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Abstract

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ELECTROLYSIS OF MELTS OF $CaO{-}Al_2O_3{-}SiO_2$

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The literature data on the electrolysis of $CaO{-}Al_2O_3{-}SiO_2$ melts are not numerous. Thus, Bockris and coauthors (^{1}) showed the applicability of Faraday's law in the evolution of oxygen in the form of CO and CO_2 at a carbon anode from $CaO{-}SiO_2$ melts. But neither they, nor Martin and Derge (^{2}), who passed current through liquid $CaO{-}Al_2O_3{-}SiO_2$ slags, detected any cathodic products. It is possible that this was due to the low specific gravity of Si, Al, and Ca, the appreciable vapor pressure and their high chemical activity, as well as the formation of ions of lower oxidation state.

In order to capture the products of the cathodic process, we used, as cathodes, liquid cast iron (4.5% C) and copper, capable of dissolving the former, Si and Al, and the latter, in addition, Ca, Mg, and Fe. The experiments were carried out, as previously (^{3}), in a cell made of fused magnesia, having an anode compartment (h = 40—45 mm; d = 15—18 mm), an intermediate compartment (h = 55 mm; d = 7 mm), and a cathode compartment (h = 55; d = 7 mm), connected by thin channels (d = 2—3 mm). The current was supplied from below to cathodes weighing from 3 to 8 g by means of tungsten or molybdenum wires. Carbon rods served as anodes. At the bottom of the intermediate compartment there was a "witness" (liquid cast iron or copper), monitoring the processes in the absence of current. The amount of electricity passed was measured with a copper coulometer. The current efficiency was determined from the change in the composition and weight of the cathode and the "witness."

As is seen from Table 1, the data of which refer to cells close

Table 1

Results of experiments on the electrolysis of $CaO{-}Al_2O_3{-}SiO_2$ melts

Fig. 1

Figure 1: Fig. 1

SiO_2	Al_2O_3	CaO	MgO	Temperature, °C	Current density, A/cm^2	Passed current, A • h	Cathode material	Si	Al	total
6.5	38.4	48.6	7.1	1385	1.29	0.99	cast iron	65.9	13.9	89.8
6.4	41.3	46.6	6.1	1370	1.03	0.95	copper	68.1	15.1	83.2
6.3	41.0	46.2	5.9	1380	1.17	0.72	cast iron	71.0	14.3	85.3
16.9	28.8	45.4	7.5	1380	1.17	0.87	copper	47.2	11.0	58.2
17.2	28.9	45.9	7.2	1375	1.29	1.11	cast iron	46.3	9.6	55.9
36.5	11.0	43.9	8.0	1370	2.47	0.59	cast iron	39.7	4.5	44.2
38.0	11.0	44.5	7.0	1380	1.17	1.02	cast iron	39.5	4.2	43.7
38.2	10.8	44.0	6.8	1380	1.17	1.17	copper	38.7	3.6	42.3
38.7	18.5	35.0	8.3	1380	1.81	1.25	cast iron	41.0	7.9	48.9
39.2	18.6	35.2	7.2	1370	1.17	1.51	cast iron	40.1	7.2	47.3
55.5	13.0	20.7	12.2	1380	1.29	0.90	cast iron	57.3	4.8	62.1
56.1	13.2	21.0	11.1	1390	1.29	0.79	copper	59.2	5.3	64.5
0.2	46.3	47.2	6.1	1440	1.81	0.82	cast iron	–	24.0	24.0

Notes. 1. The data refer to cathode compartments with $h/d = 7.5$—8.0. 2. The content of iron oxides in the slags exceeded 0.15%. 3. Magnesia was introduced into the slag to reduce corrosion of the electrolyzer walls.

size, the principal cathodic product in the electrolysis of $CaO{-}Al_2O_3{-}SiO$ melts is silicon. Its current efficiency varies from 38 to 71%, whereas for Al it is appreciably lower and does not exceed 24%. The total degree of current utilization ranges from 42 to 90%, i.e., it is often far from 100%.

Fig. 1. Current efficiencies of aluminum (A) as a function of the content of Al_2O_3 in slags at h/d of the cathode compartment equal to 8 (points a for a melt of 47% CaO, 47% Al_2O_3, 6% MgO)

To determine on what unaccounted-for process the remaining portion of the passed electricity was consumed, let us compare the dependences of the current

Fig. 2

Figure 2: Fig. 2

efficiencies of Al and Si on their content in the slag. As Fig. 1 shows, the degree of current utilization for aluminum increases regularly together with the content of Al_2O_3 in the melt. By contrast, the current efficiency of silicon, with increasing SiO_2 content, first decreases from 71 to 38%, and then rises to 59%. Its minimum corresponds to slags with the lowest viscosity. Fig. 2 illustrates a definite parallelism between the current efficiency of silicon and the viscosity values of melts taken from the literature ([4–6]). It follows from this that the decrease in the degree of current utilization is due to a process whose rate is determined by the diffusion of certain particles in the electrolyte.

In favor of this is also the regular decrease of the current efficiency of Si with increasing temperature, which lowers the viscosity. Thus, for a slag of composition 36% CaO, 18% Al_2O_3, 39% SiO_2, and 7% MgO, the current utilization was 52% at 1290°, 45% at 1350°, and 41% at 1380°. This is also evidenced by the increase in the current efficiency of Si with increasing ratio of the height of the cathode compartment (h) to its diameter (d) (Fig. 3). The latter circumstance indicates oxidation by the furnace atmosphere of particles that reduce current utilization.

Fig. 2. Current efficiencies of silicon (A) and viscosity (η) of $CaO{-}Al_2O_3{-}SiO_2$ melts for cells with $h/d = 8$

These particles are not only Fe^{3+} ions, since their reduction at the cathode to Fe^{2+} and regeneration at the boundary with the gas phase ([3]) can hardly noticeably affect the current efficiencies, owing to the low content of iron oxides in the melts (up to 0.15%) and the high current densities (up to 6 A/cm^2). As for Mg^{2+} and Ca^{2+} ions, their reduction to monovalent particles under the accepted conditions seems unlikely. To some small extent, perhaps, only the formation of Al subcompounds ([7]) should be taken into account. To this it should be added that calcium was not detected by us at all in copper cathodes, while the current efficiency of magnesium was very small and did not exceed 3-4%. Of course, it is possible that the current utilization for them was somewhat higher, since they could have been lost through evaporation.

Apparently, the most probable competing process is nevertheless the recharge of silicon ions:

$$Si^{4+} + 2e \rightarrow Si^{2+}.$$

The existence of divalent silicon in slags has been shown by a large number of observations (8), and the possibility of a charge-transfer process is indicated by the form of the corresponding polarization curves (9).

Comparatively rapid diffusion of divalent silicon to the catholyte surface and its oxidation there by the furnace atmosphere to tetravalent silicon hinder the development of the process

$$Si^{2+} + 2e \to Si$$

and thereby reduce the current efficiency for silicon.

The smaller utilization of current in the discharge of Al and Mg, as compared with Si, is in qualitative agreement with the greater strength of these oxides, more precisely, with the increasing value of the standard isobaric potential calculated with allowance for the binding energies of these oxides with the melt and the heats of formation of intermetallic compounds with the cathode (FeSi, Cu_2Mg, etc.).

Fig. 3. Dependence of the degree of current utilization (A) (for Si) on h/d of the cathode compartment for a slag of composition 47% CaO, 41% Al_2O_3, 6% SiO_2, and 6% MgO at 1390°

In conclusion, we present data on the anodic dissolution of silicon from Fe–Si (21.3% Si) and Cu–Si (17.5% Si) alloys in slags of different composition (Table 2).

Table 2

Anodic dissolution of silicon in $CaO–Al_2O_3–SiO_2$ melts

CaO	Al_2O_3	SiO_2	MgO	Temperature, °C	Anode composition before the experiment*	Current density, A/cm^2	Duration of experiment, h	Current efficiency, %
35.8	18.3	38.9	7.4	1340	Fe–Si (21.3)	1.03	1.72	104.0
44.2	11.3	37.9	6.5	1310	Fe–Si (21.3)	1.17	1.35	89.2
43.9	11.0	36.5	8.0	1370	Fe–Si (21.3)	1.03	1.17	91.0
48.2	38.7	6.3	7.0	1370	Fe–Si (21.3)	1.29	0.79	97.5
20.7	13.0	55.2	12.2	1380	Fe–Si (21.3)	1.03	0.83	95.3

CaO	Al_2O_3	SiO_2	MgO	Temperature, °C	Anode composition before the experiment*	Current density, A/cm^2	Duration of experiment, h	Current efficiency, %
47.0	46.2	1.2	7.0	1450	Cu–Si (17.5)	1.03	0.94	98.3
48.2	44.0	2.5	7.3	1450	Cu–Si (17.5)	1.17	1.12	103.2

* In parentheses—the percent Si.

As follows from Table 2, it occurs with current efficiencies from 90 to 104%. This, as well as the possibility of obtaining high cathodic current efficiencies, indicates that Faraday' s law is fulfilled in the electrolysis of CaO–Al_2O_3–SiO_2 melts.

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