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Abstract

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EQUILIBRIUM POTENTIALS OF TITANIUM IN CHLORIDE MELTS

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There are no data in the literature on the equilibrium potentials of titanium in salt melts. Since they are the most important characteristic of the processes of cathodic deposition and anodic dissolution that underlie the electrolytic production and refining of the metal, we undertook work with the aim of measuring them in electrolytes of various compositions. The present communication gives the results of studies with chloride melts.

It is known (1,2) that in chloride melts in equilibrium with metallic titanium, most of it is present in the form of divalent ions, which are strong reducing agents. Therefore, measurements of equilibrium potentials were carried out under an atmosphere of pure argon in a hermetically sealed cell (Fig. 1). It consisted of a wide quartz test tube, at the bottom of which there was a molten eutectic mixture of lithium and potassium chlorides, previously purged with dry hydrogen chloride and then kept under reduced pressure of about 0.1 mm Hg until the evolution of dissolved gases ceased.

An electrode of iodide titanium was fastened to a molybdenum current lead and immersed in a salt melt of the same composition, contained in an alundum crucible, the walls of which served as a diaphragm preventing the mixing of the electrolyte but allowing current up to 2 A to pass. For stability the crucible was enclosed in a narrow test tube, which had an opening at the bottom, and was immersed in the melt in the wide test tube so that the electrolyte level in the crucible was somewhat higher than in the rest of the cell. Titanium was introduced into the electrolyte in the alundum crucible by anodic dissolution of a metallic electrode, passing a definite quantity of electricity, which measured by means of a copper coulometer. Electrolysis was carried out with an auxiliary cathode, which consisted of a molybdenum wire placed in a separate

Fig. 1. Cell. 1 –quartz test tube, 2 –thermocouple, 3 –molybdenum current leads to the titanium and lead electrodes, 4 –alundum crucible, 5 –narrow test tube, 6 –titanium electrode, 7 –auxiliary cathode, 8 –lead reference electrode, 9 –openings in the test tubes for communication between the gas spaces, 10 – asbestos diaphragms.

Fig. 2. Temperature dependence of the emf between lead and chlorine electrodes

Figure 1: Fig. 2. Temperature dependence of the emf between lead and chlorine electrodes

Fig. 3. Temperature dependence of the emf between titanium and chlorine electrodes for different titanium concentrations in the electrolyte

Figure 2: Fig. 3. Temperature dependence of the emf between titanium and chlorine electrodes for different titanium concentrations in the electrolyte

test tube, in the wall of which there was an opening covered with an asbestos diaphragm. To prevent the deposition of alkali metal, which strongly destroys the walls of the test tube, lead chloride was added to it.

After the required concentration of titanium in the electrolyte had been reached (it was checked after the end of the experiment by chemical analysis of the contents of the corundum crucible), the desired temperature was set and the potential of the titanium electrode was measured relative to a lead reference electrode. The latter consisted of a test tube at the bottom of which there was pure molten lead, and above it a melt of the eutectic mixture of lithium and potassium chlorides containing 8.05 wt.% $PbCl_2$. In the wall of the test tube there was an opening covered with an asbestos diaphragm. Contact with the lead electrode was made by means of a molybdenum wire.

Fig. 2. Temperature dependence of the emf between lead and chlorine electrodes

Fig. 3. Temperature dependence of the emf between titanium and chlorine electrodes for different titanium concentrations in the electrolyte

In special experiments the potential of the auxiliary lead electrode was measured relative to a chlorine electrode, the construction of which was described in earlier work. Measurements of the emf of the element
$Pb/8.05\%$, $PbCl_2$, LiCl, KCl (melt.) $\|$ LiCl, KCl (melt.)/Cl_2, C
were carried out in a cell of analogous design, with the only difference that a chlorine electrode was used instead of the titanium electrode. The results of these experiments are presented graphically in Fig. 2. The experimental points, obtained in the temperature interval 450-700° C, lie on a straight line described by the empirical equation:

$$E = (1.616 - 3.21 \cdot 10^{-4} T) \pm 0.003 \text{ V}.$$

During the measurements the cell was located in a massive metal block heated in an electric resistance furnace with automatic temperature control (the temperature was measured by a thermocouple immersed in the electrolyte), which

Fig. 4. Isotherms of the emf between titanium and chlorine electrodes

Figure 3: Fig. 4. Isotherms of the emf between titanium and chlorine electrodes

could be maintained constant at the assigned value within $±$1°. The potentials accepted as reliable were those which, at the given temperature, remained constant for a long time (1-2 hours) within $±$1 mV.

The emf of the cell
Ti/X $TiCl_2$, LiCl, KCl (melt.) ‖ LiCl, KCl (melt.) ‖ 8.05% $PbCl_2$, LiCl, KCl (melt.)/Pb
was measured in the temperature interval from 410 to 710° at the following titanium concentrations in the electrolyte: 0.2; 0.32; 0.49; 0.94; 5.3 and 5.7 wt.% Ti, which corresponds to concentrations in mole fractions: $4.66 \cdot 10^{-4}$; $7.45 \cdot 10^{-4}$; $1.14 \cdot 10^{-3}$; $2.19 \cdot 10^{-3}$; $1.25 \cdot 10^{-2}$ and $1.35 \cdot 10^{-2}$.

The results of the measurements, recalculated relative to the chlorine reference electrode, are presented in Fig. 3 in the form of a graph of the temperature dependence of the emf at specified titanium concentrations in the electrolyte. As can be seen—

but the experimental points lie fairly well on straight lines (Fig. 3), to which the following empirical equations correspond:

$$\begin{aligned}
E_{0.2\%\mathrm{Ti}} &= (2.374 - 2.82 \cdot 10^{-4} T) \pm 0.002 \text{ V} \quad \text{(line 1)};\\
E_{0.32\%\mathrm{Ti}} &= (2.380 - 3.11 \cdot 10^{-4} T) \pm 0.004 \text{ V} \quad \text{(line 2)};\\
E_{0.49\%\mathrm{Ti}} &= (2.367 - 3.17 \cdot 10^{-4} T) \pm 0.002 \text{ V} \quad \text{(line 3)};\\
E_{0.94\%\mathrm{Ti}} &= (2.385 - 3.67 \cdot 10^{-4} T) \pm 0.002 \text{ V} \quad \text{(line 4)};\\
E_{5.3\%\mathrm{Ti}} &= (2.374 - 4.30 \cdot 10^{-4} T) \pm 0.001 \text{ V} \quad \text{(line 5)};\\
E_{5.7\%\mathrm{Ti}} &= (2.389 - 4.66 \cdot 10^{-4} T) \pm 0.003 \text{ V} \quad \text{(line 6)}.
\end{aligned}$$

To see how the emf changes with the concentration of titanium in the melt at constant temperature, Fig. 4 gives isotherms calculated from these empirical equations for 700, 800, 900, and 1000° K. The emf values are plotted against the logarithms of the mole-fraction concentration of titanium in the electrolyte. The recomputed experimental points lie on straight lines whose slopes are very close to the values $2.3\,RT/2F$ at the corresponding temperatures.

Fig. 4. Isotherms of the emf between titanium and chlorine electrodes

Thus, the equilibrium potential of a metallic titanium electrode in chloride melts containing up to 6 wt.% Ti varies with its mole-fraction concentration in the electrolyte in accordance with the thermodynamic equation:

$$E = E^0_{\mathrm{Ti}/\mathrm{Ti}^{2+}} + \frac{2.3RT}{2F} \lg[\mathrm{Ti}^{2+}].$$

This indicates that such melts contain predominantly ions of divalent titanium and behave as ideal solutions.

The quantity $E^0_{\mathrm{Ti/Ti^{2+}}}$ entering into this equation can be found from the experimental data obtained by excluding the thermo-emf between the molybdenum and carbon current leads to the titanium and chlorine electrodes, which is opposite in sign to the desired electrochemical potential difference (4). It is found to be equal to:

$$E^0_{\mathrm{Ti/Ti^{2+}}} = (-2.371 + 6.09 \cdot 10^{-4} T)\ \mathrm{V}$$

relative to the chlorine reference electrode.

It is of interest to compare this quantity with the value $E^0_{\mathrm{Th/Th^{2+}}}$ previously found by us for thorium. As should have been expected from the general regularities observed in the periodic system of the elements, titanium proves to be considerably more electropositive than thorium. In chloride melts containing, at equilibrium with the corresponding metals, their dichlorides, the difference

$$E^0_{\mathrm{Ti/Ti^{2+}}} - E^0_{\mathrm{Th/Th^{2+}}} = (0.82 - 4.34 \cdot 10^{-4} T)\ \mathrm{V}$$

reaches 0.4 V at 700° and 0.3 V at 900°.

It is easy to show that the decomposition voltage of pure molten titanium dichloride is equal to:

$$E_{\mathrm{decomp.}} = 0.225 \cdot 10^{-4} T - E^0_{\mathrm{Ti/Ti^{2+}}} - \frac{RT}{2F} \ln f_{\mathrm{Ti^{2+}}} \cdot f^2_{\mathrm{Cl^-}}.$$

where $f_{\mathrm{Ti^{2+}}}$ and $f_{\mathrm{Cl^-}}$ are the activity coefficients of titanium and chlorine ions in the melt of the pure salt, taking as the standard state $(f_{\mathrm{Ti^{2+}}} \cdot f^2_{\mathrm{Cl^-}} = 1)$ its dilute solutions in a molten mixture of alkali-metal chlorides—

If it is assumed that these melts behave as ideal solutions up to pure molten titanium dichloride, then for the decomposition voltage we obtain the expression:

$$E_{\mathrm{decomp}} = (2.371 - 5.86 \cdot 10^{-4} T)\ \mathrm{V}.$$

From this one can calculate the change in isobaric potential for the reaction of formation of liquid titanium dichloride from the elements:

$$\mathrm{Ti_{(s)} + Cl_{2(g)} = TiCl_{2(l)}}$$

$$\Delta Z = (-109\,360 + 27.03T)\ \mathrm{cal/mol\ TiCl_2}.$$

Consequently, $\Delta H^\circ_{\text{form}} = -109\,360$ cal/mol $TiCl_2$. From the entropy of the reaction, $\Delta S = -27.03$ cal/deg, it is easy to calculate the standard value of the entropy of liquid titanium dichloride, if $S^\circ_{\text{Ti(s)}} = 7.24$ and $S^\circ_{\text{Cl}_2\text{(g)}} = 53.29$ cal/deg$\cdot$ mol (5). It is found to be: $S^\circ_{\text{TiCl}_2\text{(l)}} = 33.5$ cal/deg $\cdot$ mol.

In the literature (6-11) there are data on the heat of formation and entropy of solid titanium dichloride. If their average values (11) are taken: $\Delta H^\circ_{\text{TiCl}_2\text{(s)}} =$ 120.6 kcal/mol and $S^\circ_{\text{TiCl}_2\text{(s)}} = 24.7$ cal/deg $\cdot$ mol, then for the heat and entropy of fusion of titanium dichloride we obtain the quantities: $\Delta H_{\text{fus}} = 11.2$ kcal/mol and $\Delta S_{\text{fus}} = 8.8$ cal/mol. According to them the salt should melt at about 1000°. In the literature (12) there are indications that the melting point of this salt lies at about 900°.

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