

# Influence of LiF, CaF<sub>2</sub>, MgF<sub>2</sub> additives and of dissolved aluminium on wetting of graphite by the cryolite-based melt

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*Dedicated to Associate Professor K. Matiašovský, DrSc.,  
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Using the “sessile drop” method the angle of contact between graphite and the cryolite-based melt was investigated. The influence of the additions of LiF, CaF<sub>2</sub>, MgF<sub>2</sub> and of dissolved aluminium on wetting of graphite by the melt was studied. It was found that the dissolved aluminium remarkably changes properties of the graphite—cryolite melt interphase while the additions of LiF, CaF<sub>2</sub>, and MgF<sub>2</sub> have only mild influence on this parameter.

It is well known that the interfacial tension on the phase boundary between graphite and the cryolite melt remarkably influences the electrode processes and corrosion of graphite and thus it affects its consumption. A review of different topics related to the consumption of anode carbon during aluminium electrolysis has been recently published in [1, 2]. Discussion of the effect of additions to the electrolyte on the wetting characteristics [2] is based mainly on the data on wetting of carbon materials by electrolyte which have been summarized in [3]. In this paper we will present the results of our investigation of the influence of additives on the angle of contact between graphite and cryolite-based melts. These results differ in some cases remarkably from the literature data [3, 4], which may affect discussion of the influence of additives on the consumption of carbon during aluminium electrolysis.

## Experimental

The angle of contact was measured using the “sessile drop” method. Images of the molten drop of electrolyte lying on the graphite plate were observed and photographed using the high-temperature microscope Leitz—Wetzlar II A-P. The graphite plates were prepared from spectral pure graphite (Elektrokarbon, Topoľčany, CSFR). Fine polishing of these plates was made with a diamond paste ( $d < 1 \mu\text{m}$ ). The plates were purified by ultrasound.

The electrolyte of desired composition was prepared in platinum crucibles. After solidification it was fine ground and pressed into small discs ( $d = 2$  mm,  $h = 2$  mm). The measurement was carried out in an argon atmosphere. Pictures of the molten drop were taken in the time intervals of 10 s and the angle of contact was read off directly from the photograph (Fig. 1). It is important that in contradistinction to the earlier works [3, 4] only negligible time dependence of the angle of contact was observed. This improves remarkably the accuracy of the measurement.

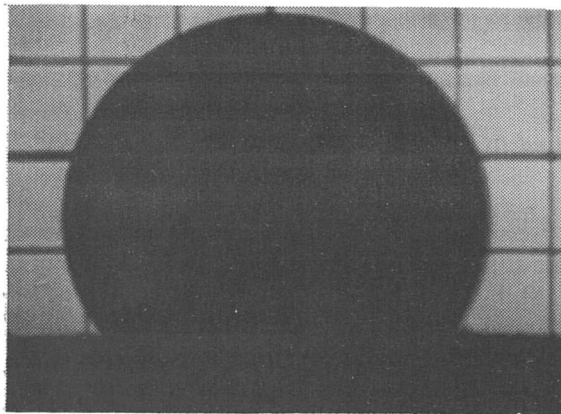


Fig. 1. Image of the molten drop of electrolyte (90 mass %  $\text{Na}_3\text{AlF}_6$  + 5 mass %  $\text{Al}_2\text{O}_3$  + 5 mass %  $\text{LiF}$ ) lying on the graphite plate.  $\theta = 1000$  °C.

## Results and discussion

The results of the experimental investigation of the influence of the addition of  $\text{LiF}$ ,  $\text{NaF}$ ,  $\text{CaF}_2$ ,  $\text{MgF}_2$ , and  $\text{AlF}_3$  on the angle of contact between the spectral graphite plate and cryolite-based melt are summarized in Table 1. The data are related to the temperature of 1000 °C. The cryolite melt contained in all cases 5 mass %  $\text{Al}_2\text{O}_3$ . The following conclusions can be made:

i) In a neutral cryolite melt (cryolite ratio  $\text{CR} = n(\text{NaF}) : n(\text{AlF}_3) = 3$ ) the addition of  $\text{LiF}$ ,  $\text{CaF}_2$ , and  $\text{MgF}_2$  increases the angle of contact between the graphite and the melt. The addition of  $\text{NaF}$  decreases the contact angle. The addition of  $\text{AlF}_3$  (lowering of the cryolite ratio) decreases the angle of contact only down to  $\text{CR} = 2.5$ . Further increase of the aluminium fluoride content has only little effect on the wetting of graphite.

ii) In the cryolite melt having the cryolite ratio 2.0 the additions of  $\text{CaF}_2$  and  $\text{MgF}_2$  have a similar effect as in the neutral melt, lithium fluoride however, has no effect on the wetting of graphite by the melt.

iii) The influence of the additions of  $\text{LiF}$ ,  $\text{CaF}_2$ , and  $\text{MgF}_2$  in basic melts ( $\text{CR} = 3.2$ ) is similar to that in cryolite melts with  $\text{CR} = 3$ .

Table 1

The influence of the addition of LiF, NaF, CaF<sub>2</sub>, MgF<sub>2</sub>, and AlF<sub>3</sub> on the angle of contact between the spectral graphite and the cryolite-based melt  
 $\theta = 1000\text{ }^{\circ}\text{C}$ ,  $w(\text{Al}_2\text{O}_3) = 5\%$

LiF	$w_i/\%$				Wetting angle $\theta/^\circ$	Standard deviation
	NaF	CaF <sub>2</sub>	MgF <sub>2</sub>	AlF <sub>3</sub>		
					112.0	3.2
2					114.3	1.9
3					123.0	1.7
5					127.7	1.1
	3.66				99.4	1.9
		3			119.3	2.1
		8			120.8	2.5
			3		120.0	2.0
			8		129.6	1.1
				7.04	103.9	3.2
				15.84	104.4	6.1
5	3.66				112.7	0.8
	3.66	8			113.0	1.2
	3.66		8		120.7	1.5
5				15.84	103.8	2.7
		8		15.84	125.0	1.2
			8	15.84	115.4	0.8

The influence of cryolite ratio, *i.e.* the influence of the addition of NaF or AlF<sub>3</sub> found in this work is in a fairly good qualitative agreement with literature data [3]. The same can be said about the influence of alumina, though in these two cases the numerical values of the angle of contact between graphite and cryolite melt are slightly different.

However, the data on the influence of additives LiF, MgF<sub>2</sub>, CaF<sub>2</sub> on the wetting of graphite presented in this work differ from those reported by *Belyaev et al.* [4] (see also [3]). The cited authors claim that the additions of LiF, CaF<sub>2</sub>, and MgF<sub>2</sub> have practically no influence on the angle of wetting. This is true only for LiF in acidic melts. In all other cases the additions of LiF, CaF<sub>2</sub>, and MgF<sub>2</sub> increase the angle of contact between graphite and cryolite melt and thus they decrease also the wetting of graphite by the melt.

#### *Influence of dissolved aluminium on the angle of contact*

The results of investigation of the effect of dissolved aluminium on the angle of contact between the graphite and cryolite-based melt can be considered only as qualitative because it is difficult to determine precisely the content of the

dissolved metal in the melt. (A small grain of aluminium was pressed together with the powdered electrolyte.) As it can be seen from Fig. 2 the dissolved aluminium changes remarkably the wetting of graphite by the cryolite melt. The contact angle between graphite and the aluminium-containing melt is lower than  $90^\circ$ . Thus, in this case, graphite is wetted by the melt. This fact is probably very important in the discussion of interaction between carbon materials and the Hall—Héroult bath which can contain dissolved metal. It is not quite clear in which form the dissolved metal is present in the melt.

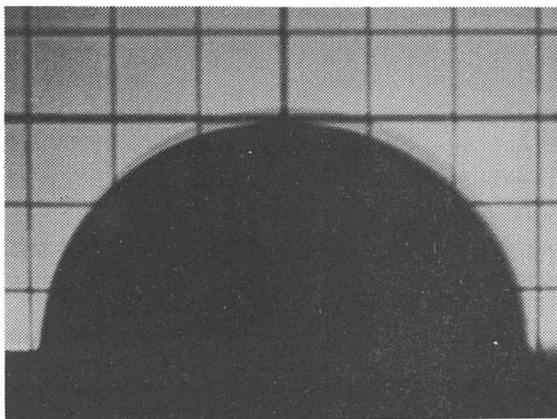


Fig. 2. Image of the molten drop of electrolyte containing dissolved aluminium lying on the graphite plate. Composition of the basic electrolyte and its temperature are the same as those given in Fig. 1.

It is open to discussion whether near the anode where is a surplus of anode gas the dissolved metal can exist at all.

Nevertheless the influence of dissolved aluminium on the behaviour of carbon particles in the aluminium electrolyte has to be taken into account.

### References

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