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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Current Efficiency of Strontium Deposition into an Alloy with Zinc and Cadmium in Electrolysis of Chloride and Oxide–Chloride Melts

A. V. Volkovich, V. I. Zhuravlev, and I. S. Trofimov

Novomoskovsk Institute of the State Educational Institution for Higher Professional Education, Mendeleev Russian University of Chemical Engineering, Tula oblast, Novomoskovsk, Russia

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Abstract—Effect of the current density and electrolysis duration on the cathodic current efficiency by strontium was studied in chloride and oxide–chloride melts.

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One of the most important characteristics of the electrolysis of molten salts with liquid cathodes is the current efficiency by a metal being deposited into an alloy with the cathode metal. It is known that, in contact with the ambient atmosphere in open baths, the technological process occurs with a poor current efficiency. Reasons for such a behavior have not been elucidated so far. It can, however, be assumed that a possible reason is that an oxide is formed in the melt. This communication presents the results obtained in a study of the current efficiency of strontium deposition into an alloy with zinc and cadmium in electrolysis of a chloride melt $(K–Na)Cl_{equiv}$ + 26 mol % $SrCl_2$. In a separate set of experiments, SrO was introduced into the melt.

EXPERIMENTAL

Experiments were performed at a temperature of 973±3 K in the atmosphere of dry purified argon. The electrochemical cell used was described in detail in [2]. All salts of analytically pure grade and strontium oxide of pure grade were preliminarily dried in a vacuum drying box for 48 h, with the temperature gradually raised to 250°C. Immediately before the beginning of an experiment, the salt melt was bubbled through with dry hydrogen chloride and then vacuum-treated until the gas evolution ceased. The gas space of the cell was filled with argon. Zinc of Ts-0 brand and cadmium of Kd-0 brand were used as the cathode materials. The variation of the potentials of the alloys with time was recorded with a TES-2730 digital voltmeter.

The effect of the current density on the current efficiency (CE) of strontium deposition into an alloy with zinc and cadmium is illustrated by Fig. 1. The electrolysis was performed so as to obtain alloys containing 1 mol % Sr. It can be seen that the curves show a peak at the current densities, corresponding to the highest current efficiency by strontium (87 and 95% for alloys with zinc and cadmium, respectively). The rise in the CE of strontium deposition into the zinc and cadmium electrodes upon an increase in the cathode current density is described by the equation [3]:

$$\mathrm{CE} = \frac{i_c - i_{res}}{i_c}, \qquad (1)$$

where i_{res} is the residual current density (A cm^{-2}), equal to 0.008 and 0.003 A cm^{-2} for the zinc and cadmium cathodes, respectively.

As the current density increases further, the current efficiency by strontium decreases in both cases. This occurs because the cathode potential shifts to more electronegative values at which sodium ions can be discharged.

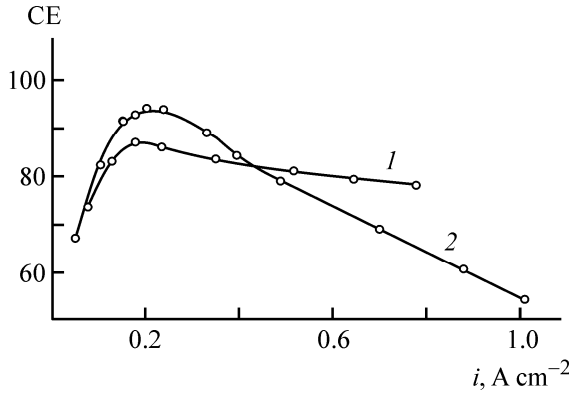

Fig. 1. Effect of the current density i on the current efficiency CE of strontium deposition into an alloy with (*1*) zinc and (*2*) cadmium in electrolysis of a chloride melt.

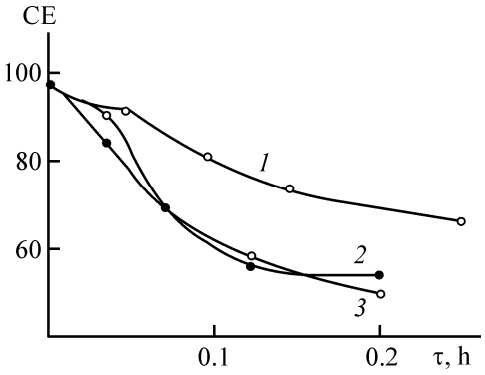

Fig. 2. Effect of the electrolysis duration τ on the current efficiency CE of strontium deposition into an alloy with cadmium. (*1*) Experiment; calculation: (*2*) by Eq. (12) and (*3*) by Eq. (13).

To evaluate the selectivity of liquid-metal electrodes in joint deposition of two metals, strontium and sodium in the given case, and the current efficiencies by strontium, it is advisable to use the selectivity coefficient Θ' [4] of the liquid metallic electrode:

$$\Theta' = X_{Sr}/X_{Na}, \quad (2)$$

where X_{Sr} and X_{Na} are, respectively, the concentrations of strontium and sodium in the alloy (mol fraction).

The separation coefficient Θ and the selectivity coefficient are related by the expression [5]

$$\Theta = \Theta' X_{Na^+}/X_{Sr^{2+}}. \quad (3)$$

If the concentration of strontium in the electrolyte varies only slightly in the course of electrolysis, it can be assumed that its activity coefficient in the melt remains constant. In such a case, it is appropriate to introduce, by analogy with the conditional standard potential of the alloy (E^{**}), the notion of a "conditional equilibrium potential of the alloy" (E^*_{eq}). Then the values of E^*_{eq} for the Sr–Cd and Na–Cd alloys can be found from the expressions

$$E^*_{eq}(Sr^{2+}/Sr\text{–}Cd) = E^{**}(Sr^{2+}/Sr\text{–}Cd) + \frac{RT}{2F}\ln X_{Sr^{2+}}, \quad (4)$$

$$E^*_{eq}(Na^{+}/Na\text{–}Cd) = E^{**}(Na^{+}/Na\text{–}Cd) + \frac{RT}{F}\ln X_{Na^{+}}. \quad (5)$$

Simultaneous solution of the equations of the potential isotherms for the alloys [5]:

$$E^*_{eq}(Sr\text{–}Cd) = E^*_{eq}(Sr^{2+}/Sr\text{–}Cd) + \frac{RT}{2F}\ln X_{Sr\text{–}Cd}, \quad (6)$$

$$E^*_{eq}(Na\text{–}Cd) = E^*_{eq}(Na^{+}/Na\text{–}Cd) + \frac{RT}{2F}\ln X_{Na\text{–}Cd} \quad (7)$$

with account taken of the fact that equilibrium is attained in the melt between all the oxidized and reduced forms of the components of the system [2], gives the following expression for Θ':

$$\Theta' = \ln\frac{X_{Sr}}{X_{Na}} = \frac{F[2E^*_{eq}(Sr\text{–}Cd) - E^*_{eq}(Na\text{–}Cd) - E]}{RT}. \quad (8)$$

Because the total current density i_c consumed for joint deposition of strontium and sodium is i_c–i_{res}, it is appropriate to evaluate the partial current density corresponding to deposition of strontium. At a selectivity coefficient Θ', the quantity of electricity consumed for deposition of strontium and sodium is $X_{Sr}2F$ and $X_{Na}F$, respectively. Then the distribution coefficient K of the quantity of passed electricity is given by

$$K = \frac{X_{Sr}2F}{X_{Na}F} = 2\Theta'. \quad (9)$$

Calculated content of sodium in Sr–Cd and Sr–Zn alloys

Cathode metal	Content in an alloy, $X\times10^2$, mol fraction		Θ'
	strontium	sodium	
Cadmium	0.5	0.25	2.0
	1.0	0.35	2.9
	2.0	0.50	4.0
	5.0	0.79	6.3
Zinc	0.3	0.014	21.5
	1.0	0.014	71
	1.5	0.014	107
	5.0	0.014	357

The fraction K' of current density consumed for deposition of strontium, i_{Sr}, can be calculated using the expression

$$K' = \frac{i_{Sr}}{i_{Sr} + i_{Na}}. \quad (10)$$

K' can be expressed in terms of the selectivity coefficient at a given alloy potential as

$$K' = \frac{2\Theta'}{2\Theta' + 1}. \quad (11)$$

Then the current efficiency of strontium deposition into the alloy can be written at a given current density, with account of the residual current density and the selectivity coefficient, as

$$CE = \frac{i_c - i_{res}}{i_c} K'. \quad (12)$$

The table lists the calculated amounts of sodium in the Sr–Cd and Sr–Zn alloys.

It can be seen that the content of sodium in Sr–Cd alloys increases. The zinc electrode has a higher selectivity toward strontium, compared with the cadmium cathode.

Calculations by Eq. (8) are justified in the case when the activity coefficient of sodium in the alloys remains unchanged upon addition of strontium. The theoretically calculated, by Eq. (12) derived from Eqs. (8) and (11), current efficiency of strontium deposition into an alloy with cadmium and zinc, and its experimental values are presented in Figs. 2 and 3. The same figures also show the differential current efficiency of strontium deposition into an alloy with cadmium, CE*, calculated by the equation

$$CE^* = \frac{m_n - m_m}{m_n^{theor} - m_m^{theor}}, \quad (13)$$

where m_n and m_m are the masses of strontium deposited into the alloy during time intervals n and m; m_n^{theor} and m_n^{theor} are the calculated masses of strontium deposited into the alloy during time intervals n and m, respectively.

As can be seen in Fig. 2 (curve *1*), the current efficiency of strontium deposition into the alloy with cadmium decreases from 94 to 66% as the electrolysis duration increases. This is accounted for by the increase in the amount of sodium deposited into the metallic phase. The calculated curves are in satisfactory agreement with that obtained experimentally. In the case of alloys of the system Sr–Zn, the amount of sodium in the metallic phase remains nearly unchanged, which is due to the low solubility of Na in zinc [6] and narrow existence domain of liquid Sr–Zn alloys [7]. In the course of electrolysis, the alloys rapidly become two-phase.

In the case of the zinc cathode (Fig. 3), the decrease in the current efficiency is due to growth of dendrites of the intermetallic compound $SrZn_{13}$ on the electrode surface, which is accompanied by phase polarization. The cathode current density decreases to become equal to the residual current density.

Figure 4 shows the E–τ curve for galvanostatic electrolysis with a zinc electrode at a current density of 0.234 A cm^{-2}. The quantity of passed electricity corresponded to obtaining an alloy containing 5 mol % Sr. The monotonic shift of the alloy potential to electronegative values, observed at the beginning of electrolysis, corresponds to accumulation of strontium in zinc. In 400 s, the alloy potential abruptly shifts into the region of negative values, and in 1200 s, reaches the potential of the two-phase alloy under current flow conditions (–2.92 V). The subsequent shift of the

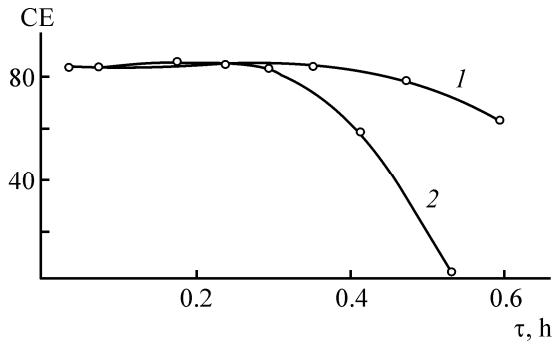

Fig. 3. Effect of the electrolysis duration τ on the current efficiency CE of strontium deposition into an alloy with zinc. Curve: (*1*) experimental and (*2*) differential.

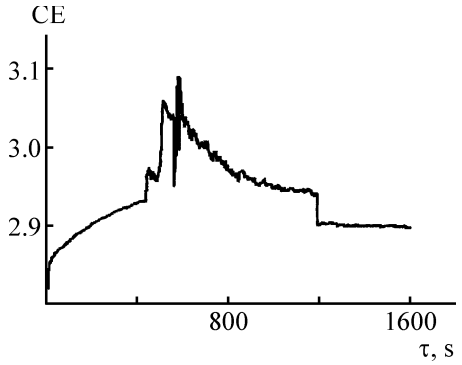

Fig. 4. Zinc potential E vs. the electrolysis time τ of a chloride melt.

potential in the positive direction is due to an increase in the cathode surface area because of the intense growth of crystals of the intermetallic compound $SrZn_{13}$, which leads to a decrease in the actual current density. The growth of the cathode surface area was also observed in [8]. As a result, the current efficiency by strontium decreases to 2%, with the content of strontium in the alloy changing from 4 to 5 mol %.

It has been shown previously that residual currents increase on passing to oxide–chloride alloys [9]. In electrolysis of alloys of composition $(K–Na)Cl_{equiv}$ + 26 mol % $SrCl_2$ + 1.81–3.62 mol % SrO at current densities in the range 0.03–1.0 A cm^{-2}, only trace amounts of strontium were found in liquid zinc and cadmium cathodes. A probable explanation of this fact is that, after a zinc or cadmium electrode is submerged into a melt of this kind, zinc or cadmium ions pass into the electrolyte as a result of corrosion. The products of this process are oxides, which partly settle onto the electrode surface and partly remain in the electrolyte bulk as a finely dispersed suspension [9]. It has been shown [9] that, in oxide–chloride melts, the reduction of strontium ions to give the alloy is preceded by the reaction of metallothermic reduction of CdO and ZnO by subions of the alkali metal and metallic strontium

$$ZnO + Sr = Zn + SrO. \quad (14)$$

The latter can be formed as a finely dispersed powder in the reaction of disproportionation of strontium subions [10]. Therefore, reaction (14) proceeds both at the cathode surface and in the melt bulk. This leads to an additional expenditure of strontium ions, which, in turn, requires an additional quantity of electricity. It was found that Sr–Zn and Sr–Cd alloys with a noticeable content of strontium can be obtained if the content of strontium oxide in the electrolyte does not exceed 0.36 mol %.

The results of experiments on determining the current efficiency by strontium in electrolysis of the melt $(K–Na)Cl_{equiv}$ + 26 mol % $SrCl_2$ + 0.36 mol % SrO_2 at 973 K on liquid zinc and cadmium cathodes are shown in Fig. 5. The general run of curves *1* and *2* is similar to that shown in Fig. 1. However, there are quantitative distinctions. For example, the current efficiency of strontium deposition into an alloy with zinc is almost twice lower in this melt. For the cadmium cathode at a current density of 0.52 A cm^{-2}, the current efficiency by strontium decreases from 92% (Fig. 1, curve *2*) to 59%, respectively. The general decrease in the current efficiency of strontium deposition into the alloy with zinc and cadmium, observed under these conditions, is due to an increase in the residual current density because of the occurrence of reaction (14) and to a rise in the recharging current density of Sr^{2+} ions to Sr+ in the presence of strontium oxide. In the oxide–chloride melt, the potential of the cadmium electrode shifts toward values by 0.01–0.02 V more electronegative than those in the chloride electrolyte. As a result, the fraction of current consumed for reduction of alkali metals increases, which leads to a decrease in the current efficiency of strontium deposition into the alloy with cadmium.

To determine the influence exerted by the electrolysis duration on the current efficiency of strontium deposition into an alloy with cadmium and zinc, the given melt was subjected to electrolysis at a current density of 0.39 A cm^{-2}. The calculated strontium content of the alloy was varied from 0.5×10^{-2} to 5×10^{-2} mol fraction. The results obtained are shown in Fig. 6. The run of the curves is similar to that in Figs. 2 and 3. However, the current efficiency by strontium in

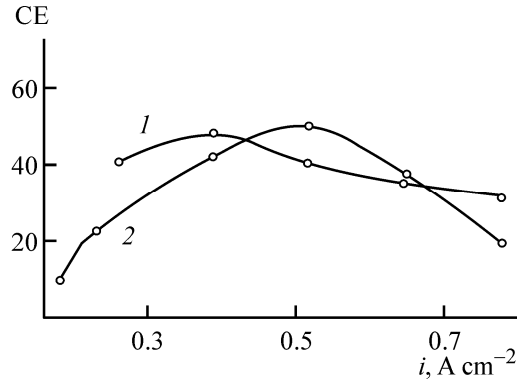

Fig. 5. Effect of the current density *i* on the current efficiency CE of strontium deposition into an alloy with (*1*) zinc and (*2*) cadmium in electrolysis of an oxide–chloride melt.

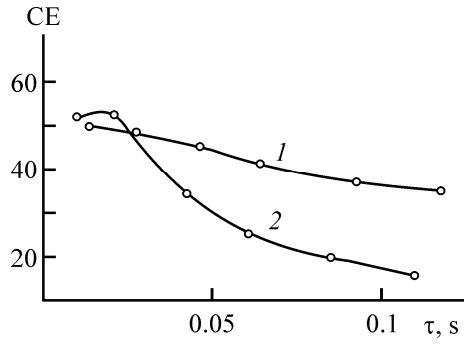

Fig. 6. Current efficiency CE of strontium deposition into an alloy with (*1*) zinc and (*2*) cadmium vs. the duration τ of electrolysis of an oxide–chloride melt.

this alloy is lower. For example, the current efficiency decreased from 94% (Fig. 2) to 51% at a current density of 0.39 A cm^{-2} for the alloy with cadmium, and from 85% (Fig. 3) to 50% at the same current density for the zinc cathode. This satisfactorily coincides with the data on the current efficiency by strontium as a function of the polarizing current density. The current efficiency of strontium deposition into an alloy decreases with time less steeply with a zinc cathode, compared with the cadmium cathode.

CONCLUSIONS

(1) In the electrolysis of chloride and oxide chloride melts, the run of the dependences of the current efficiency of strontium deposition into an alloy with cadmium and zinc on the current density and electrolysis duration is the same.

(2) In electrolysis of a chloride melt, the maximum current efficiencies of strontium deposition into alloys with cadmium and zinc are 94 and 85% at current densities of 0.18 and 0.23 A cm^{-2}, respectively. The decrease in the current efficiency by strontium is attributed to joint discharge with sodium ions for deposition into an alloy with cadmium and to growth of dendrites of the intermetallic compound $SrZn_{13}$ on the electrode surface for the zinc cathode.

(3) In the oxide–chloride melt, the current efficiency of strontium deposition into an alloy with zinc and cadmium decreases nearly twice as compared with the chloride melt because of the increase in the residual current density.

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