collected from carbon cathode surface. The regular bath samples had normal excess AlF_3 in line with normal bath compositions, while those collected at the carbon cathode surface were considerably more basic (depleted in AlF_3). This difference in acidity is believed to arise from reactions between the carbon cathode and the bath moving under the aluminium pad. It is proposed that the observed changes in bath acidity is an important factor that must be included in an explanation of the observed carbon cathode wear, especially for the wear reaction, but also the transport of carbon from the cathode surface.

Due to the interaction between the bath and the carbon cathode, causing a more basic bath composition at the carbon surface, a mechanism involving initiation and termination of the cathode wear process is proposed. This can be understood from Figure 2 were the liquidus curves for normal bath compositions with 5 wt% CaF_2 and different amounts of Al_2O_3 are shown as function of excess AlF_3 [7]. Within the range of normal superheat, a depletion of AlF_3 will cause the bath to reach the liquidus curve were solid cryolite is formed. This is indicated by the blue dashed arrow in Figure 43 using 15 °C superheat. As a result, the cathode wear will slow down. It may be noticed that a variation in alumina content between 2 and 4 wt% corresponds to about 10 °C difference in the liquidus curve. This may have implications both for bath freezing, e.g., in connection with alumina feeding, although alumina has a positive effect on lowering the bath liquidus curve, as well for exceeding the peak in the liquidus curve. In the last case, this may prevent the bath on the cathode surface to freeze out in spite of being depleted in AlF_3 and the explained stopping mechanism will not be effective before the bath is nearly completely depleted in AlF_3, i.e., until the formation of solid NaF (with Al_2O_3 and CaF_2) may take place.

The proposed main governing wear reaction can be expressed by the following equation:

$$3\ \mathrm{Na_3AlF_6(l)} + 4\ \mathrm{Na(in\ C)} + \mathrm{C} = \mathrm{Na_3Al_3CF_8(diss)} + 10\ \mathrm{NaF(l)} \quad (1)$$

In this equation, the dissolution of carbide in the bath is included. When the bath is saturated in carbide, Al_4C_3 can form on the carbon surface according to the following equation:

$$4\ \mathrm{Na_3AlF_6(l)} + 12\ \mathrm{Na(in\ C)} + 3\ \mathrm{C} = \mathrm{Al_4C_3(s)} + 24\ \mathrm{NaF(l)} \quad (2)$$

A thin carbide layer is usually observed in the pores of used cathodes, supporting that aluminium carbide formation is the main driving force for cathode wear.

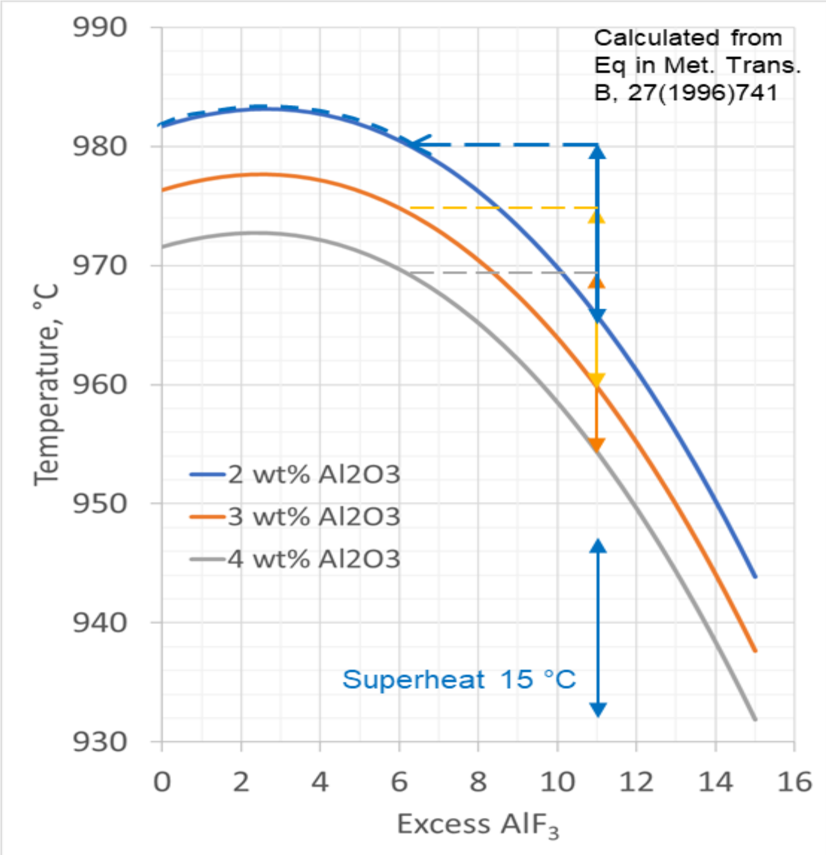

Figure 43. The liquidus curve for normal bath compositions with 5 wt% CaF_2 as function of excess AlF_3 and various Al_2O_3 contents.

3. Conclusion

The average coke grains were observed to be different from that of the pitting cavities. A relatively uniform wear cutting across both the coke aggregates and the binder matrix of the carbon material was observed at the carbon-electrolyte interface. A wear mechanism involving an initiation and termination of the wear process due to changes in bath chemistry on the cathode surface is proposed. No correlation between the average pitting size and the coke aggregate size, as well as the observation of a relatively uniform worn surface at the carbon-electrolyte interface, suggest pitting occurs by a chemical wear process under electrochemical conditions causing high sodium activity.

4. Acknowledgement

Financial support from the Norwegian Research Council and the industrial partners Hydro Aluminium, Alcoa, Elkem Carbon and Skamol through the project "CaRMa - Reactivity of Carbon and Refractory Materials used in metal production technology" is acknowledged.

5. References

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