Chemical Reactions in the System Na_3AlF_6—SiO_2—Al

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The chemical reactions in the system $Na_3AlF_6-SiO_2-Al$ have been studied with regard to the aluminium electrolysis and to the potential significance of this system in the electrolytic production of Si-alloys. It was found that dissolved silica and metallic aluminium reacted to form Al_2O_3 and the Al—Si alloy. Possible consequences of this reaction for the electrolysis have been pointed out.

The study of chemical reactions in molten $Na_3AlF_6-SiO_2$ mixtures is of interest with regard to the Al electrolysis, since silica can be present as an impurity in the electrolyte. On the other hand, it is also possible that a mixture of this type could be used for the electrolytic deposition of silicon and silicon alloys. Reactions of SiO_2 in cryolite melts must also be considered in relation to their effect on the reproducibility of all physico-chemical measurements in these melts.

A number of workers [1—7] have shown that silica reacts with cryolite or aluminium fluoride with the formation of volatile SiF_4:

$$4Na_3AlF_6(s) + 3SiO_2(s) = 3SiF_4(g) + 12NaF(s) + 2Al_2O_3(s), \qquad (1)$$

$$4AlF_3(g) + 3SiO_2(s) = 3SiF_4(g) + 2Al_2O_3(s). \qquad (2)$$

According to *Snow* [8], the reaction between SiO_2 and NaF is also possible:

$$4NaF(s) + SiO_2(s) = 2Na_2O(s) + SiF_4(g). \qquad (3)$$

Ivanova [5] investigated the thermodynamics of the reaction (*1*) and (*2*), and reported the following Gibbs free energies at 1300°K:

$$\text{reaction } (1)\text{: } \Delta G^0_{1300^\circ K} = -19 \text{ kcal},$$

$$\text{reaction } (2)\text{: } \Delta G^0_{1300^\circ K} = -42 \text{ kcal}.$$

The formation of SiF_4 is therefore thermodynamically possible, however, regarding the reaction (*1*) it should be pointed out that in the melt the activities of components would differ considerably from the unity. AlF_3 can be ascribed a certain activity, but the reaction (*2*) will hardly follow the given scheme. The same, to some degree, is valid for the reaction (*3*).

This was also confirmed experimentally. *Weill* and *Fyfe* [9] reported that the maximum amount of trapped gas (which possibly includes some volatile fluorides such as SiF_4 and probably $NaAlF_4$), which might be formed in the melt, would be too small to effect the results. *Monier* and *Barakat* [10] also assume that the rate of reactions (*1*) and (*2*) is fairly low. This means that any changes in the chemical composition of the melt would be negligible.

When metallic aluminium is present in the system Na_3AlF_6—SiO_2, it is necessary to consider the possibility of a reaction between silica and aluminium. It is well known that silicon can be prepared by the thermal reduction of SiO_2 or SiX_4 (X = = halide ion) by means of magnesium, aluminium or carbon. As early as 1864, *Winkler* [11] prepared Al—Si alloys by melting aluminium with cryolite in which the silica powder or water glass was dissolved. A similar preparation of silicon had been described by *Wöhler* [12] eight years earlier. The content of silicon in the alloy was up to 80%.

In those experiments, silicon was prepared according to the reaction

$$3SiO_2(s) + 4Al(l) = 2Al_2O_3(s) + 3Si(s), \qquad (4)$$

$$\Delta G^0_{1300\,°K} = -139.55 \text{ kcal}.$$

It is evident that the thermodynamics of the reaction (*4*) favours the formation of the product. This paper reports the results of preliminary experiments on the kinetics of this reaction in the medium of molten cryolite.

Experimental

The following reagents were used: Al — pure (99.9%) supplied by Lachema, Czechoslovakia, Na_3AlF_6 — hand-picked natural Greenland cryolite, SiO_2 — pure, precipitated, low in alkali, supplied by Reanal, Hungary.

Aluminium (40 g) was placed on the bottom of a graphite crucible (d = 45 mm, h = = 60 mm) and melted with cryolite saturated with silica (100 g of the mixture) in a furnace at 1000 ± 10°C. The surface area of the boundary between the liquid metal and the melt was *ca.* 20 cm². All experiments were carried out in an argon atmosphere. At the conclusion of the reaction period, the liquid Al—Si alloy was cast into an iron mould and cooled. Analysis of the Al—Si alloys was carried out using standard analytical methods [13].

In order to determine the distribution of silicon in the alloy, the crucible in which the alloy was cooled was cross sectioned and the metal was analyzed spectroscopically. The silicon distribution was found to be relatively constant, *e.g.* 5.4 weight % at the surface and 4.8 weight % in the middle of the cross section.

In the first series of experiments the melt containing 5 weight % of silica was used with addition of no supplementary SiO_2. From the reaction (*4*) it follows that the content of silica in the melt is not constant over the reaction period.

In the second series of experiments a graphite crucible with a silica lining was used. The other conditions were the same as above. The lining dissolved during the experiments, thus introducing additional silica into the melt.

In the last series of experiments a graphite crucible with a silica lining was used and the melt was stirred by blowing argon through a graphite tube (d = 3 mm). The flow rate of the gas was appr. equal to the amount of gas evolved during electrolysis using a graphite anode at a current of 5 A.

Results and Discussion

The experimental results are presented in Table 1 and the average values are graphically presented in Fig. 1.

These results confirm the assumption, based on the thermodynamic calculation, that the thermodynamics of the reaction (*4*) favours the formation of silicon.

Table 1

Kinetics of the reaction between Al and SiO_2

t (hrs)	Concentration of Si in Al—Si alloy (weight %)		
	No supplementary addition of SiO_2	Graphite crucible with SiO_2-lining	
		without stirring	with stirring
0.5	0.7	1.0	1.7
	0.8	1.3	—
1.0	1.4	2.2	2.8
	1.6	2.5	—
1.5	2.4	3.2	3.9
	2.8	3.4	4.2
2.0	3.2	4.1	5.3
	3.5	4.5	5.7
2.5	3.9	5.2	—
	4.3	5.7	—
3.0	4.8	5.9	—
	4.9	6.0	—
3.5	5.1	—	—
	5.3	—	—
4.0	5.0	—	—
	5.4	—	—
	5.7	—	—

From the shape of the graphical curves some conclusions can be made about the factors which determine the rate of the reaction (*4*). It was evident that if no supplementary SiO_2 was added during the experiment (first series of experiments), the rate of the reaction (*4*) slowed down after appr. 3 hours, evidently due to the de-

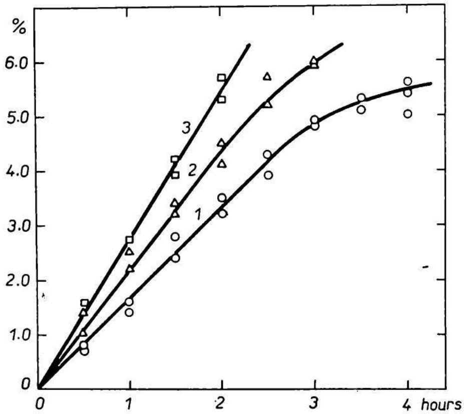

Fig. 1. Dependence of the concentration of silicon in Al—Si alloy (weight %) on the experimental conditions (time in hours).
1. no supplementary addition of SiO_2, no stirring; *2.* SiO_2-lining, no stirring; *3.* SiO_2-lining, stirring.

crease in the concentration of dissolved SiO_2 in the melt at the melt—aluminium boundary. The same phenomenon was observed in the second series of experiment when a graphite crucible with a silica lining was used. In this case, the reaction rate was somewhat higher, but the rate of reaction decreased as the experiment was prolonged. In the last series of experiments, when the melt was stirred by bubbling inert gas through it, the exchange reaction was faster and no decline in the reaction rate was observed during the experimental period. This is evidently due to the maintenance of a constant concentration of SiO_2 at the reaction boundary.

Thus, it can be concluded that under the given experimental conditions, the rate of the reaction (*4*) is a function of the concentration of dissolved SiO_2 at the boundary melt—Al and it is limited by the diffusion rate of the dissolved aluminium.

Since the crucible is situated in a part of the furnace where there is practically no vertical temperature gradient, it can be assumed that there is practically no mixing due to the thermal convection in the melt. Thus the transport of dissolved silica towards the reaction boundary will depend only on diffusion. This assumption is confirmed by the results of the last series of experiments.

Any consideration on the prospective use of cryolite—silica mixtures for the electrolytic deposition of silicon in the form of Si—Al alloys using an Al cathode, must take into account the influence of dissolved alumina on the decomposition potential of silica. In the determination of the decomposition potential only the concentrations of the compounds at the electrodes are important. It is thus evident that the dissolved alumina resulting from reaction (*4*) will exert a significant effect on the decomposition voltage of silica since its concentration at the melt—aluminium boundary can be comparatively high.

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