

# Some aspects of the electrolytic preparation of silicon alloys

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The possibility of preparation of silicon alloys by the electrolysis of silica dissolved in cryolite was studied. The data on temperature of primary crystallization, density, and specific conductivity of  $\text{Na}_3\text{AlF}_6\text{—SiO}_2\text{—Al}_2\text{O}_3$  mixtures, important from the aspect of the electrolysis, are presented. Furthermore, decomposition voltage of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  under different conditions and the results on the current efficiency measurements in the electrolytic preparation of Al—Si, Cu—Si, Cu—Al, and Cu—Si—Al alloys are reported.

The idea of the electrolytic preparation of silicon and its alloys is not new. As early as 1865, *Ullik* [1] prepared pure silicon and metallic potassium by the electrolysis of a molten  $\text{K}_2\text{SiF}_6\text{—KF}$  mixture. A review of these attempts is described in [2, 3]. The analysis of the published data leads to the conclusion that the most suitable methods for the preparation of silicon and its alloys are those based on the electrolysis of cryolite ( $\text{Na}_3\text{AlF}_6$ ) systems.

Apart from the theoretical aspect, the preparation of silicon and its alloys by the electrolysis can be attractive from the technical point of view. The desired alloys can be obtained in one step and their purity can be higher than that of alloys produced from thermally prepared silicon. The electrolysis of cryolite melts containing silica can be performed at a relatively low temperature (approx. 1000°C) and it is actually a modification of the well-known Hall—Hérault process for aluminium production. This analogy brings many technical and technological advantages.

In this paper, the results of measurements of some physicochemical properties of  $\text{Na}_3\text{AlF}_6\text{—SiO}_2\text{—Al}_2\text{O}_3$  mixtures which are in relation to the electrolysis of these mixtures are presented. Furthermore, data concerning the electrolytic preparation of Al—Si, Cu—Si, Cu—Al, and Cu—Si—Al alloys are reported.

## Experimental

The temperature of the primary crystallization of  $\text{Na}_3\text{AlF}_6\text{—SiO}_2\text{—Al}_2\text{O}_3$  mixtures was determined by the cooling curve method using a Pt/Pt10Rh thermocouple at a cooling rate of 1°C/min.

The density of the  $\text{Na}_3\text{AlF}_6\text{—SiO}_2\text{—Al}_2\text{O}_3$  mixtures was measured by means of the hydrostatic method. The accuracy of the measured density values was determined to be better than  $\pm 0.5\%$ . For a detailed description of the apparatus see [4].

The specific conductivity of the cryolite mixtures was measured by a double Thompson bridge using platinum electrodes with accuracy better than  $\pm 3\%$ . For a detailed description of the measuring technique see [5].

The determination of the decomposition voltage  $E_d$  of silica and alumina was based on the extrapolation method of  $I-E$  curves to zero current. The experiments were carried out in a graphite crucible using a graphite anode. Temperature was kept constant with an accuracy of  $\pm 2^\circ\text{C}$ . For the electrolysis, a d.c. power supply working at constant current or constant voltage (range 0–5 A, 0–24 V) was used. In this work, the electrolysis was carried out at constant current. The current efficiency (CE) was determined by the analysis of cathodic alloys. For a more detailed description of the apparatus see [2, 6, 7].

## Results and discussion

### *Liquidus curves of $\text{Na}_3\text{AlF}_6-\text{SiO}_2-\text{Al}_2\text{O}_3$ mixtures*

The fusibility data of  $\text{Na}_3\text{AlF}_6-\text{SiO}_2-\text{Al}_2\text{O}_3$  mixtures are presented in Table 1.

*Weill* and *Fyfe* [8] studied the phase equilibria in this system and published the isothermal sections of the system at 800 and 1010°C. From these data it may be seen that the solubility of silica in pure cryolite is rather low (less than 5 wt % at 1010°C). However,

Table 1

Fusibility data [ $^\circ\text{C}$ ], density [ $\text{g cm}^{-3}$ ] and specific conductivity [ $\text{cm}^{-1} \text{ohm}^{-1}$ ] of  $\text{Na}_3\text{AlF}_6-\text{SiO}_2-\text{Al}_2\text{O}_3$  mixtures\*

wt % $\text{Al}_2\text{O}_3$	wt % $\text{SiO}_2$						
	0	2	4	6	8	10	
0	[ $^\circ\text{C}$ ]	1005	1001	995	989	991	993
	[ $\text{g cm}^{-3}$ ]	2.102	2.100	2.099	2.098		
	[ $\text{cm}^{-1} \text{ohm}^{-1}$ ]	2.80	2.63	2.57	2.50		
	[ $^\circ\text{C}$ ]	994	989	993	994	995	995
3.0	[ $\text{g cm}^{-3}$ ]	2.078	2.084	2.087	2.088		
	[ $\text{cm}^{-1} \text{ohm}^{-1}$ ]	2.68	2.57	2.49	2.42		
5.0	[ $^\circ\text{C}$ ]	982	983	987	989	990	990
6.0	[ $\text{g cm}^{-3}$ ]	2.061	2.071	2.078	2.083		
	[ $\text{cm}^{-1} \text{ohm}^{-1}$ ]	2.53	2.41	2.31	2.26		
7.5	[ $^\circ\text{C}$ ]	973	976	980	983	984	984
9.0	[ $\text{g cm}^{-3}$ ]	2.048	2.060	2.070	2.075		
	[ $\text{cm}^{-1} \text{ohm}^{-1}$ ]	2.38	2.28	2.23	2.18		
12.0	[ $\text{g cm}^{-3}$ ]	2.038	2.051	2.060			
	[ $\text{cm}^{-1} \text{ohm}^{-1}$ ]	2.22	2.18	2.15	2.10		

\* Density and conductivity values hold for 1000°C.

increasing the content of alumina in the melt the solubility of silica increases up to 69 wt % of  $\text{SiO}_2$  in the invariant point. It can be assumed that the activity coefficient of silica decreases with increasing content of alumina.

Taking into account the reproducibility of the physicochemical measurements, the possibility of chemical reactions between silica and different constituents of the cryolite melt should be discussed. According to [9] the chemical reaction between silica and cryolite is thermodynamically possible, however, the rate of this reaction being low, any changes in the chemical composition of the melt are negligible.

#### *Density of molten $\text{Na}_3\text{AlF}_6$ — $\text{SiO}_2$ — $\text{Al}_2\text{O}_3$ mixtures*

The densities of molten  $\text{Na}_3\text{AlF}_6$ — $\text{SiO}_2$ — $\text{Al}_2\text{O}_3$  mixtures were measured within the concentration range from 0 to 12 wt %  $\text{Al}_2\text{O}_3$  and from 0 to 5 wt %  $\text{SiO}_2$ , which are approximately the solubility values of silica and alumina, respectively, in molten cryolite at 1000°C. The experimental data are presented in Table 1.

#### *Specific conductivity of molten $\text{Na}_3\text{AlF}_6$ — $\text{SiO}_2$ — $\text{Al}_2\text{O}_3$ mixtures*

The experimental values of the specific conductivity of the studied system are presented in Table 1. There is a great discrepancy between the measured values and those presented by Belyaev [10], this being due to an inadequate measuring technique used in [10].

#### *Decomposition voltage of $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$ in cryolite mixtures*

The results of decomposition voltage measurements are presented in Table 2. It is evident that the measured  $E_d$  values depend on the composition of the electrolyte and on the material of the cathode.

One can object that this method is not sensitive enough. However, it is close to the technical electrolysis and thus it can give a valuable information on the overall cell process.

The standard decomposition voltage  $E^0$  of silica and alumina, calculated from the change in Gibbs free energy at 1300 K, is 1.675 and 2.17 V, respectively. Using a carbon

Table 2

Experimentally determined values of the decomposition voltage of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  under different experimental conditions with a graphite anode

Composition of the electrolyte [wt %]	Cathode	Temperature [°C]	$E_d$ ( $\text{SiO}_2$ ) [V]	$E_d$ ( $\text{Al}_2\text{O}_3$ ) [V]
95% $\text{Na}_3\text{AlF}_6$ + 5% $\text{SiO}_2$	graphite	1000 ± 2	1.00 ± 0.05	—
95% $\text{Na}_3\text{AlF}_6$ + 5% $\text{SiO}_2$	Al	1000 ± 2	1.15 ± 0.05	—
95% $\text{Na}_3\text{AlF}_6$ + 5% $\text{SiO}_2$	Cu	1030 ± 2	1.10 ± 0.05	—
90% $\text{Na}_3\text{AlF}_6$ + 10% $\text{Al}_2\text{O}_3$	Al	1000 ± 2	—	1.45 ± 0.05
90% $\text{Na}_3\text{AlF}_6$ + 10% $\text{Al}_2\text{O}_3$	87.5% Al	1000 ± 2	—	1.25 ± 0.05
	12.5% Si	1000 ± 2	—	1.25 ± 0.05
90% $\text{Na}_3\text{AlF}_6$ + 10% $\text{Al}_2\text{O}_3$	Cu	1030 ± 2	—	1.50 ± 0.05
85% $\text{Na}_3\text{AlF}_6$ + 5% $\text{SiO}_2$ + 10% $\text{Al}_2\text{O}_3$	Cu	1030 ± 2	1.30 ± 0.05	—
85% $\text{Na}_3\text{AlF}_6$ + 5% $\text{SiO}_2$ + 10% $\text{Al}_2\text{O}_3$	Al	1000 ± 2	1.25 ± 0.05	—

Table 3

Kinetics of reaction between Al and SiO<sub>2</sub> dissolved in cryolite at 1000°C\*

Time [hours]	Si wt % in Al—Si alloy		
	Non-constant concentration SiO <sub>2</sub>	Constant concentration SiO <sub>2</sub>	
	without stirring	without stirring	with stirring
0.5	0.7	0.75	—
1.0	1.4	2.2	2.75
2.0	3.2	4.5	5.2
2.0	3.5	—	5.65
3.0	4.8	5.15	—
3.0	5.1	6.0	—
4.0	5.0	—	—
4.0	5.6	—	—

\* Surface of Al 25 cm<sup>2</sup>, weight of Al 40 g, weight of the melt 100 g.

Table 4

Si and Al deposit in the electrolysis of silica and alumina dissolved in cryolite using Al cathode\*

Time [hours]	Weight of deposited Si [g]		Weight of deposited Al [g]
	5 wt % SiO <sub>2</sub>	5 wt % SiO <sub>2</sub> + + 10 wt % Al <sub>2</sub> O <sub>3</sub>	5 wt % SiO <sub>2</sub> + + 10 wt % Al <sub>2</sub> O <sub>3</sub>
1	2.00	1.15	0.45
	—	1.35	0.65
2	3.50	2.70	1.40
	3.75	—	1.95
3	5.75	3.85	2.30
	5.95	4.30	—
4	7.20	—	—
	7.55	—	—

\* Total current 5 A.

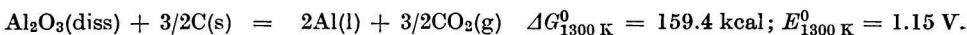
Table 5

Dependence of the current efficiency on the cathodic current density in the electrolysis of SiO<sub>2</sub> (5 wt %) dissolved in cryolite\*

Current density [A cm <sup>-2</sup> ]	Deposited Si [g] Al cathode	CE [%]
		Graphite cathode
0.25	4.75	33
0.50	3.50	45
	3.70	50
1.00	3.25	51
	—	56
1.50	2.85	54
	3.00	56

\* 10 Ah passed through the cell.

anode, and assuming  $\text{CO}_2$  to be a primary anodic product, the following decomposition voltages  $E^0$  calculated on the base of thermodynamic data [11] were obtained



From the thermodynamic considerations it follows that if the unit activity of the components is assumed the metal deposited on the cathode should be silicon. However, the values of experimental decomposition voltage,  $E_d$ , presented in Table 2 were not obtained under standard conditions, this being due to the non-unit activity of the components of electrolyte and by polarization phenomena at the electrodes. It gives a possibility for simultaneous deposition of both metals, silicon and aluminium. A more detailed discussion of these problems can be found in [6].

#### *Chemical reaction between aluminium and silica dissolved in cryolite*

Using aluminium cathode, one must take into consideration the chemical reaction between metallic aluminium and silica dissolved in cryolite. By this reaction, Al—Si alloys have been prepared more than 100 years ago [12]. The results of our experiments on the kinetics of this reaction are summarized in Table 3.

Three series of experiments were carried out. In all experiments, the melt (100 g) was in connection with molten metallic aluminium (surface  $25 \text{ cm}^2$ ) which was placed on the bottom of the graphite crucible. In the first series, the melt contained 5 wt % of silica at the beginning of the experiment. The content of silica decreased in the course of the experiment as a consequence of the chemical reaction between silica and aluminium.

In the second series the content of silica was kept constant.

In the third series, the electrolyte was stirred in order to simulate the conditions existing during electrolysis. A more detailed discussion on this problem may be found in [9].

#### *Current efficiency in the electrolysis of the $\text{Na}_3\text{AlF}_6$ — $\text{SiO}_2$ — $\text{Al}_2\text{O}_3$ mixtures*

##### *Aluminium cathode*

According to Faraday's law, one ampere-hour deposits theoretically 0.2617 g of silicon or 0.335 g of aluminium.

The electrolysis was carried out at  $1000 \pm 2^\circ\text{C}$ , the interpolar distance being 45 mm. The other conditions of the experiment are stated in Tables 4, 5 summarizing the experimental results. For a detailed discussion of this problem see also [6].

##### *Copper cathode*

The electrolysis was carried out at  $1030^\circ\text{C}$ , the interpolar distance being 25 mm. The cathode was formed by a copper disc (diameter 20 mm). The other conditions of the electrolysis are listed in Tables 6—8 summarizing the experimental results.

In the case of copper cathode, silicon diffused to the bulk of cathode. If the surface concentration was, e.g., 0.52 wt % Si, 3.5 mm under the surface the concentration was 0.15 wt % Si and 5 mm under the surface 0.06 wt % Si, respectively.

Table 6

Dependence of the current efficiency in the electrolysis of SiO<sub>2</sub> (5 wt %) using Cu cathode on the time of the electrolysis\*

Time [hours]	2	4	5	7
CE (%)	26.7	30.2	26.2	30.0
CE (%)	28.5	—	28.8	28.4

\* Total current 2 A.

Table 7

Dependence of the current efficiency in the electrolysis of SiO<sub>2</sub> (5 wt %) and Al<sub>2</sub>O<sub>3</sub> (7.5 wt %), respectively, dissolved in molten cryolite using Cu cathode on the total current passing through the cell

Current [A]	2	3	4	5
CE <sub>Si</sub> (%)	26.7	29.6	33.2	34.9
	28.5	—	31.3	—
CE <sub>Al</sub> (%)	41.5	42.6	46.5	52.0
	39.5	—	46.2	—

Table 8

Dependence of Si and Al deposit in the electrolysis of SiO<sub>2</sub> (5 wt %) and Al<sub>2</sub>O<sub>3</sub> (5 wt %) (column A) and of SiO<sub>2</sub> (5 wt %) and Al<sub>2</sub>O<sub>3</sub> (10 wt %) (column B) dissolved in molten cryolite using Cu cathode on the total current passing through the cell\*

Current [A]	1		2		3		4		5	
	A	B	A	B	A	B	A	B	A	B
Si [g]	0.305	—	0.351	0.362	—	0.373	0.372	0.384	0.370	0.395
Al [g]	0.000	—	0.000	0.008	—	0.032	0.110	0.086	0.138	0.183
Si [g]	—	—	0.370	—	—	—	0.392	0.366	0.405	0.390
Al [g]	—	—	0.012	—	—	—	0.076	0.112	—	—

\* 5 Ah passed through the cell.

## Conclusions

From this study it follows that the preparation of silicon alloys by the electrolysis SiO<sub>2</sub> dissolved in cryolite is possible and that it can be attractive also from the technical point of view. In this paper, the preparation of Al—Si, Cu—Si, and Cu—Al—Si alloys was studied. Under the experimental conditions, the prepared Al—Si alloys were liquid and silicon was distributed homogeneously in the alloy. Using the copper cathode, the

Cu—Si, Cu—Al or Cu—Si—Al alloys were formed only on the surface of the cathode and silicon diffused to the bulk of the cathode. However, some other silicon alloys can be prepared in a similar way. A modification of the described process can be used for the electrolytic refining of silicon or for the deposition of thin layers on the surface of the metal.

The relatively low current efficiency found in these experiments is due to the laboratory experimental conditions (small interpolar distance) and we may assume that in the technical electrolysis, the CE would be approximately the same as in the aluminium electrolysis (about 90%).

The fact that the activity of components of an alloy is lower than that of pure metals influences favourably the CE and the decomposition voltage. Besides, in this process, instead of pure silica and pure alumina, some suitable mineral containing both SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> could be used.

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