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Degradation mechanisms and development of silicon carbide refractories

Ron Etzion

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Abstract

The lifetime of aluminium reduction cells is of considerable importance in the operating economics of an aluminium smelter. Not only are the cell materials costly, but cell life is also key in minimizing production downtime and the waste material generated in the cutting-out and relining of a reduction cell. This lifetime is increasingly driven by two components of the cell lining: the carbon cathode and the sidewall refractories which are the primary containment of the metal and electrolyte.

Silicon nitride bonded silicon carbide (SNBSC) refractories are the current state-of-the-art sidewall materials. These materials are formed by encapsulation of SiC particles in a silicon nitride matrix, by nitridation of silicon at high temperatures under a nitrogen atmosphere. In this study the mechanisms of the corrosion of silicon nitride bonded silicon carbide refractories in an aluminium reduction cell environment were examined.

Microstructural analysis of SNBSC materials by: X-ray diffraction, solid state NMR, Raman spectroscopy, XPS, and SEM, identified variations in α/β Si_3N_4 ratio and porosity in the binder phase, with higher porosity levels and β Si_3N_4 content found in the interior part of the brick. Unreacted metallic silicon was observed only as a crystalline phase inside SiC grains and is not associated with the binder phase.

SNBSC samples from eight different commercial refractory manufacturers were tested in an industrial aluminium cell environment, both by immersion in industrial cells and in the laboratory. The samples showed extensive attack and considerable differentiation between the samples. The effects on the corrosion rate of porosity levels, amount of binder, α/β Si_3N_4 ratio, free Si content in the binder, and different factors in the environment were examined in the laboratory scale trials. A laboratory scale testing rig with some novel features, such as a rotating anode, was developed to examine corrosion resistance of samples under electrolysis conditions in molten cryolite at up to 1000 ^{o}C.

Corrosion test results, supported by thermodynamic calculations, identified the Si_3N_4 binder as the reactive phase in SNBSC materials, especially in the gas phase above the bath level. High porosity levels and high β Si_3N_4 fraction in the binder showed a statistically significant contribution to the corrosion rate in lab-scale corrosion trials. Commercial materials are also

highly inhomogeneous in the distribution of the β Si_3N_4 phase as mentioned above, which complicates sample selection and the interpretation of corrosion test results.

The crystal morphology of β Si_3N_4 is suggested as the reason for the high reactivity of these materials. This morphology characterised by elongated rod-like shape crystals with hexagonal cross section, presents a higher surface area compared to α Si_3N_4 crystals containing mainly flat matte crystals. In the light of this observation, the binder phase in selected samples was deliberately modified to convert a significant fraction of the α Si_3N_4 to β Si_3N_4. Corrosion rates measured from these modified samples in general support the argument that the crystallographic form of silicon nitride contributes to corrosion rate.

The proposed corrosion mechanism for SNBSC materials in the aluminium reduction cell atmosphere is based on combination of oxidation of the binder followed by attack of corrosive gases to produce volatile SiF_4. Thus the binder phase is initially passivated below the electrolyte level on the sidewall, where exposure to corrosive gases is limited, but occurs more rapidly in the area above the electrolyte/air interface. The intrusion of electrolyte into the refractory and capillary transport up the sidewall is a key in accelerating this reaction.

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