

NOVEL ELECTROCHEMICAL PROCESSES AND TECHNOLOGIES IN IONIC MELTS

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A significant progress in the solution of problems of extracting and refining nonferrous and rare metals (Sn, In, Bi, Zn, Ga, etc) from secondary raw materials and alloys can be achieved by using ionic melts as reaction media.

Electrochemical processes in ionic melts ensure:

- a high rate of mass exchange through effecting chemical and electrochemical transformations in liquid phase (operating temperature range: 210-900°C) and the possibility to use high current densities (up to $1 \cdot 10^4$ A/m²) and compounds in the lowest oxidation states;
- a high selectivity of metal extraction and high refining quality through effecting different variants of mass exchange between the electrodes: from anode to cathode and in the opposite direction, without mass exchange, under filtration conditions (Table 1), using bipolar electrodes and special-purpose materials, e.g. modified β -alumina;
- low specific electrical energy and reagent consumption through the possibility to carry out electrolysis at very small electrode spacing (of the order of 0.5-1.0 mm).

Table 1. Variants of mass exchange between the electrodes in ionic melt electrolysis.

| Transfer | Processes at the electrodes | |
|---|--|--|
| | at the cathode | at the anode |
| Conventional transfer (from anode to cathode) | $Me_1^{n+} + ne^- = Me_1^0$ | $Me_1^0 = Me_1^{n+} + ne^-$ |
| Intermetallide transfer (from cathode to anode) | $Me_2^{i+} + le^- = Me_2^0$ $xMe_2 + yMe_1 =$ $= Me_{2x}Me_{1y}$ | $Me_{2x}Me_{1y} =$ $xMe_2 + yMe_1^{n+} + yne^-$ |
| Without mass exchange | $Me^{m+} + (m-n)e^- = Me^{n+}$ | $Me^{n+} = Me^{m+} + (m-n)e^-$ |
| Owing to filtration | Change in surface tension | Change in surface tension |

An examination of the capabilities of currently known electrochemical technologies showed electrochemical processes in the cells with molten electrolytes and porous materials to be most suitable for the solution of the above problems.

The peculiarities of mass transfer in devices of such type make it possible not only to reduce substantially the specific electrical energy and electrolyte consumption, but also to decrease noticeably the impurity transfer from anode to cathode and hence to improve the quality of metal refining.

Characteristics of indium purification by the conventional method and in the cells with porous diaphragm are listed in Table 2

Table 2. Comparative characterization of indium purification by the conventional electrolysis and electrolysis through porous diaphragm ($i = 1600$ A/m², $t = 220$ °C).

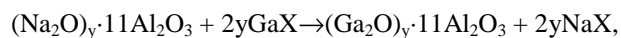
| Metallic impurity | Impurity content (wt %) | | |
|-------------------|-------------------------|---------------------------|--|
| | Before purification | After purification | |
| | | Conventional electrolysis | Electrolysis through thin porous diaphragm |
| Pb | 0.03 | 0.003 | 0.0004 |
| Sn | 0.02 | 0.001 | 0.0002 |
| Cu | 0.02 | 0.0001 | 0.00001 |
| Ni | 0.01 | 0.0001 | 0.00002 |

It has been found that when electrolyzing some metals, e.g. bismuth, gallium, there is either no mass exchange between the electrodes, or it occurs under filtration conditions.

For example, gallium acquire under certain polarization conditions the ability to change the surface tension and, depending on its magnitude, either to leak freely through the porous dielectric material or not. In the case of gallium, this effect manifests itself in hydroxide electrolytes at certain electrode potential values. Anodic polarization of a gallium electrode leads to a decrease in surface tension and to infiltration of gallium through the porous dielectric. Electrode polarization in the opposite direction increases the surface tension, and there is no infiltration.

The effect revealed was used to develop a process for gallium purification by filtration method. It is known that the gallium purification technology involves the operation of filtering off mechanical impurities, which is generally carried out by a vacuum technique. The use of the electrochemical method makes it possible to drop the vacuum technique and to greatly simplify this operation.

It has been found that β -alumina can be used to fill the interelectrode space. This material is notable not only for having a high ionic conductivity but also for the possibility of inverse isomorphous substitution of sodium cations by other cations, for example by monovalent gallium cations, without considerable distortion of the main fragments of the gallium structure:



where X⁻ is halide ions.

β -Alumina modified by cations of the metals to be refined decreases the transfer of metallic impurities from anode to cathode. The use of it for gallium refining makes it possible to obtain the metal of 99.9999% purity with a current efficiency close to the theoretical value.

The use of liquid bipolar electrodes also hinders the transfer of metallic impurities from anode to cathode and makes it possible to obtain on the cathode a metal with a total impurity content of the order of $(1-8) \cdot 10^{-5}\%$.

The effects revealed were used to develop new processes for the separation of nonferrous alloys in ionic melts; most of them have been put into practice in nonferrous metallurgy.