Light Metals 2016
Edited by: Edward Williams
TMS (The Minerals, Metals & Materials Society), 2016

EFFECT OF CARBON DUST ON THE ELECTRICAL RESISTIVITY OF CRYOLITE BATH

Louis Bugnion, Jean-Claude Fischer
R&D Carbon; Sierre, Switzerland

Keywords: Carbon dust, bath resistivity, ACD squeeze, cell stability

Abstract

For many years anode dusting has been an issue for aluminum producers. Suspended carbon particles enhance the electrical resistivity of the cryolite bath, setting off a chain reaction of adverse effects for the pot. Many studies have documented the negative influence of carbon dust on current efficiency or bath temperature which are indirect effects of contaminated bath. The dependence of bath resistivity on the amount and on the size of carbon particles is poorly understood though. Tube-type cell experiments were performed to determine the electrical resistivity at 980 °C of standard bath mixtures added with carbon dust. The carbon content ranged from 0.06 to 1.01% in weight with mean particle size of 2 µm. A bath resistivity increase of 70% was measured when comparing the bath with the lowest carbon concentration with the one with the highest. From a bath with a carbon content of 0.06% to a one with 0.16%, the change in resistivity was equal to 13%. Thus the difference in bath resistivity between a benchmark bath with 0.03% carbon content and a bath from a dusty pot will be even larger. These results agree with variations of voltage measured during the ACD squeeze of groups of clean and dusty pots.

Introduction

Carbon is one of the impurities present in electrolytic bath along with iron, silicon or sulfur. In contrast to other impurities, carbon does not dissolve in bath. Coarse particles float at the bath surface whereas finer ones are suspended in the electrolyte. Carbon particles have a size ranging from micron to centimeter scale with an average size between 1 and 10 µm [1, 2]. The average carbon concentration in the bath is of the order of 0.05% and varies as a function of bath depth (see Figure 1). It is larger at the bath-metal interface and close to the bath surface where the coarse particles are found. In dusty pots, the average carbon concentration in the bath can reach values as high as 0.4% [3] with severe consequences for the pot performance.

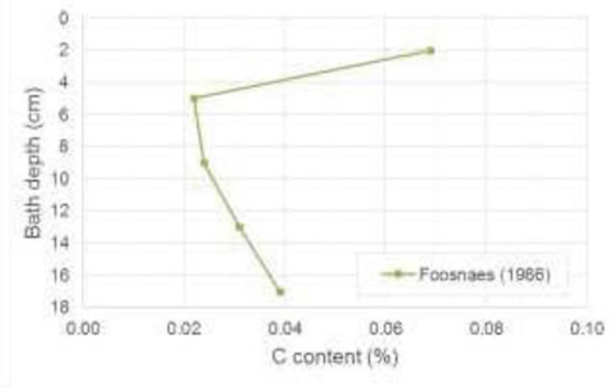

Figure 1. Carbon content as a function of bath depth as measured over 5 prebake pots by Foosnaes [2].

Carbon dust mainly originates from selective burning of the anodes in contact with CO_2 or air. The binder matrix is preferentially burnt, loosening carbon particles into the bath or within the crust/anode cover. The combustion reactions take place at the anode surface or in the anode bulk where the gases are able to permeate. The reaction rates depend on the temperature, surface structure, permeability and reactivity of the anodes constituents [4].

Other sources of carbon dust are identified such as cathode and ramming paste wear. Carbon fines entrained by the fumes and captured by the dry scrubber system return to the pot through secondary alumina feeding. Likewise, recycled anode cover contains carbon particles which contaminate the bath when falling into it.

The cycle of carbon dust in the electrolytic bath is complex and mechanisms of generation of fine particles, combustion rate and accumulation patterns of suspended particles, impact on bath properties are poorly understood. Carbon excess consumption figures give a hint about the total amount of anode carbon which is not used for the electrochemical reactions but fall short on predicting how much, where and for how long carbon dust remains in the bath. Over the years, strategies were developed with the objective of preventing the formation of carbon dust, monitoring the carbon concentration (e.g. in the secondary alumina) and removing carbon dust from the electrolyte.

The primary effect of carbon dust is to increase the electrical resistivity of the bath. Since the cell voltage is prescribed by the process control, a higher dusting level will result in an ACD squeeze. Enhanced bath resistivity is the starting point for a chain reaction of adverse effects. A lower ACD will affect pot stability and current efficiency [5], increasing bath temperature. As a result, the cell performance is reduced and the propensity to dusting is enhanced.

The dependence of bath resistivity on carbon concentration is little documented. Early work by Vetyukov [6] reported significant impact of carbon content in comparison with other bath constituents [7, 8] as shown in Figure 2. However, at levels of carbon content encountered in industrial pots, the increase of bath resistivity found was small i.e. approximately 10% at 1% concentration. It failed to explain the disturbance caused by carbon dust at levels as low as 0.1%. Foosnaes [2] developed a simple model to account for the resistivity increase as the result of a reduction of the conducting cross-section due to suspended particles. The prediction of the model is also represented in Figure 2. The same remark as for [6] applies though, when considering the impact of typically measured carbon dust concentration values.

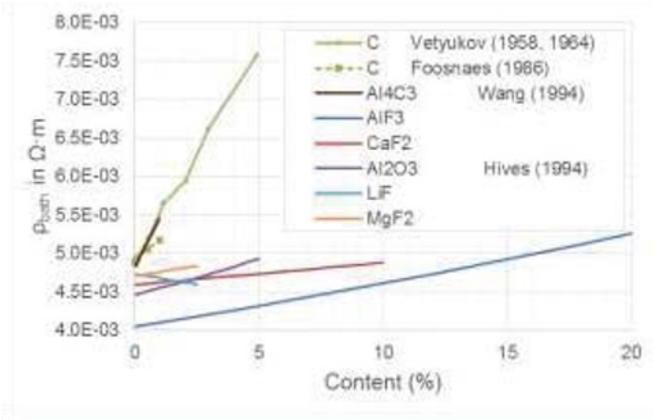

Figure 2. Bath resistivity as a function of its components concentration.

Experimental setup

In order to measure the electrical resistivity of cryolite bath as a function of carbon content, a tube-type cell was used. The cell, also used for the Rapoport cathode test, consists of a graphite crucible with 120 mm outer diameter and 92 mm inner diameter acting as the anode. The bottom of the crucible is insulated electrically by a fused alumina disk. The cathode is made by a 100 mm high graphite cylinder with diameter 30 mm lying on top of the alumina disk. Thus the anode-cathode distance is 31 mm. Solid bath is poured in the crucible and heated up at 980 °C for two hours. The crucible is covered by a graphite cover insulated from the current output by a fused alumina ring. The pressure between the cylinder/crucible and current output/input is ensured by a hydraulic cylinder. The atmosphere of the furnace is controlled through a continuous argon flow. A schematic drawing of the apparatus is shown in Figure 3.

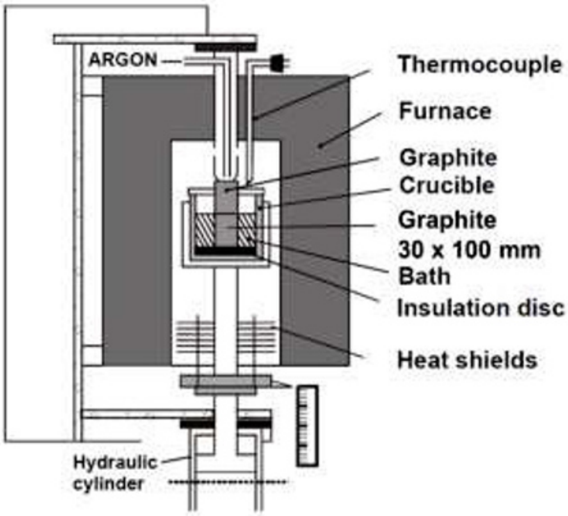

Figure 3. Schematic drawing of the test apparatus.

Bath samples were prepared in another furnace in a graphite crucible according to the following recipe: 80% Na_3AlF_6, 12% AlF_3, 5% CaF_2 and 3% Al_2O_3. The carbon dust was obtained from coke crushed with a vibrating cup mill. The carbon particles have a mean size of 1.9 µm with 90% of volume > 0.5 µm and 10% > 6.3 µm. Three different experiments were performed adding 1%, 0.1% and 0% carbon dust to the bath for a total sample mass of 250 g. The carbon contents of the clean bath and of the bath with 1% were measured separately using the LECO method to assess the sample preparation method and in particular the contamination of the clean bath by the graphite crucible used to melt the ingredients. Three 1 g samples of both baths were analyzed and yielded a mean content of 0.06% ± 0.02% for the clean bath and of 1.01% ± 0.05% for the bath with 1% carbon. Thus the carbon content of the bath samples used in the three experiments was corrected to 1.01%, 0.16% and 0.06%. We assume that carbon dust is uniformly spread in the bath. In industrial pots it is reasonable to admit that the carbon concentration is fairly constant away from the bath surface (see Figure 1) i.e. where most of the current flows. In our experimental setup the bath recirculation might be weaker than in an industrial pot though, causing segregation or clustering of the carbon particles to occur. Thus the measured impact of carbon shall be considered as a lower bound estimate.

Results and discussion

After preheating, voltage (3.87 V) was imposed at fixed power and the current was measured within 30 seconds to avoid changes in bath composition resulting from electrochemical reactions. The current was larger for bath samples with lower carbon content as reported in Table 1. To interpret the current values, we assume the following voltage decomposition:

$$U = C + (R_{bath} + R_{ext})\cdot I \qquad (1)$$

where C is a constant, R_{bath} is the bath resistance and R_{ext} is the external resistance. The validity of Eq. (1) in the investigated current range was verified by varying the voltage for the bath sample with 0.06% carbon and by fitting the current data linearly (see Figure 5). The constant C = 2.1255 V is obtained as the y intercept value. It shall not be interpreted as the sum of the reversible decomposition voltage and of the overvoltages since the latter are not linear functions of the current. Since R_{ext} is unknown, R_{bath} was determined through modeling of the cell with the clean bath sample assuming a bath resistivity of $4.63\cdot10^{-3}$ Ω·m. The current distribution was computed using ANSYS (see Figure 6) yielding first $R_{bath} = U_{bath}/I$ with U_{bath} = 647 mV and second R_{ext} using Eq. (1). R_{ext} was considered to be constant for the two other experiments.

Figure 4. Section of the crucible after two hours of electrolysis for the experiment with the bath sample containing 0.16% carbon

dust. A torus of aluminum around the cylinder bottom is visible as well as the attack of the insulation disk on the sides.

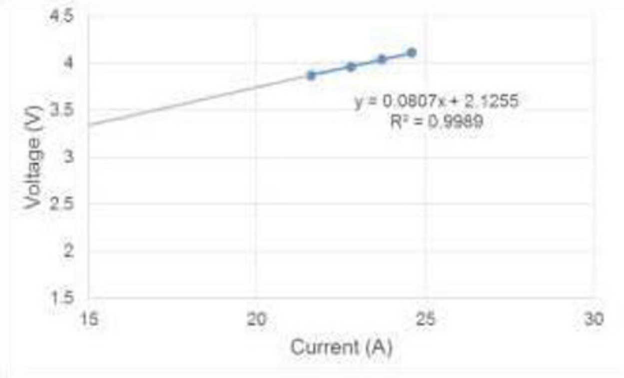

Figure 5. Linear fitting of the voltage as a function of current for the experiment with the bath sample with 0.06% carbon content and determination of the constant C = 2.1255 V.

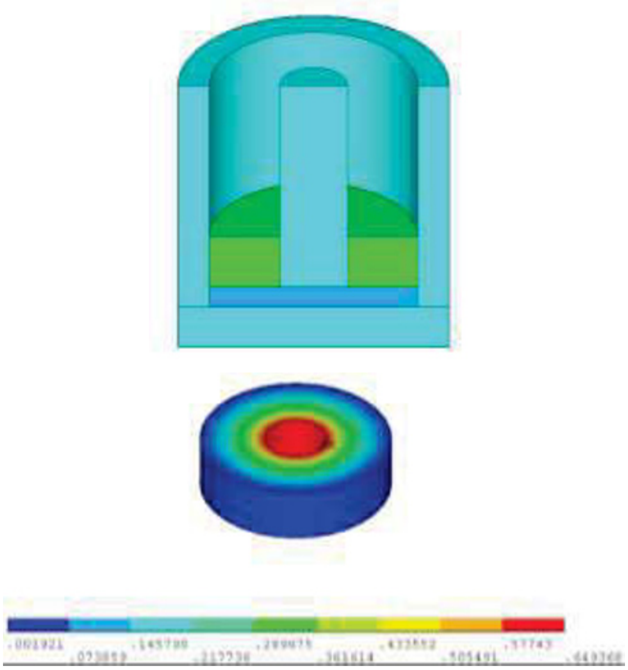

Figure 6. Solid model of the crucible and electric potential in the bath for the experiment with clean bath.

The bath resistance for the three experiments is reported in Table 1 and Figure 7. If we assume that the current distribution is similar for all experiments, R_{bath} is proportional to ρ_{bath}. As a result we conclude that the presence of carbon dust affects the bath resistivity to a larger extent than what has been measured or modeled up to now (Figure 2). At the carbon content of 0.16%, possibly found in a dusty industrial pot, the increase in bath resistivity is equal to 13% with respect to the resistivity of the bath at 0.06% and shall attain 20% with respect to the resistivity of a benchmark bath at 0.03%. The experimental procedure does not allow to measure the resistivity of cleaner bath since a low quantity of carbon is present as a consequence of the bath preparation method.

Table 1. Summary of the three experiments. ρ_{bath} stands for the bath resistivity.

C content	%	1.01	0.16	0.06
I_{init}	A	17.4	20.8	21.8
U	V	3.87	3.87	3.87
R_{bath}	Ω	0.0499	0.0335	0.0297
$\rho_{bath}/\rho_{bath,0.06\%}$	%	168	113	100
R_{ext}	Ω	0.0503	0.0503	0.0503

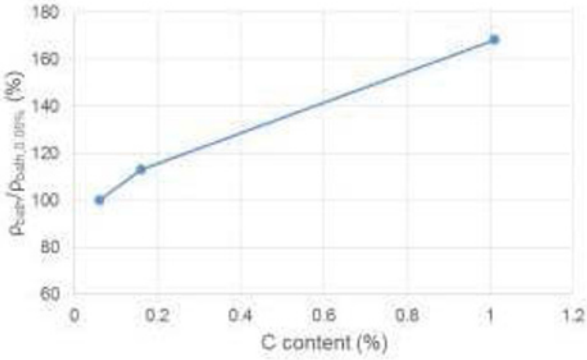

Figure 7. $\rho_{bath}/\rho_{bath,0.06\%}$ versus C content.

Squeeze test of clean and dusty pots

In order to assess the impact of carbon dust on bath resistivity and on the resulting ACD squeeze, a simple method was applied on two groups of pots with different bath carbon content. The beam was moved downwards by a few mm and it was kept at that very position during 10 min until it was moved downwards again. The cell voltage and beam position were recorded as a function of time. The test was stopped when the pot started to oscillate. In order to improve precision and to assess the reproducibility of the measurement, the same operation was repeated with upwards beam displacements. Cell voltage and beam position yield following quantities: 1) the increase of noise level as a function of ACD decrease and 2) the variation of pot voltage per mm of modified ACD. 1) provides information on the stability margin of the pot whereas 2) quantifies the bath electrical resistivity. The test was performed on two groups of pots in one potline: a first group composed of four clean pots and a second group with two dusty pots. Carbon content of bath samples from all 6 pots was determined using LECO method and XRF as control (see Table 2). The samples were taken from the tapping hole at approximately bath mid-height. The average carbon content was equal to 0.07% for the clean pots and 0.11% for the dusty pots. In Figure 8, the voltage of one pot from each group is plotted versus time during the downwards beam movements.

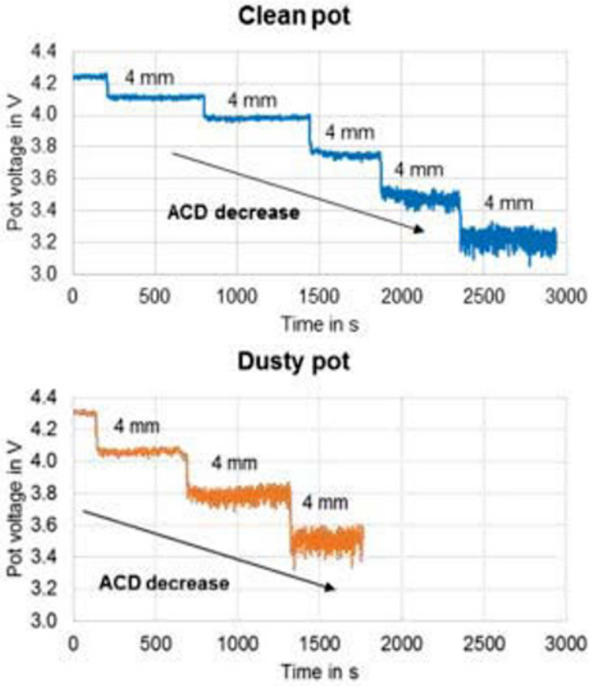

Figure 8: Pot voltage versus time during ACD squeeze in a clean pot and in a dusty pot.

One observes that the increase in noise level occurs earlier for the dusty pot. It is well visible when plotting the noise level (standard deviation of the cell voltage) as a function of the ACD decrease for the two pots (see Figure 9).

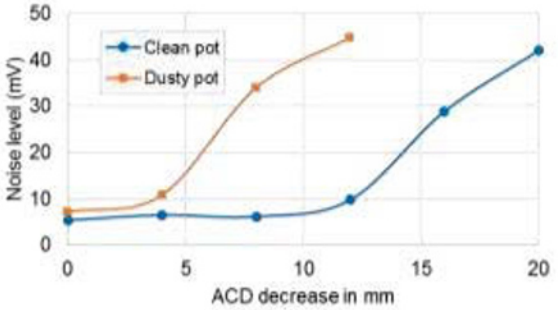

Figure 9: Noise level versus ACD decrease during ACD squeeze in a clean pot and in a dusty pot.

The acceptable noise level limit of 20 mV is exceeded after 6 mm of ACD decrease for the dusty pot and after 14 mm for the clean pot. Since pot design and pot operation are the same, the discrepancy is mainly explained by the fact that the initial ACD levels are not equal (the initial pot voltage values are). This is confirmed by the analysis of the variation of pot voltage per mm of modified ACD which is expected to be proportional to bath resistivity $\Delta U/\Delta ACD = \rho_{bath} \cdot I/S$ with S the total anode surface (see Table 2). Only data points with noise level below 20 mV are considered - at higher noise level, effects related to changing fanning factor and oscillations of the bath-metal interface distort the proportionality relationship - and data points are averaged over each group of pots. From the squeeze test, one obtains that the voltage variation per mm of modified ACD is equal to 47 mV/mm for the clean pots and 61 mV/mm for dusty pots. This represents a 30% larger bath resistivity which can be partly attributed to the presence of carbon dust in the electrolyte. Indeed the voltage variation per mm of modified ACD predicted by the bath resistivity formula [8] using the bath temperature and bath composition data is equal to 42 mV/mm and 41 mV/mm for the clean and dusty pots respectively. Other factors such as poor anode current distribution or bath height might also affect the quantity ΔU/ΔACD.

Table 2. Variation of pot voltage per mm of modified ACD for the two groups of pots.

	# pots	ΔU/ΔACD Squeeze test mV/mm	ΔU/ΔACD Bath res. formula mV/mm	Carbon content Leco %
Clean pots	4	47	42	0.07
Dusty pots	2	61	41	0.11

Conclusions

Maintaining a low and steady concentration of carbon dust in the electrolyte bath is a difficult task. It requires careful selection of raw materials and know-how in the manufacturing and rodding of anodes. At operation level, thermally balanced pots, low bath temperature and uniform anode current distribution reduce the risk of dusting. The optimal cost/benefit ratio in terms of raw materials, anode manufacturing optimization and anode cycle time shall be determined. The present work aimed at understanding the root cause for the loss of pot performance due to carbon dust that is the increase of bath resistivity.

Laboratory measurements with a tube-type cell showed that bath resistivity increases significantly with carbon content. A bath resistivity increase of 70% was measured when comparing a bath with 0.06% carbon content with a one with 1.01%. From a bath with a 0.06% carbon content to a one with 0.16%, the change in resistivity was equal to 13%. Thus the difference in bath resistivity between a benchmark bath with a 0.03% carbon content and a bath from a dusty pot will be even larger. Squeezing tests of groups of pots with different bath carbon content confirmed that high levels of dusting affect bath resistivity and consequently the stability margin of the pots.

In this perspective, an objective assessment of the costs generated by carbon dust shall be realized. Under enhanced stress - current creep to increase aluminum production, ACD squeeze to limit specific energy consumption, change in anode recipe - pots shall react very differently depending on carbon dust concentration and stability margin. A comprehensive monitoring of anode quality, carbon content of the bath, butts properties is thus of prime importance.

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