

Structure and Porosity in Anodes for Aluminum Production

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Abstract. Aluminium production involves electrochemical reduction of aluminium oxide by carbon anodes. The paper summarises structure of anodes and assesses the related roles of binder pitch and grist coke. Bonding at interfaces is discussed and the beneficial roles of QI in pitch are listed. It is concluded that the size, number and strength of the binder coke bridges influence the overall porosity and strength of the carbon anode. Porosity has to be minimised to increase density and shift-life, to minimise secondary internal gasification and to minimise dusting.

Introduction

The aluminium industry is the largest single user of carbon. In the production of aluminium from aluminium oxide via electrolytic reduction, it is the carbon anode which removes the oxygen as carbon dioxide. Each tonne of aluminium requires a theoretical minimum of 0.33 tonne of carbon. In practice, more carbon than this is consumed because of (a) reaction of the CO_2 with the carbon anode to produce CO, (b) gasification of the hot anode by air, (c) "dusting" where carbon particles break away from the anode.

The carbon anodes are made on the same site as the electrolysis cells. A traditional method of manufacture of these baked anodes is used whereby a binder pitch is intimately mixed with a grist (filler) coke of known sizes and small pieces of recovered butts. The green mix is moulded (vibrated) to the required shape and size, at $\sim 120^\circ\text{C}$ and then cooled and baked at about 1200°C . The baked anode is attached to its 'conducting rod' at the position of a pre-made socket and is ultimately fitted into the cell, where a shift-life in excess of 20 days can be expected.

Quality control over the anodes is essential and this necessitates not only rigorous monitoring of all stages of manufacture but also of the specifications assigned to the binder pitch and the grist coke. In recent times, it has been difficult to maintain supplies of binder pitch and grist coke of consistent quality. This, in turn, has prompted a critical examination of the related properties of binder pitch and grist coke and of the anode itself.

The objective of this paper is to summarise structure within carbon anodes and to assess the

related roles of binder pitch and grist coke.

Grist coke. This material is the medium quality, sponge or regular coke of the delayed-coker and must be used dry. It must be adequately calcined (maximum strength and minimum volatile matter) and have an optical texture of adequate size (coarse-grained mosaics, $10\text{ }\mu\text{m}$ dia. and larger).

Figure 1 is a scanning electron micrograph (SEM) of a particle of grist coke. The extremes of surface roughness are visible as well as macroporosity in the particle interior, $\sim 250\text{ }\mu\text{m}$ diameter. Figure 2 is a SEM micrograph of smaller sized particles of grist coke, broken so as not to contain the macroporosity $\sim 250\text{ }\mu\text{m}$ dia. The upper particle of Figure 2 exhibits a cross-section perimeter which is relatively smooth, the lower particle having a higher surface roughness factor. The binder pitch has to flow over and wet such surfaces to be effective as a binder. It is apparent that it will enter into the macroporosity of Figure 1.

Binder pitch. This material must have a sufficiently low viscosity such that, at the green anode stage, it will flow over/between/around the grist coke particles to establish a uniform, mouldable mix. However, during baking, the viscosity has to be high enough to prevent slumping/deformation of the anode and possible run-out from the surfaces of the grist coke (resulting in a weak anode). Binder pitch is usually a coal-tar pitch containing primary and secondary QI, or can be a petroleum pitch without QI. The primary QI can have five beneficial roles: (i) during mixing the QI may accumulate on grist coke surfaces forming a QI filter-cake and preventing unnecessary filling of porosity within the grist coke (ii) QI enhances viscosity of meso-phase formed during pyrolysis (iii) QI reduces size

of optical texture of mesophase so enhancing strength of binder-coke bridges (iv) QI filter-cake in surface roughness carbonizes to a relatively strong material. (v) the presence of QI may enhance carbon yield from the pitch. The binder pitch at the mesophase stage, incorporates the smallest size of grist coke. This enhances the size of binder coke bridges and anode strength. Petroleum pitch without QI could have a higher chemical reactivity for mesophase formation than coal-tar pitch (ctp), and hence forms mesophase at lower temperatures. It is an advantage to manufacturing operations for pitch to form the higher viscosity mesophase at as low a temperature as possible to prevent run-out.

Heating of green anode. The distribution and size/shape of the binder pitch component of the green anode would appear to change on heating to baking temperatures. Figure 3 is a diagram of the essential feature of a carbon anode as assessed by microscopy. The particles of grist coke are bonded together by binder-coke bridges. These coke bridges must have adopted the morphology of binder pitch bridges created by flow of the pitch. Thus, the formation of the binder-coke bridges must represent a critical balance between the decreasing viscosity of the pitch (increasing temperature), the restraining effects of incorporated solid material on viscosity, and the rapid increase in viscosity associated with the onset of mesophase formation. It is via the mesophase material that the morphology of the pitch bridge is transferred to the coke bridge.

The carbon anode. The essential features of the carbon anode are represented diagrammatically in Figure 3. The larger sized particles of grist coke are bonded together by binder-coke bridges (from binder pitch) to form a 3-dimensional inter-locked system containing about 25% of porosity. The anode must have (a) a minimum resistivity, $<60\mu\Omega\text{m}$, (b) a maximum compressive strength ($>200\text{ kg cm}^{-2}$) and (c) a minimum reactivity to CO_2/O_2 . Resistivity and strength are related (i) to "crystallinity" (optical texture) and porosity of the filler coke, (ii) to the quality of contact at the interface between the binder-coke and filler coke and (iii) to the "crystallinity", shape, size, number and porosity of the binder-coke bridges. The reactivity of the anode relates to both the binder coke and grist coke, preferential gasification of the former leading to enhanced porosity and decreased strength with dusting.

The Interface: binder and grist. The binder pitch has to be a good 'adhesive' and hence (i) it must adequately wet the coke surface in order to create intimate contact (ii) it may enter macroporosity of the grist coke (iii) the pitch system must become more viscous and finally solidify during baking (via mesophase) (iv) the solid phase must accommodate the internal stresses of thermal shrinkage. Bonding at interfaces is of three types: mechanical (keying-in), chemical and electrical. Wetting of grist coke by pitch does not guarantee bonding of binder coke to grist coke. Current evidence suggests that the interface is bonded mechanically. The surface roughness of the grist coke may provide the necessary keying-in action without recourse to pore filling. Mesophase in porosity can adopt a carbon fibre structure.

Conclusions

The above discussion indicates that the number (frequency), size, shape and structure of binder-

coke bridges influence the overall porosity and strength of the carbon anode. The formation of the binder-coke bridges is intimately related to factors which control the viscosity of the pitch and the onset and properties of mesophase. An industrial objective is to minimise porosity in order to (i) increase density and shift-life (ii) minimise secondary gaseous oxidation (reactivity) and (iii) minimise dusting. Temperatures in pitch and coke must be minimised to reduce catalytic promotion of secondary oxidation.

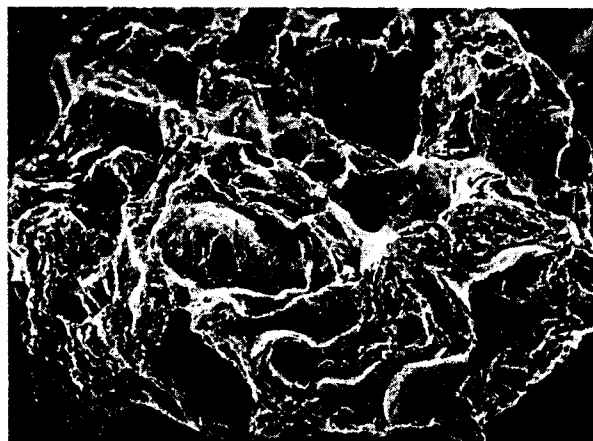


Figure 1. SEM micrograph of grist coke. 500 μm

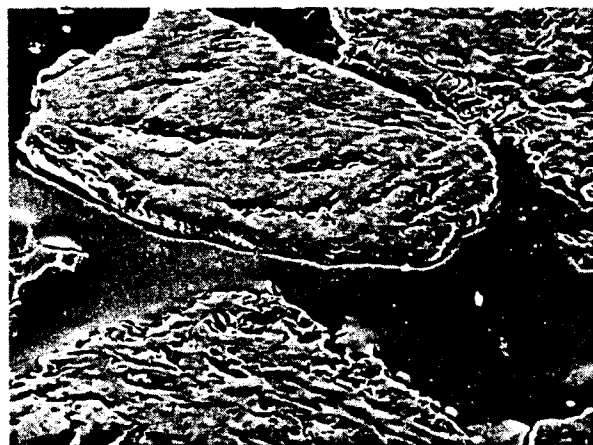


Figure 2. SEM micrograph of grist coke. 100 μm

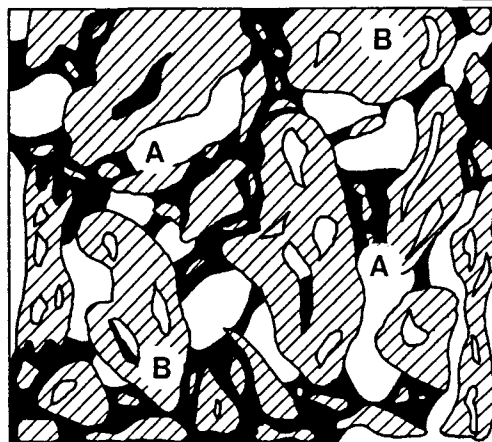


Figure 3. Diagram of structure of carbon anode. A: pitch coke bridges, B: grist coke.