Role of Pitting in the Formation of Potholes in Carbon Cathodes - A Review

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Abstract



The formation of potholes on carbon cathodes is one of the main causes of pot failure in the aluminium industry. A single pothole deep enough to cause the molten metal pad to come in contact with the collector bar is enough to fail a pot. Based on current theories, the cathode wear mechanisms, industrial experiences in formation of potholes and their characteristics and the role of pitting in the formation of potholes, are discussed. Pitting, a highly localized form of cathode erosion that produces relatively small pits on the cathode surface is a phenomenon observed in potholes of the cathode block during autopsies of spent pot linings. The presence of pitting within these potholes shows that pitting plays an important role in their formation.

Keywords: Pitting of cathode carbon blocks; potholes in carbon blocks; cathode erosion; carbon cathode.

1. Introduction

Cathode life is still one of the major challenges for the primary aluminium industry due to the major costs involved in replacing pot linings, loss in production and disposal of spent pot linings [1]. Reduced cathode service time has evolved in parallel to the demand for higher productivity, either through increased amperages in existing cathode technologies or introduction of modern high amperage cathodes. In addition to increasing amperage, changes towards more acidic compositions of the cryolite bath have also taken place [2]. Traditional amorphous/anthracite based carbon cathodes are less suitable for the emerging higher amperage regimes due to their higher electrical resistance and sodium swelling, and the industry has largely moved to graphitized blocks with lower electrical resistance, higher thermal conductivity and energy efficiency of the aluminium industry [3], but faster cathode wear have become a major challenge due to reduced lifetime of the cells [1]. Autopsies of shut down cells have also demonstrated that the cathode wear is not even, but typically shows a so-called W or WW wear pattern [1]. Understanding the underlying mechanism(s) for these uneven wear is therefore of paramount importance in order to increase the lifetime of the cells.

The mechanisms for the cathode wear have been the subject of several studies in the past [1]. The mechanisms discussed in the literature will be reviewed in this paper. Moreover, industrial experiences have also shown that the cathode erosion is irregular and occurs through the formation of potholes on the carbon cathodes. In the worst cases, a single pothole is deep enough to reach the collector bars, which may fail a pot as the molten metal pad will dissolve the collector bar and potentially cause cell tap out [1]. The industrial experiences are

summarized in this review with attention to potholes and particularly pitting of the carbon cathode, which may act as precursors to the potholes.

2. Mechanisms for Cathode Wear

Cathode wear have previously been discussed in relation to several mechanisms involving pure mechanical erosion and mechanisms related to chemical and electrochemical reactions.

Physical or mechanical wear is today proposed to occur mainly through cavity cleaning in connection with metal tapping and anode change operations as well as alumina particles scratching the surface of the cathode blocks [1]. Tests by Toda and Wakasa [4] showed that graphitized blocks had lower abrasion resistance than their more amorphic and anthracitic counterparts. This may, to some extent, explain the observation of the graphitized cathode blocks being more eroded than the narrow joints (rammed joints) between them [5]. Erosion measurements performed in reduction cells by Wilkening and Reny [6], however, showed that graphite cathodes with superior mechanical abrasion resistance index displayed poorer wear resistance. This supports the conclusion that mechanical abrasion is not the key mechanism for cathode wear.

Cathode wear may also be chemical involving the formation and dissolution of aluminium carbide (Al4C3). This is because the reaction between aluminium and carbon as shown in reaction (1) is thermodynamically favourable (Gibbs energy of -147 kJ at 970 °C) at all temperatures of concern in electrolytic aluminium production [1].

$$4Al(l) + 3C(s) \rightarrow Al_4C_3(s) \tag{1}$$

The formation and dissolution of aluminium carbide from the carbon block under the metal pad is enhanced by the presence of cryolite based melts [1]. Laboratory tests conducted by Novak et al. [7] showed the presence of an oxide film between the metallic aluminium and the carbon cathode. This oxide film prevents wetting of aluminium on carbon [8]. Thus for any direct carbide formation to occur, aluminium must diffuse through the oxide film to react with carbon [9]. The dynamics, however, change when cryolite melt is introduced to the system. The cryolite melt act as a wetting agent by dissolving the oxide film (thereby increasing the wettability of aluminium on carbon) and paving the way for carbide formation [8].

Absorbed sodium in carbon can also react with carbon and cryolite or alumina to form aluminium carbide within the pores of the carbon cathode as shown in Reactions 2 and 3 below [1]. High activity of sodium is necessary for any of these two reactions to be the dominant aluminium carbide forming reaction [10].

$$4Na_{3}AlF_{6}(l) + 12Na(in C) + 3C = Al_{4}C_{3}(s) + 24NaF(l)$$
(2)

$$8Al_2O_3(s) + 12Na(in C) + 3C(s) = Al_4C_3(s) + 12NaAlO_2(s)$$
(3)

Øye and Lossius [11] analysed different industrial cathode samples by drilling core samples covering the whole depth of the bottom linings at different locations. Aluminium carbide was observed as one of the phases within the cathode samples. They also observed that Al_4C_3 was both formed at the surface as well as inside the pores of the cathode.

eventually formed. Upon the formation of a pothole, contact with the collector bar(s) may be reached and a tapout may be encountered if no drastic measures are taken. It is a common industrial practice to fill these potholes with recrystallized alumina once contact is made with the collector bar(s) [1] to stop or delay tapout. The strap to the affected collector bar(s) may also be cut to reduce the temperature and current density at the pothole area and allow bath to freeze around the recrystallized alumina and seal the pothole [1].

3. Conclusion

Cathode wear as discussed in this paper is a combination of mechanical, chemical and electrochemical wear mechanisms. None of these mechanisms can alone explain all of the cathode wear patterns observed in industry and laboratory tests. However, laboratory tests as well as industrial autopsies show that electrochemical induced wear is probably the most dominant mechanism. The current trend of reduction in cathode life as amperage is increased is better explained by the electrochemical wear mechanisms.

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5. Reference

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