Porosity Measurements in Prebaked Pitch-Coke Artifacts

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Introduction

Anodes for the aluminium industry are made of petroleum coke particles and pitch binder. During the mixing of the components and the shaping of the artefact the pitch binder partly penetrates into the porosity of the coke particles and partly occupies the interparticle voids. Upon carbonization the volume of binder decreases. The purpose of this study is to measure the volume of binder present into the intra and the interparticle porosity of the coke particles at different stages of baking and to investigate the effect of compaction of the electrode on the carbonization process of the pitch.

Experimental

A petroleum coke (particle size 1.18-2.0 mm in diameter) has been mixed at 170° C with a coal tar pitch (softening point 111° C). The pitch content is equal to 19 % in weight in all samples. The green paste was divided into two parts : a non compacted one (NC) and a compacted one (C). The compacted sample C was obtained by moulding the green paste into a cylindrical electrode for use in a pilot plant (apparent green density 1.56 g/cm³). Both types of samples C and NC were then heated under flowing nitrogen at 250, 450, 550 and 1000°C at a heating reate of 16°C/hour.

Mercury density and mercury intrusion measurements were made on uncoated and pitch coated particles. In order to avoid any interparticle porosity, the artefacts were fragmented back to the coke grains. In that operation the artefacts cleave into the binder phase and restitute coke particles coated with pitch. Mercury intrusion experiments were carried out on a Carlo Erba (2000 kgf/cm²) porosimeter.

Porosity and Pitch Volumes Measurements

Due to the small intraporosity of petroleum coke, corrections for the compressibility of the coke and of the pitch were made. The porous volume of coke v_c obtained by mercury intrusion is equal to $82 \text{ mm}^3/\text{g}$ for pore radius ranging from 7.5 μ m to 10 nm. In a similar way the pore volume of binder coated particles v_c^* is determined. Hence the volume of binder present in the intraparticle porosity of the coke, V_b int is given by

$$V_{b} int = av_{c} - v_{c}^{*}$$
(1)

with a = weight fraction of coke in the coated sample.

The volume of binder present on the particle surface (i.e. in the interparticle porosity of the artefact) V_b ext is determined from the difference in mercury density of the coated and the uncoated particles :

$$J_{\rm b} \, \text{ext} = \frac{1}{\rho^*} - \frac{a}{\rho} \tag{2}$$

 ρ and ρ^{\star} are respectively the mercury density of the uncoated and coated particles.

It has to be noted that V_b int and V_b ext are calculated from independant measurements. Therefore, the total volume of binder V_bT verifies the following the relation

 $V_b T = V_b \text{ int } + V_b \text{ ext}$ (3)

For unbaked artefacts in which the total volume of binder is known, Equation (3) was indeed verified thus confirming the validity of Equations (1) and (2).

Results and Discussion

The change in pitch volume V_b int, V_b ext and V_bT as a function of temperature for NC and C samples are shown in figures 1 and 2 respectively. At 250°C V_b int represents about 85 % of the intraparticle porosity of the coke for both types of samples. Hence the filling up of the pores by the binder is high at that temperature.

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Figure 1. Change in binder volume with temperature for non compacted sample.

Between 250 and 450 °C V_b int decreases for NC sample whereas V_b ext slightly increases. Since the pitch is liquid in that temperature range the binder flows out of the pores and accumulates at the particle surface where it distillates. Above 450 °C carbonization of the pitch leads to a decrease of its volume both in and outside the pores of the coke particles. At 1000 °C 40 % of the initially present volume of binder remain in NC sample, the major part being located on the particle surface.

In the case of compacted sample the change in binder volume is rather different. Between 250 and 450°C Vb int decreases less than in the non compacted system. In contrast, in the interval 450-550°C, a pronounced expulsion of pitch (20 mm³/g) from the pores occurs which lead to an equivalent increase in Vb ext. Hence no change in the total volume of binder is detected in this temperature range. Effectively no significant weight loss of C sample is found between 450 and 500°C (less than 1.5 % in weight) whereas NC sample undergoes an 11 % weight loss. Above 550°C $V_{\rm b}$ ext decreases while $V_{\rm b}$ int almost remains constant. At 1000°C the remaining volume of binder is higher than in the case of a non compacted artefact. Moreover the volume fraction of binder inside to pore is about three time larger than for NC sample.



Figure 2. Change in binder volume with temperature for compacted sample.

These results show that the volume change of binder during the carbonization differs widely for compacted and non compacted artefacts. In particular between 450 and 550°C when mesophase starts growing the binder is expulsed from the pores without significant weight loss of the electrode. It might therefore be expected that the carbonization process of NC and N samples is somewhat different. Optical microscope observations of polished sections of carbonized samples at 550°C indeed show that the anisotropic domains in the binder phase are less developed in compacted artefact. Although the precise cause of the binder expulsion is not yet clearly established, it appears however that a longer residence of the pitch in the coke porosity hinders the growth of the anisotropic domains.

Conclusions

The repartition of the pitch binder in the intra and interporosity of coke particles during the baking process depends on the degree of compaction of the artefact. In a compacted system the binder is expulsed out of the coke porosity in the temperature range where mesophase starts growing. Additional work is presently undertaken to explain this phenomenon.

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