

Chemical reactions in molten $\text{Na}_3\text{AlF}_6\text{--SiO}_2\text{--Al}_2\text{O}_3\text{--AlF}_3$ mixtures

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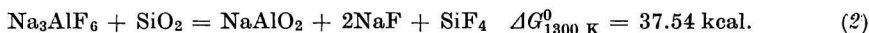
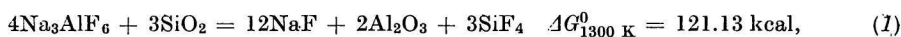
The system $\text{Na}_3\text{AlF}_6\text{--SiO}_2\text{--Al}_2\text{O}_3\text{--AlF}_3$ was studied with regard to the possibility of a one-step production of Al–Si alloy by the electrolysis of the cryolite-based melts. It was found that in the above system the components react and SiF_4 is formed. The dependence of the SiO_2 losses on the melt composition and on the interaction of silica and alumina in a cryolite melt is discussed.

The study of cryolite melts containing silica is interesting from both theoretical and technical aspect. In aluminium electrolysis silica is generally considered to be an undesirable admixture in the electrolyte. But on the other hand SiO_2 can be added to the electrolyte purposely with the intention of a one-step electrolytic preparation of silumine or other silicon-containing alloys [1, 2]. Regarding the possibility of the preparation of silicon alloys by the electrolysis of melts on the basis of cryolite, the study of the kinetics of chemical reactions in the system $\text{Na}_3\text{AlF}_6\text{--SiO}_2\text{--Al}_2\text{O}_3\text{--AlF}_3$ appears to be of prime importance.

Literature data on chemical reactions in a molten system containing silica and alumina dissolved in molten cryolite are very scarce. In the study of the phase equilibria in the system $\text{Na}_3\text{AlF}_6\text{--SiO}_2\text{--Al}_2\text{O}_3$ *Weill* and *Fyfe* [3] determined that the changes in the composition of the melt owing to the formation of volatile SiF_4 were negligible and did not affect significantly the composition of the melt. However, it should be pointed out that the experiments were carried out in a closed system, the sample being sealed in a Pt vial. According to *Monnier* and *Barakat* [4] who carried out the electrolysis of SiO_2 dissolved in a cryolite melt containing 90% Na_3AlF_6 , 5% Al_2O_3 , and 5% CaF_2 , the content of silica decreased after one hour of electrolysis by approx. 10% (from 3.00% to 2.75%) owing to the chemical reactions among the components of the melt.

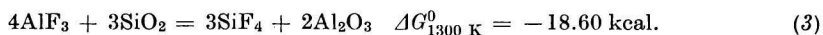
The aim of this work was to determine the influence of different parameters, mainly of the melt composition, on the losses of SiO_2 (and subsequently on the losses of fluorine) from the cryolite melt. Since the silica losses in the form of SiF_4 depend on the kinetics of chemical reactions as well as on the transport properties of the melt and the activity of SiO_2 changes during the reaction of silica with the melt owing to the interaction of silica with alumina which is formed by the above reaction, the determination of the rate constants of these reactions would be only formal. Therefore the experimental results are presented in a tabular form.

Cryolite may react with silica according to the following schemes:



The thermodynamic data for the calculation of ΔG^0 values were taken from [5–7]. The change in the Gibbs energy referring to 1 mole of SiO_2 or SiF_4 according to the respective equations appears to be almost equal. Thus the chemical equilibrium should be shifted markedly to the starting substances and the chemical reactions should not take place. But in an open system, where the newly formed SiF_4 can escape into the atmosphere, the equilibrium is not established. Besides, one should take into consideration that in the molten system $\text{Na}_3\text{AlF}_6\text{--SiO}_2\text{--Al}_2\text{O}_3$ the activities of components taking part in the reaction are not known.

In a melt containing besides cryolite a certain amount of free AlF_3 (the melts of this type are used in the industrial production of aluminium) also the possibility of the occurrence of the reaction should be considered:



From the calculated value of the Gibbs energy it follows that in this case the equilibrium is shifted to the right side and the reaction will occur also in the solid phase with unit activities of components.

From the experimental results of this work it follows that the main problem concerning the explanation of the SiO_2 losses in the system $\text{Na}_3\text{AlF}_6\text{--SiO}_2\text{--Al}_2\text{O}_3$ appears to be the interaction of silica and alumina in the cryolite melt. The existence of such an interaction is confirmed by the increasing solubility of silica in the cryolite melt with an increasing concentration of alumina. According to *Weill* and *Fyfe* [3] only 5% SiO_2 dissolves in molten cryolite at 1010°C , but in a melt containing 14% Al_2O_3 the solubility of silica increases up to 69%. It may be assumed that Al_2O_3 and SiO_2 dissolve in molten cryolite with the formation of complex ions containing both oxygen and fluorine similarly as it is assumed in the case of the $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{O}_3$ mixtures [8].

Experimental

Chemicals

For the preparation of samples the following chemicals were used: hand-picked natural Greenland cryolite (m.p. 1006°C , 54.7% F), precipitated SiO_2 with a low alkali content (Laboratory BDH Reagent), 35–40% hydrofluoric acid "for semi-conductors" (0.025% Si). The other chemicals were of reagent grade.

Working procedure

A homogenized sample (40.00 g) was put into a graphite crucible ($d = 30 \text{ mm}$, $h = 40 \text{ mm}$). The crucible in a steel support was placed into the vertical shaft (Degussite tube, $d = 50 \text{ mm}$) of a resistance furnace with a Kanthal winding. The shaft was closed by two water-cooled brass heads sealed by means of silicon rubber rings. The temperature was measured close to the surface of the melt using a Pt/Pt10Rh thermocouple and was kept constant during the experiment within $\pm 1^\circ\text{C}$ by means of a potentiometric controller. The experiments were carried out in an inert atmosphere by passing a constant stream of argon (1 l/min. controlled by a manostat) through the shaft. After passing through the furnace, the carrier gas containing the reaction products was bubbled through absorbers containing hydrofluoric acid where SiF_4 was absorbed in the form of H_2SiF_6 . The silicon content in the hydrofluoric acid was determined spectrophotometrically as the yellow α -silicomolybdenic acid [9].

Table 1

 Losses of SiO₂ from cryolite melts at 1030°C as a function of the melt composition

No.	Composition of the melt [wt %]				Time [hrs]	Losses of SiO ₂		Comment
	Na ₃ AlF ₆	SiO ₂	Al ₂ O ₃	AlF ₃		[mg]	[%]	
1	95.00	5.00	—	—	4	1.4	4.4	Sample 0.6260 g sealed in a Pt vial
2	90.95	5.00	—	4.05	4	2.4	8.3	Sample 0.5720 g sealed in a Pt vial C.R. = 2.7
3	100.00	—	—	—	0	0		
					1	5.0		
					4	10.0		
4a	95.00	5.00	—	—	0	10	0.50	
					1	228	11.40	
					4	281	14.05	
4b	95.00	5.00	—	—	0	20	1.00	
					1	82	4.10	
					4	260	13.00	
5	90.00	5.00	5.00	—	0	1	0.05	
					1	5	0.25	
					4	21	1.05	
6	85.00	5.00	10.00	—	0	3	0.15	
					1	4	0.20	
					4	17	0.85	
7	90.95	5.00	—	4.05	0	61	3.05	
					1	120	6.00	C.R. = 2.7
					4	305	15.25	
8	81.37	5.00	10.00	3.63	0	4	0.20	
					1	7	0.35	C.R. = 2.7
					4	22	1.10	
9	86.06	5.00	5.00	3.94	0	2	0.10	
					1	3	0.15	C.R. = 2.7
					4	15	0.75	
10	90.00	1.10	8.90	—	0	2	0.45	SiO ₂ + Al ₂ O ₃
					1	2	0.45	mixture from
					4	7	1.60	Závod SNP

The abbreviation C.R. denotes the cryolite ratio (the molar ratio NaF/AlF₃) in the melt.

For the purpose of comparison in some cases the sample was sealed in a Pt vial. After the experiment the sample was dissolved in the hydrofluoric acid and the silicon content was determined [9].

The results of measurements carried out at 1030°C are in Table 1.

Results and discussion

The experimental results are summarized in Table 1. The experiments Nos. 1 and 2 were carried out in a sealed Pt vial. The samples were heated at 1030°C for 4 hours. The silicon losses were small in both cases. It may be assumed that the newly formed SiF_4 was reduced to a small extent by platinum with the formation of platinum silicides or of metallic silicon, this being indicated by the presence of a few small light-ochre coloured grains in the calcined samples. In the course of this reaction the pressure of gases in a sealed vial increases. However, no deformation of the vial was observed even in the case when the melt contained free AlF_3 which is an indirect evidence of the small amount of the formed SiF_4 .

The following experiments were carried out in a graphite crucible by the procedure described in the Experimental. The samples were placed into a cold furnace. The time "0" denotes the moment when the working temperature was reached, *i.e.* approx. after one hour of heating. In Table 1 the total loss of SiO_2 from the beginning of the experiment is reported. *E.g.* in the sample No 4a 10 mg SiO_2 escaped while the sample was heated up to 1030°C, whereas the SiO_2 loss after one hour at 1030°C made 218 mg. Thus from the beginning of the experiment 228 mg of SiO_2 escaped. During the following 3 hours the loss of SiO_2 increased by 53 mg. The total loss during the entire period was 281 mg of SiO_2 . It should be mentioned that this evaluation of the experimental results which comprises the total SiO_2 losses represents also the total experimental error.

The sample No. 5 corresponds to "pure" cryolite. An analysis has shown that this cryolite contains 0.03% Si; this corresponds approximately to 0.06% SiO_2 [9]. When studying the kinetics of the reaction of SiO_2 with components of the cryolite melt, the measurement with "pure" cryolite was several times repeated and the results were found to be reproducible.

The measurements Nos. 4a and 4b represent the limiting values in a series of experiments with samples containing 5% SiO_2 dissolved in cryolite at the beginning of the experiment. Comparison of the experimental results shows that there is a poor reproducibility of the values determined after 1 hour at 1030°C. But after 4 hours the losses of SiO_2 determined in different series of experiments equalized. This is caused most probably by different thermal "history" of the sample during the heating period.

As mentioned above, SiO_2 dissolved in molten cryolite reacts to some extent with the solvent forming Al_2O_3 which dissolves in the melt with the formation of complex ions containing both silicon and aluminium. Consequently, it may be assumed that in the presence of alumina, the reaction ability of SiO_2 will decrease. This assumption was confirmed experimentally (experiments Nos. 5 and 6). From the tabulated data it is evident that in the presence of Al_2O_3 the losses of SiO_2 resulting from the chemical reaction of silica with cryolite melt are strongly reduced.

With regard to the change of the Gibbs energy for the reaction of SiO_2 with AlF_3 (see equation (3)) it can be expected that this reaction will take place even in the solid phase. This assumption was confirmed experimentally (experiment No. 7). But also in this case the rate of the above reaction decreases in the presence of alumina (experiments Nos. 8 and 9).

In the experiments No. 10, the silicon losses were determined in case when a mixture of silica and alumina, prepared from bauxite by a technology used in the Al industry, was added into cryolite (the sample was supplied by Závod SNP in Žiar nad Hronom).

Tentatively, also the influence of an addition of CaF_2 on the SiO_2 losses was determined. It has been found that this addition does not affect substantially the reaction of SiO_2 with the constituents of the melt; however, it decreases the temperature of the primary crystallization of the electrolyte, thus enabling to lower the working temperature in the electrolysis and consequently the silicon losses. This assumption was confirmed experimentally: the silicon losses measured at 970°C in a melt corresponding to the cryolite ratio (NaF/AlF_3 molar ratio) 2.7 containing 5% CaF_2 , 5% Al_2O_3 , and 5% SiO_2 were found to be within a range corresponding to the experimental error (± 1 mg SiO_2).

In all experiments a white substance condensed on the water-cooled closures of the furnace shaft. Comparison of the X-ray diffraction record with the tabulated data [10] showed that this substance consists mostly of NaAlF_4 . No silicon compounds were determined in the condensate.

The study of chemical reactions in the system $\text{Na}_3\text{AlF}_6\text{--SiO}_2\text{--Al}_2\text{O}_3$ thus confirmed the assumption on a pronounced interaction between silica and alumina dissolved in molten cryolite which evidently influences the magnitude of the SiO_2 losses. It was found that under certain conditions this system is fairly stable and might find a technical application in the electrolytic production of silicon alloys.

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