Solubility and Rate of Dissolution of Alumina in Cryolite-Based AlF_3-Rich Melts with Additions of LiF, CaF_2, and MgF_2

[a]Ž. LUBYOVÁ, [b]P. FELLNER, and [b]J. GABČOVÁ

[a]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, CS-842 36 Bratislava*

[b]*Department of Inorganic Technology, Faculty of Chemical Technology, Slovak Technical University, CS-812 37 Bratislava*

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Equilibrium solubility of alumina in the cryolite melts containing 26 mass % excess AlF_3 and additions of LiF (up to 7 mass %), CaF_2 (3.5 mass %), and/or MgF_2 (up to 10 mass %) was determined. Rate of dissolution of alumina in the melts of given composition was investigated. It was found that the experimental data can be described by a hyperbolic relationship with two adjustable parameters. One parameter corresponds to the equilibrium solubility of alumina in the melts. The other parameter characterizes the used alumina, temperature, and composition of the melt.

Cryolite (Na_3AlF_6) melts which are a good solvent for alumina are used as the electrolytes for electrowinning of aluminium. The temperature of melting of cryolite is 1012 °C [1]. Conventional electrolytes used for aluminium production contain (in mass %) 6—14 % AlF_3, 3—8 % CaF_2, and 2—5 % Al_2O_3. Their temperature of primary crystallization is in the range of 945—970 °C. It might be of advantage to use the electrolytes with lower temperature of primary crystallization [2—4]. One of the possibilities how to decrease remarkably the melting temperature is to increase the content of AlF_3 in the melt [2]. This change in composition has, however, also unfavourable influence on some properties of the electrolyte. One of the negative effects is the lowering of solubility and of the rate of dissolution of alumina in cryolite melts. This work is a contribution to the investigation of this issue.

EXPERIMENTAL

NaF was of anal. grade (Lachema, Brno). Sublimed AlF_3 (Faculty of Chemical Technology, Slovak Technical University, Bratislava) was used. LiF, CaF_2, and MgF_2 were of grade "for monocrystals" (Monokrystaly, Turnov). Aluminium chloride hydrate used for dissolution of solid cryolite electrolyte during the analysis of alumina was of grade "crystalline" (Lachema, Brno).

Al_2O_3 of anal. grade (Fluka) was used for investigation of saturation of melts with alumina. For investigation of the rate of dissolution alumina produced in the Slovak Aluminium Plant Žiar nad Hronom was also used. These two types of alumina have different phase composition, size of particles and specific surface areas. They will be characterized in more detail in the discussion.

Determination of Solubility and Rate of Dissolution of Alumina

Solubility and rate of dissolution of alumina in cryolite-based melts were investigated using the same method. This method was based on the determination of changing of content of alumina in the melt with time. In the case of determination of solubility, 4 g of Al_2O_3 (Fluka) were added to 40 g of the melt. The molten cryolite-based mixture was kept at a constant temperature of 850, 900, and 950 °C and homogenized by stirring. The first sample was taken after 45 min, the other samples were taken in 30 min intervals. Sampling was carried out by sucking the melt in a silica tube connected with a syringe. Solidified electrolyte could be removed easily from this tube. The method used for determination of alumina will be described later.

The rate of dissolution of alumina was studied in a similar way to that described above. In this case 50 g of mixture containing no alumina was heated in a platinum crucible at 900 °C. Alumina was added to the melt using a silica tube. The amount of added alumina corresponded exactly to that required for saturation of the melt at given composition and temperature. In this case sampling of the melt was carried out more frequently at the beginning of measurement, *e.g.* in the time intervals 5, 10, 30, 60, 90, 120, and 150 min.

Determination of Content of Alumina in the Sample

The sample was ground and sieved with a fine mesh sieve (d < 0.05 mm). Exactly 1.000 g of the powdered sample was added to a boiling solution of 30 % $AlCl_3$ (50 cm^3), boiled for 10 min (± 2 s), then cooled for 30 min (± 2 min) and filtered. The filter was dried at 120 °C and calcined at 950 °C. The mass of the residue, which corresponds to the content of alumina in the sample, was determined by weighing. It was found that the standard deviation of this method corresponds to 0.2 mass % of alumina in the sample.

RESULTS AND DISCUSSION

Solubility of Alumina

The equilibrium solubility of alumina was investigated at the temperatures of 850, 900, and 950 °C in the melts of the following composition (mass %):

1. 74 % Na_3AlF_6 + 26 % AlF_3 (it is denoted as MIX)
2. 96.5 % of MIX + 3.5 % LiF
3. 93.0 % of MIX + 7.0 % LiF
4. 96.5 % of MIX + 3.5 % CaF_2
5. 92.0 % of MIX + 3.0 % CaF_2 + 5.0 % MgF_2
6. 87.0 % of MIX + 3.0 % CaF_2 + + 10.0 % MgF_2
7. 89.0 % of MIX + 3.0 % CaF_2 + + 5.0 % MgF_2 + 3.0 % LiF

Table 1. Solubility of Alumina in Cryolite-Based Melts

Melt	θ/°C	w_1(sat) / mass % This paper	w_2(sat) / mass % Ref. [5]	$w_1 - w_2$ / mass %
1	850	4.9	4.8	0.1
1	900	5.9	5.8	0.1
1	950	7.4	6.9	0.5
2	850	4.5	4.3	0.2
2	900	5.6	5.4	0.2
2	950	7.1	6.7	0.4
3	850	4.0	3.8	0.2
3	900	5.3	5.1	0.2
3	950	6.8	6.5	0.3
4	850	4.4	4.4	0.0
4	900	5.5	5.3	0.2
4	950	6.4	6.3	0.1
5	850	3.3	3.8	- 0.5
5	900	5.2	4.6	0.6
5	950	6.3	5.4	0.9
6	850	2.8	3.2	- 0.4
6	900	4.1	3.8	0.3
6	950	5.4	4.6	0.8
7	850	3.1	3.3	- 0.2
7	900	5.0	4.2	0.8
7	950	6.1	5.2	0.9

The results obtained are summarized in Table 1. *Skybakmoen, Solheim,* and *Sterten* [5] investigated the solubility of alumina in cryolite melts by the method based on the determination of mass loss of an alumina disc. The results reported in paper [5] have been presented in the form of a regression equation. The data calculated from the cited work are compared with this investigation in Table 1. It follows that in most cases the agreement between our and literature data is good and it does not exceed the experimental error in the analytical determination of alumina used in this work. Greater deviations are only in the case of melts containing larger amount of additions. Because Skybakmoen *et al.* have not given accuracy of their equation it is difficult to estimate whether the difference is statistically significant.

Rate of Dissolution of Alumina

Rate of dissolution of alumina was investigated in two different melts, *viz.* the melts denoted as No. *1* containing no additions and No. *7* containing all admixtures. The temperature of the bath was 900 °C. Two different types of alumina were used. They were characterized by X-ray phase analysis and electron microscopy (Figs. 1*a* and 1*b*). It was found that alumina supplied by Fluka consists only of α-phase, while alumina from Závod SNP contains also 30 % of ϑ-phase. Mean diameter of alumina grains was determined by scanning microscopy. The mean diameter of Fluka alumina was 4.7 µm and that of the grains from ZSNP equals 16.9 µm. The mechanism of dissolution of alumina in cryolite melts is complicated because the process of dissolution consists of endothermic chemical reaction, heat transfer and transport of dissolved alumina from grain boundaries. In this work it was found that the experimental data can be described by an empirical equation of the type

$$m = \frac{t}{A + Bt} \qquad (1)$$

where m is the mass of dissolved alumina and t is the time of dissolution. The reciprocal value of A corresponds to the initial rate of dissolution at time t = 0

$$\left(\frac{dm}{dt}\right)_{t=0} = \frac{1}{A} \qquad (2)$$

The reciprocal value of B approaches at time $t \to \infty$ the maximum amount of dissolved alumina (saturation of the melt). The experimental data are summarized in Table 2. In Fig. 2, linearized relationships

$$\frac{t}{m} = A + Bt \qquad (3)$$

are plotted.

a)

b)

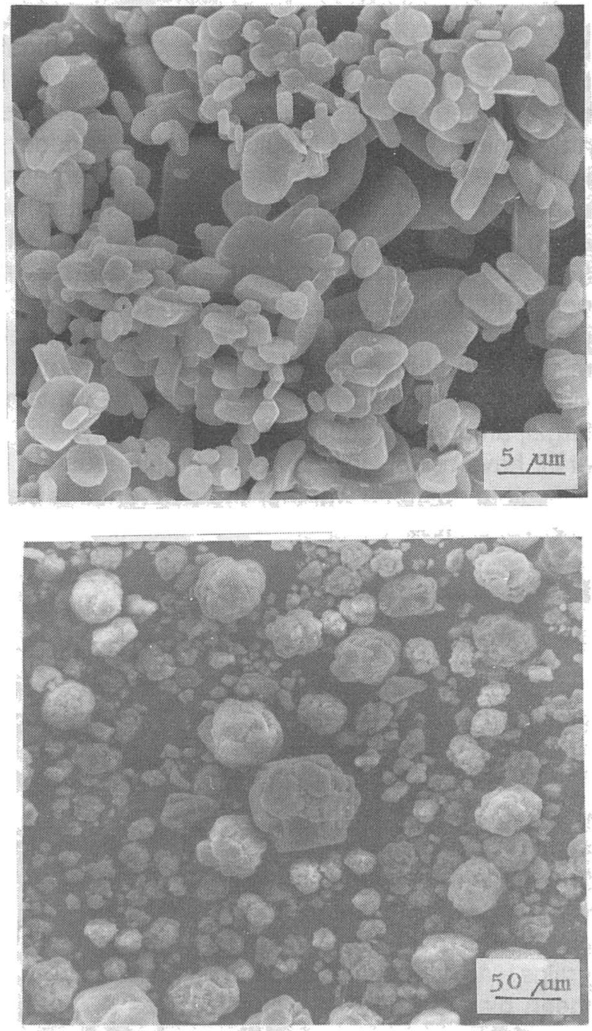

Fig. 1. Electron micrograph of alumina grains. *a*) Fluka, anal. grade; *b*) ZSNP.

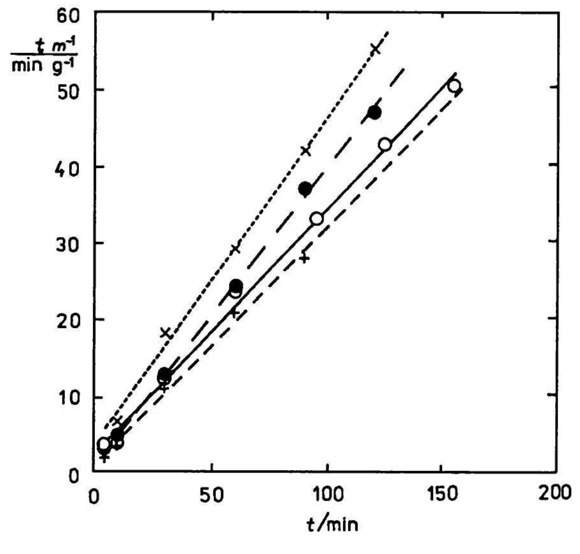

Fig. 2. The dependence $t/m = A + Bt$ for two grades of alumina and two different melts. ○ Al_2O_3 Fluka, anal. grade, melt No. *1*; + Al_2O_3 ZSNP, melt No. *1*; × Al_2O_3 Fluka, anal. grade, melt No. *7*; ● Al_2O_3 ZSNP, melt No. *7*.

Table 2. Mass of Dissolved Al_2O_3 as a Function of Time (θ = 900 °C)

Al_2O_3 (Fluka) in the melt *1*			Al_2O_3 (ZSNP) in the melt *1*		
$m(Al_2O_3)$/g	t/min	$t\ m^{-1}$/(min g^{-1})	$m(Al_2O_3)$/g	t/min	$t\ m^{-1}$/(min g^{-1})
1.30	5	3.846	2.44	5	2.049
2.30	10	4.348	2.49	10	4.016
2.40	30	12.500	2.70	30	11.111
2.55	60	23.529	2.86	60	20.979
2.86	95	33.217	3.24	90	27.778
2.92	125	42.808			
3.08	155	50.325			
Al_2O_3 (Fluka) in the melt *7*			**Al_2O_3 (ZSNP) in the melt *7***		
$m(Al_2O_3)$/g	t/min	$t\ m^{-1}$/(min g^{-1})	$m(Al_2O_3)$/g	t/min	$t\ m^{-1}$/(min g^{-1})
1.43	10	6.993	1.72	5	2.907
1.63	30	18.405	1.95	10	5.128
2.06	60	29.126	2.33	30	12.875
2.15	90	41.860	2.48	60	24.194
2.18	120	55.046	2.43	90	37.037
			2.56	120	46.875

Table 3. The Parameters *A*, *B* and Mass of Alumina Needed for Saturation of the Melts, m_{sat}

Melt	Alumina	A/(s g^{-1})	B/g^{-1}	B^{-1}/g	m_{sat}/g
1	Fluka	2.64	0.317	3.15	3.13
	ZSNP	1.22	0.306	3.27	3.13
7	Fluka	3.90	0.426	2.35	2.53
	ZSNP	1.26	0.386	2.59	2.53

It is evident that this empirical equation describes the experimental data well. The constants *A*, *B* obtained by the linear regression of the experimental data are given in Table 3. The reciprocal value of *B* equals the maximum amount of dissolved alumina. The reciprocal value of *A* characterizes the initial rate of dissolution. It depends on the properties of alumina, composition and temperature of the melts and on the experimental conditions of dissolution. Thus if all parameters except of quality of alumina are the same, this parameter can be used for characterizing the solubility rate of alumina in cryolite melts.

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