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Electrochemical refining of tin through thin-layers of molten electrolytes

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A new principle of tin refining in molten electrolytes is proposed. Its main feature is mass transfer between electrodes through a thin porous diaphragm of $(0.5\text{–}1.0) \times 10^{-3}$ m thickness, which is impregnated with molten electrolyte. The distance between the electrodes is equal to the diaphragm thickness. A mixture of zinc chlorides, alkali chlorides and tin chlorides is proposed as an electrolyte. It is shown that thin layer electrolysis makes it possible to produce tin with an impurity content no more than 1×10^{-3}%. The thin layer electrolysis in melts reduces the specific electrical energy by a factor of 1.5–2.0 and the electrolyte consumption by a factor of 2.5–6.0 per ton of purified tin in comparison with current practice. The results show the proposed method of thin layer electrolysis in molten electrolytes to be promising for tin refining.

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1. Introduction

At the present time, electrolyser designs of the 'crucible in crucible' type have found the widest use in the production and refining of heavy nonferrous metals in molten electrolytes [1–3]. These units are reliable and simple to operate but are characterized by a nonuniform distribution of current density and mass transport intensity on the electrodes [3], making it impossible to control the metal separation and refining processes and causing a decrease in efficiency.

Electrochemical reactors for refining nonferrous metals, such as aluminium, by the three-layer electrolysis method [4, 5] are free from such disadvantages.

One of the main reasons which complicated the use of such reactors for producing and refining heavy nonferrous metals (such as tin, lead, bismuth, indium etc.) was the problem of separating the liquid salt and metal phase independent of their density.

An original technical solution of this problem was proposed in the early sixties [6]. It was suggested to separate the liquid metal and salt phase by means of porous materials, which do not hinder the mass transport of metals in ionic form by the action of electric current and also prevent mechanical infiltration. Porous ceramic materials of different composition and porosity were investigated [6].

As the industrial production of thermally stable ceramic and fibrous porous materials was brought to the commercial level, investigations in this direction were continued independently in Great Britain [7–10] for developing methods for separating lead–antimony, lead–bismuth, lead–zinc alloys and refining aluminium and zinc; in the former USSR [11–15] for developing methods for separating lead–bismuth alloys and refining indium, in US [16–18] and Japan [19–22] for developing a method for refining aluminium.

Many types of electrochemical reactor with different porous materials are described in these papers. Most of them [16–22] are intended for the electrochemical refining of aluminium.

In electrolysis through porous materials, a stable mass exchange between the different liquid electrodes is observed at very small interelectrode distances (of the order of $(0.5\text{–}1.0) \times 10^{-3}$ m) [23], which are equal to the thickness of the porous dielectric, and that the amount of molten electrolyte contained in its pores is sufficient for carrying out electrolysis. The current density on the electrodes can reach 50–80 kA m^{-2} without short circuit, and both the cathodic and anodic yield of metal agrees with the theoretical value within determination error.

It was proposed [23] to call this method 'thin layer electrolysis in molten electrolytes' and to use it for refining heavy nonferrous metals. Thin layer electrolysis in molten electrolytes is an effective method for refining indium, lead and bismuth [23, 24]. This process provides a considerable reduction in specific electric energy and electrolyte consumption due to the very small interelectrode distances [23, 24] and an improvement in refined metal quality [25].

This paper presents a study of mass transfer of tin and accompanying impurities from the anode to the cathode during thin layer electrolysis.

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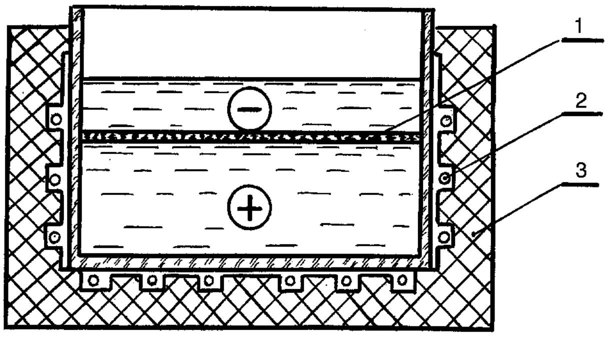

Fig. 1. Schematic diagram of reactor for tin refining by thin layer electrolysis in molten electrolytes. (1) porous dielectric, separating electrodes; (2) heating elements and (3) heat insulator.

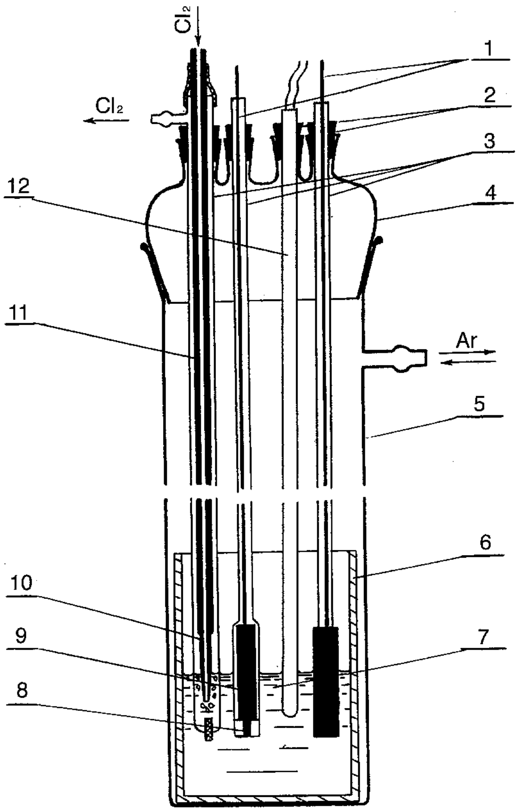

Fig. 2. Cell for electrochemical investigations. (1) Molybdenum current lead, (2) rubber stopper, (3) Pyrex tube, (4) reactor cover, (5) Pyrex reactor, (6) corundum glass, (7) electrolyte, (8) glassy carbon, (9) graphite muff, (10) graphite tube, (11) reference electrode carbon tube and (12) thermocouple.

2. Experimental details

A schematic diagram of the apparatus is shown in Fig. 1. Liquid metal electrodes are separated by a thin porous dielectric material and are located so that their working surfaces are parallel and of equal area, and also that the interelectrode distance is equal to the thickness of the dielectric. The molten electrolyte only occupies the pores of the diaphragm separating the electrodes. Thermally stable textile materials were used as diaphragms. Industrial samples of such materials can withstand a molten metal layer which gives a load of $(6.0 \pm 0.5) \times 10^3\,\mathrm{N\,m^{-2}}$ without mechanical infiltration of metal, permitting them to be used in industrial electrolysers.

The ionization of metal at the anode, transport of formed ions through the electrolyte, and ion discharge at the cathode take place under the action of direct current.

The electrochemical behaviour of heavy nonferrous metals in a molten chloride electrolyte was investigated by cyclic voltammetry under dynamic potential conditions with a potential sweep rate of $2\,\mathrm{mV\,s^{-1}}$ and at 300 °C. The voltammograms were taken in a three-electrode cell with glassy-carbon electrodes which were soldered in molybdenum glass. The cell assembly for electrochemical investigations is shown in Fig. 2.

The cathodic metal was analysed by spectral and atomic absorption methods.

3. Results and discussion

Mixtures of alkali chlorides and zinc chloride were used as electrolyte. These mixtures have a low fusion point, and the metals have more electronegative potentials against tin.

Discharge potential values of tin and accompanying metal impurities in a thoroughly dehydrated eutectic mixture of zinc, sodium and potassium chlorides with 203 °C fusion point are presented in Table 1. These values are given relative to tin for convenience of comparison. Typical discharge voltammograms for different nonferrous metal ions in a molten eutectic mixture of sodium, potassium and zinc chlorides are presented in Fig. 3.

Analytical treatment of the voltammograms indicates that the ion discharge of tin and accompanying impurities occurs reversibly in one stage and is

Table 1. Quantitative characteristics of voltammograms

Metal being discharged	*Deposition potential/V*	*RT/nF/V*		*No. electrons taking part in electrode reaction*	*Convective diffusion coefficient* $10^6 K_d/\mathrm{m\,s^{-1}}$
		theoretical	*experimental*		
Zinc	−0.18	0.025	–	–	–
Lead	−0.07	0.025	0.024	2	8.5
Tin	0.00	0.025	0.024	2	4.2
Copper	0.17	0.025	0.028	2	5.6
Silver	0.25	0.049	0.045	1	9.7
Antimony	0.28	0.016	0.014	3	4.0
Bismuth	0.44	0.016	0.017	3	4.1

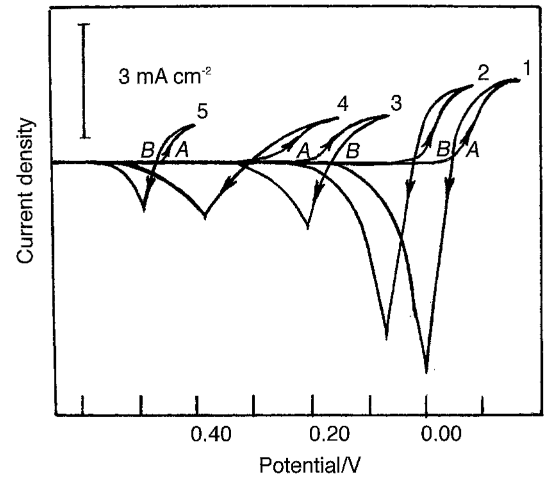

Fig. 3. Typical voltammograms of ion discharge: (1) lead, (2) tin, (3) copper, (4) silver and (5) bismuth.

diffusion controlled. The discharge of each ion has only one wave, whose height is directly proportional to the concentration of metal ions being discharged; the difference between the beginning of the cathodic (point A) and anodic (point B) branches of voltammetric curves is not greater than +40 mV, indicating reversibility. The direct proportionality between the wave height and the concentration of metal impurities in the electrolyte made it possible to calculate the convective diffusion coefficients K_d from the equation

$$i_d = z_i F \frac{D_i}{\delta} C_i = z_i F K_d C_i \qquad (1)$$

Analytical treatment of the voltammograms by a conventional method [2] in V against $\ln(i_d - i)$ coordinates allowed determination of the number of electrons, taking part in the reaction. The quantitative characteristics of cathodic reduction of different nonferrous metal ions from a molten eutectic mixture of zinc chlorides and alkali chlorides are presented in Table 1. The data demonstrate the possibility of selectively depositing tin from the anode on to the cathode. In this case, more electropositive metal impurities (copper, silver, antimony, bismuth) accumulate in the anodic residue, and more electronegative ones disperse in the electrolyte.

To check the operation of a thin layer electrochemical reactor, the yield of tin was investigated at different current densities and tin chloride electrolyte concentrations. Tin with a total impurity content of no more than 1×10^{-4} wt % was used in this experiment. From the data of Table 2 it is clear that stable electrolysis is possible over a wide current density range. The current yield of tin at the electrodes corresponds, within experimental error, to the theoretical in terms of divalent tin, which indicates that there is no mechanical infiltration of liquid metal through the porous diaphragm and mixing of the metallic anodic and cathodic phases. A decrease in tin chloride concentration causes a reduction in cathodic current efficiency and an increase in zinc concentration in the cathodic metal. In this case, the zinc concentration in the cathodic metal depends on the time of electrolysis and decreases with increasing quantity of charge passed as shown in Table 3.

Table 2. Tin transport from the anode to the cathode during thin layer electrolysis

Electrolysis conditions		*Current efficiency*		*Zinc concentration in cathodic metal*/wt %
Current density $10^3 i$/A m^{-2}	*Concentration of tin in electrolyte*/wt %	*anodic*/%	*cathodic*/%	
2.0	0	99.0	95.0	1.08
2.0	5.0	98.5	98.2	0.016
2.0	11.4	99.5	99.0	0.003
2.0	30.0	99.9	98.1	0.0001
0.5	30.0	100.0	99.5	–
1.0	30.0	99.8	99.4	–
5.0	30.0	99.9	99.0	0.0001
10.0	30.0	99.7	98.5	0.0001

Conditions: 300 °C, $Q = 6.0$ A h, interelectrode distance 5×10^{-4} m

This is due to saturation of electrolyte by tin chloride during electrolysis and to tin ion discharge becoming the predominant cathodic reaction.

To elucidate the behaviour of metal impurities during the thin layer electrolysis, crude tin containing 0.0014 wt % zinc, 2.11 wt % bismuth, 2.35 wt % antimony and 2.07 wt % copper was electrolysed. The anode was loaded with 0.200 kg of crude tin. Electrolysis was carried out at 270 °C at different current densities and electrolye tin chloride concentrations with which the diaphragm was impregnated. In all experiments, the quantity of charge passed was the same and corresponded to 60% tin deposited on the cathode. Data on the transfer of metal impurities during the thin layer electrolysis are given in Table 4. The cathodic metal was analysed by spectral and atomic-absorption methods. From Table 4 it is clear

Table 3. Dependence of zinc concentration in the cathodic metal on quantity of electricity passed

Quantity of electricity passed/A h	6.0	10.0	15.0	21.0	27.0
Zinc concentration /wt %	1.08	0.08	0.45	0.32	0.21

Table 4. Metal impurity transport during tin refining by thin-layer electrolysis

Electrolysis conditions		*Concentrations of impurities in cathodic tin*			
Current density $10^3 i$/A m^{-2}	*Tin concentration in electrolyte* /wt %	*zinc* /wt %	*copper* /wt %	*antimony* /wt %	*bismuth* /wt %
2.1	0	0.110	–	0.0010	0.0010
2.1	11.4	0.0010	–	0.0010	0.0010
2.1	30.0	–	–	0.0005	0.0010
3.4	30.0	0.0010	–	0.0005	0.0010
0.5	30.0	0.0010	–	0.0012	0.0020
1.0	30.0	0.0013	–	0.0013	0.0012
2.0	30.0	0.0014	0.040	0.0012	0.0010
3.0	30.0	0.0014	0.040	0.0012	0.0011
5.0	30.0	0.0018	–	0.0012	0.0011
7.0	30.0	0.0020	0.040	0.0010	0.0012
8.0	30.0	0.0066	–	0.0010	0.0012

that the thin layer electrolysis provides an effective removal of electropositive metal impurities such as copper, antimony and bismuth from tin. Removal of zinc from tin through the passing of zinc into the salt phase is also observed. The concentration of tin chloride in the electrolyte does not practically affect the transfer of electropositive impurities, but it has a great influence on the removal of zinc impurity. In the electrolysis of an electrolyte containing 30 wt % tin chloride the zinc impurity concentration in the cathodic metal is not greater than 1×10^{-4} wt %.

The dependence of the zinc content, which is less noble than tin, in the cathodic metal on tin chloride concentration in the electrolyte may be represented as follows. A necessary condition for the codischarge of several elements on the cathode is the equality of their electrode potentials. It is generally considered [2] that the overwhelming majority of nonferrous metals in the molten state, including tin and zinc, are practically nonpolarizable electrodes. In view of this, the dependence of the potential of these metals on the electrolyte composition can be represented, as a first approximation, by the Nernst equation. From the electrode potential equality condition (necessary for codischarge)

$$\begin{aligned} E_{\mathrm{Zn}} = E^0_{\mathrm{Sn}} &= E^0_{\mathrm{Zn}} + \frac{RT}{2F} \ln\left(\frac{a^{2+}_{\mathrm{Zn}}}{a^0_{\mathrm{Zn}}}\right) \\ &\equiv E^0_{\mathrm{Sn}} + \frac{RT}{2F} \ln\left(\frac{a^{2+}_{\mathrm{Sn}}}{a^0_{\mathrm{Sn}}}\right) \qquad (2) \end{aligned}$$

it follows that

$$\ln a^0_{\mathrm{Zn}} \equiv \frac{2F}{RT}(E_{\mathrm{Zn}} - E_{\mathrm{Sn}}) + \ln\left(\frac{a^{2+}_{\mathrm{Zn}} a^0_{\mathrm{Sn}}}{a^{2+}_{\mathrm{Sn}}}\right) \qquad (3)$$

It is evident from Equation 3 that the activity (and hence the content) of zinc in the cathodic metal is dependent, not only on the electrode potential difference, but also on the salt phase and metal phase composition. In the case of electrolysis with a tin cathode ($a_{\mathrm{Sn}} \approx 1$), the zinc content of the cathodic metal must be the lower, the higher the tin chloride concentration. The less the $a^{2+}_{\mathrm{Zn}}/a^{2+}_{\mathrm{Sn}}$ ratio than unity, the lower must be the zinc activity on the cathode. If we assume that the electrode potential difference of zinc and tin is equal to the deposition potential difference of the metals and is −0.18 V, as follows from Table 1, at 300 °C and $a^{2+}_{\mathrm{Zn}}/a^{2+}_{\mathrm{Sn}} = 1$ the zinc activity is estimated to be of the order 6.7×10^{-4}. This parameter can actually have a somewhat different value since the difference between equilibrium electrode potentials and between deposition potentials is not always the same. The behaviour of other less noble metal impurities can be represented in a similar way. In this case it should be taken into account that $a^{2+}_{\mathrm{Zn}}/a^{2+}_{\mathrm{Sn}} \ll 1$.

It was found that the transfer of electropositive impurities is independent of current density in the interval $(2-5) \times 10^3$ A m^{-2}. This may be explained by the fact that transfer is mainly controlled by diffusion and takes place under limiting current conditions. The limiting current value is independent of the total current flowing through the electrolyser. An increase in current density results in a slight increase in zinc concentration in the cathodic metal. This is caused by the fact that at higher current densities, due to concentration polarization, conditions for the codischarge of tin and zinc are attained.

An analytical treatment of experimental data shows that an increase in electrolysis temperature contributes to the enhancement of impurity transfer to the cathode.

It was found [1], that when tin is refined by a conventional method using large amounts of electrolyte, the specific energy consumption is 500–600 kW h, and the electrolyte consumption is 20–50 kg per ton of purified metal.

For the thin layer electrolysis these parameters are 300–400 kW h and 8–9 kg of electrolyte per ton of purified tin. Thus, the results obtained indicate the use of the thin layer electrolysis for tin refining to be highly effective and promising.

4. Conclusion

A new method for refining tin in molten electrolytes has been developed. The essence of the method developed consists in the fact that mass exchange between the liquid electrodes is effected through a thin layer of porous dielectric material impregnated with molten electrolyte, the interelectrode distance being equal to the dielectric thickness $(0.5–1.0) \times 10^{-3}$ m.

In comparison with established practice, the new principle of refining decreases the specific energy consumption by a factor of 1.5–2.0 and the specific electrolyte consumption by a factor of 2.5–6.0 per ton of purified metal.

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