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Stationary Potential and Corrosion of Metals in Molten Salts

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Very often we encounter corrosion of metals in molten salts, where the oxidizer and the corrosion products are present in ionic form. At high temperatures, ion discharge and ionization of metals in these media proceed without significant difficulty, as a result of which thermodynamic equilibrium should exist between the corroding metal and its ions, and also between the ions of the oxidizer and its reduced form in the layer of melt adjacent to the metal. And this means that the equilibrium potential of the metal relative to its ions in the near-electrode layer of the electrolyte

$$E_1 = E^0_{\mathrm{Me/Me}^{n+}} + \frac{RT}{nF}\ln[\mathrm{Me}^{n+}]$$

is equal to the oxidation-reduction potential of the medium immediately near the electrode

$$E_2 = E^0_{\mathrm{oxid/red}} + \frac{RT}{nF}\ln\frac{[\mathrm{oxid}]_S}{[\mathrm{red}]_S}.$$

At the first moment after immersion in the melt, when thermodynamic equilibrium has not yet had time to become established, the electrode potential of the metal has a substantially more electronegative value than the oxidation-reduction potential of the surrounding medium. As a consequence of this, reduction of the oxidizer begins: oxid. (melt) $+me \to$ red. (melt), which proceeds at the expense of dissolution (corrosion) of the metal: $\mathrm{Me} - ne \to \mathrm{Me}^{n+}$ (melt). As the corrosion products (Me^{n+} and the reduced form of the oxidizer) accumulate in the near-electrode layer, the electrode potential of the metal shifts toward more positive values, while the oxidation-reduction potential, conversely, shifts toward more negative values. Equilibrium is reached when these potentials become equal, i.e., a definite stationary potential is established on the metal,

$$\varphi_{\mathrm{stat}} = E_1 = E_2.$$

It will be maintained as long as the corrosion conditions remain unchanged (the temperature and the oxidation-reduction potential of the medium).

The layer of melt adjacent to the metal, however, is not in equilibrium with the entire volume of the medium. Because of this, corrosion does not cease when the stationary potential is established. It continues, but now at a constant rate determined by diffusion of the oxidizer to the metal and of the products of its corrosion into the bulk of the melt. In those cases where the concentrations of ions of the corroding metal and of the reduced form of the oxidizer in the melt are practically equal to zero, and the concentration of the oxidizer is maintained unchanged, one may write, from the conditions of linear diffusion:

$$nFD_{\mathrm{Me}^{n+}}\frac{C^S_{\mathrm{Me}^{n+}}}{\delta} = nFD_{\mathrm{red}}\frac{C^S_{\mathrm{red}}}{\delta} = nFD_{\mathrm{oxid}}\frac{C_{\mathrm{oxid}} - C^S_{\mathrm{oxid}}}{\delta} = i_{\mathrm{cor}}.$$

These equalities are a direct consequence of the condition of thermodynamic equilibrium between the corroding metal and the corresponding ions in the layer of melt adjacent to it, since the corrosion products Me^{n+} and the reduced form of the oxidizer are formed simultaneously and, moreover, in a strictly definite ratio.

From a practical point of view, the greatest interest is presented by an equation relating the corrosion rate of a metal, expressed as the current i_{cor} (A/cm^2), to the values of its electrode potential, $E^0_{\mathrm{Me/Me}^{n+}}$, and the diffusion coefficient of its ions, $D_{\mathrm{Me}^{n+}}$, in the given medium. From the conditions of linear diffusion it follows that the concentration of ions, Me^{n+}, expressed in g-ions/cm^3 of melt in the near-electrode layer, is equal to $C^S_{\mathrm{Me}^{n+}} = \dfrac{\delta i_{\mathrm{cor}}}{nFD_{\mathrm{Me}^{n+}}}$, or, passing to mole-fraction concentration,

$$[\mathrm{Me}^{n+}]_S = \frac{M_{kx}}{d_{kx}}\,\frac{\delta i_{\mathrm{cor}}}{nFD_{\mathrm{Me}^{n+}}}.$$

Here M_{kx} and d_{kx} are the molecular weight and density of the molten salt.

Substituting this value into the corresponding equation for the stationary potential, we obtain the desired relation between the value of the stationary potential of the metal and the rate of its corrosion (in A/cm^2), expressed through the thermodynamic $\left(E^0_{\mathrm{Me/Me}^{n+}}\right)$ and kinetic $(D_{\mathrm{Me}^{n+}})$ characteristics of its ions in the given medium:

$$\varphi_{\mathrm{stat}} = E^0_{\mathrm{Me/Me}^{n+}} + \frac{RT}{nF}\ln\frac{M_{kx}}{d_{kx}}\,\frac{\delta i_{\mathrm{cor}}}{n\cdot F\cdot D_{\mathrm{Me}^{n+}}}.$$

In an analogous way one can derive an equation relating the stationary potential and the corrosion current through the thermodynamic $\left(E^0_{\mathrm{ox/red}}\right)$ and kinetic parameters (D_{ox} and D_{red}) of the medium in which corrosion proceeds:

$$\varphi_{\text{stat}} = E^0_{\text{ox/red}} + \frac{RT}{mF} \ln \left(\frac{nFD_{\text{red}}}{\delta i_{\text{cor}}} \frac{M_{kx}}{d_{kx}} [\text{ox.}] - \frac{D_{\text{red}}}{D_{\text{ox}}} \right).$$

Here [ox.] is the mole-fraction concentration of the oxidizer in the salt melt.

The stationary potential is an important quantitative characteristic of the corrosion of metals in salt melts, having an electrochemical nature. The special value of this process parameter lies in the fact that it is easily accessible to direct measurements. Knowing $E^0_{\text{Me/Me}^{n+}}$ and $D_{\text{Me}^{n+}}$ for the ions of the metal corroding in the given medium, one can calculate from the value of the stationary potential the current (i.e., the rate) of corrosion:

$$\lg i_{\text{cor}} = 5{,}040 \, \frac{n}{T} \left(\varphi_{\text{stat}} - E^0_{\text{Me/Me}^{n+}} \right) + \lg \frac{nFD_{\text{Me}^{n+}}}{\delta} \frac{d_{kx}}{M_{kx}}.$$

The role of oxidizers may be played by cations of the salt medium, which occurs, for example, during corrosion in pure melts of chlorides of alkali metals freed from foreign impurities. The process here proceeds by recharge of cations of ordinary valences to subions

$$2n\,\text{K (melt)} + ne \to n\,\text{K}_2^+ \text{ (melt)}$$

$$\text{Me} - ne \to \text{Me}^{n+} \text{ (melt)}$$

Some authors say that displacement of alkali metals occurs. However, in reality they are not liberated in the free state, but form solutions in melts of their chlorides. There are many grounds for believing that atomic-ion groupings of the type of the subions K_2^+ are formed in this case.

In order to test experimentally the considerations we have expressed concerning the possible mechanism of corrosion of metals in salt melts, we studied the behavior of metallic zirconium in a molten equimolar mixture of NaCl—KCl, subjected to careful purification from impurities. All experiments were carried out under an atmosphere of pure argon, which

excluded access of oxidants to the melt from outside. The stationary potentials of zirconium relative to a chlorine reference electrode were measured at 700, 800, and 900°. The results are presented graphically in Fig. 1. The experimental points fit quite satisfactorily on a straight line corresponding to the empirical equation: $\varphi_{\text{stat}} = 2.47 - 2.2 \cdot 10^{-4} T$ V.

The system Zr—NaCl—KCl melt was chosen by us not accidentally. It had previously been established that in NaCl—KCl melts dilute with respect to zirconium

Fig. 1. Temperature dependence of the stationary potential of zirconium in NaCl—KCl.

Figure 1: Fig. 1. Temperature dependence of the stationary potential of zirconium in NaCl—KCl.

and in equilibrium with the metal, the overwhelming fraction of its ions is accounted for by Zr^{2+}, and the values of the electrode potential $E^0_{Zr/Zr^{2+}}$ (^{1}) and the diffusion coefficient $D_{Zr^{2+}}$ (^{2}) were found in the temperature range investigated by us. For the density of the NaCl—KCl melt, data from other authors (^{3}) were used. Table 1 gives the results of calculating the corrosion current for the indicated temperatures, under the assumption that the thickness of the diffusion layer of the melt at the metal surface is equal to 10^{-1} cm.

Fig. 1. Temperature dependence of the stationary potential of zirconium in NaCl—KCl.

Then direct determinations were carried out (from the loss of weight of the specimens and analysis of the salt melts) of the corrosion of zirconium under the very same conditions in which its stationary potential was measured. The duration of exposure of the metal in the salt melt was different in individual experiments, the results of which are presented in Table 2.

The corrosion currents found by the direct method, within the limits of possible errors of determinations and measurements, agree sufficiently well with those calculated from the values of the stationary potentials.

As was shown above, the value of the stationary potential can also be related to the diffusion flux of the second corrosion product—subions of alkali metals.

Table 1

T-ra, °C	φ_{stat}, V	$E^0_{Zr/Zr^{2+}}$, V	$D_{Zr^{2+}} \cdot 10^5$, cm^2/sec	$d_{NaCl—KCl}$, g/cm^3	$i_{corr} \cdot 10^4$, A/cm^2
700	−2.26	−1.898	3.29	1.590	3.1
800	−2.23	−1.831	5.38	1.528	4.0
900	−2.21	−1.764	8.06	1.467	4.8

Table 2

Fig. 2. Polarization of a molybdenum cathode in NaCl—KCl: 1 —700°, 2 —800°, 3 —900°

Figure 2: Fig. 2. Polarization of a molybdenum cathode in NaCl—KCl: 1 —700°, 2 —800°, 3 —900°

T-ra, °C	Holding time, h	Corrosion of specimen, g · 10^{-3}	Final concentration of zirconium in the melt, mol. fractions · 10^{-4}	Corrosion rate, g · cm^{-2} · h^{-1} · 10^{-4}	$i_{corr} \cdot 10^4$, A/cm^2
700	4.3	10.7	0.52	3.3	1.94
700	9.25	21.9	1.06	3.3	1.94
800	4	19.0	0.92	6.1	3.6
800	4	22.9	1.11	7.4	4.35
800	6	21.7	1.05	5.2	3.06
800	11.75	39.0	1.90	5.0	2.94
900	4	30.6	1.49	9.3	5.48
900	6	29.7	1.44	6.7	3.94

The correctness of this assumption is also amenable to experimental verification. For this purpose zirconium should be replaced by a more electropositive metal, for example molybdenum, and it should be polarized cathodically under the same conditions. Then, obviously, at a potential equal to the stationary potential of zirconium, the polarizing current must coincide with the corrosion current. Figure 2 shows polarization curves recorded on a molybdenum cathode in NaCl—KCl melt relative to a chlorine reference electrode.

As can be seen, at potentials corresponding to the stationary potentials of zirconium at the same temperatures, the polarizing currents are close to the corrosion currents.

The magnitude of the corrosion current can also be judged from the anodic-polarization curves of zirconium (^{4}). When the polarizing current i is less than the self-dissolution current

tion (corrosion) of the metal, its potential remains practically constant and equal to the stationary value. When $i \gg i_{cor}$, the anode potential begins to increase, and linearly with the current density as a result of concentration polarization. Figure 3 shows polarization curves for a zirconium anode, obtained in a NaCl—KCl melt at 700, 800, and 900° relative to a chlorine reference electrode.

Fig. 2. Polarization of a molybdenum cathode in NaCl—KCl:

Fig. 3. Polarization of a zirconium anode in NaCl—KCl: 1 –700°, 2 –800°, 3 –900°

Figure 3: Fig. 3. Polarization of a zirconium anode in NaCl—KCl: 1 –700°, 2 –800°, 3 –900°

1 –700°, 2 –800°, 3 –900°

Fig. 3. Polarization of a zirconium anode in NaCl—KCl:
1 –700°, 2 –800°, 3 –900°

The points of intersection of the extended rectilinear portions of the curves correspond to a polarizing current close in magnitude to the corrosion current of zirconium under the same conditions. A similar picture is observed in the case of beryllium (5), titanium (6), hafnium (4), and uranium (7).

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Note: Figure translations are in progress. See original paper for figures.