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V. V. KHLYNOV and O. A. ESIN

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Abstract

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V. V. KHLYNOV and O. A. ESIN

ELECTROCAPILLARY MOTIONS IN MOLTEN SLAGS

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In the slags of nonferrous metallurgy, metal and its compounds are lost not only as a result of dissolution, but chiefly owing to the formation of a suspension of both small and comparatively large droplets (^{1}). Whereas dissolved metal can be extracted by electrolysis (^{2}), the possibility of extracting droplets by electrophoresis is unlikely because of the high concentration and mobility of slag ions (^{3}).

However, in aqueous solutions a number of investigators ($^{4–7}$) have observed so-called electrocapillary motions, i.e., the displacement of mercury droplets in electrolytes under the influence of an electric field. A quantitative theory of these phenomena was given by Frumkin and Levich ($^{8–10}$). It follows from it that electrocapillary motions in molten slags are quite possible, since liquid metals and sulfides immersed in them are electrically charged (^{11,12}).

Accordingly, in the present work we found, at temperatures of 1370–1500° C, displacement toward a definite electrode of droplets of Cu, Ni, Mn, Ag, and Ni_3S_2 over the surface of a slag containing 52% CaO, 41% Al_2O_3, and 7% SiO_2.

A cell made of fused magnesia with a Π-shaped cavity was filled with slag, whose depth in the horizontal channel reached 3 mm. Graphite current leads were lowered to the lower part of the vertical channels through special inclined cavities. A droplet, whose diameter was measured beforehand and was 0.5–3 mm, was carefully placed on the surface of the slag. It did not spread (the exception was FeS) and did not sink in it. The droplet size in the cell was additionally checked with a telescope fitted with an ocular scale. When a direct current was switched on (of strength 0.5–5 A), the droplet moved along the horizontal channel, and the time of its passage was recorded with a stopwatch. By changing the direction of the current, it was possible to make the droplet move in either direction an unlimited number of times. In a number of experiments, using liquid electrodes of Ni_3S_2 with graphite current leads, it was possible to observe the simultaneous motion of a large number (20-30) of droplets of different sizes (from 0.5 to 3 mm).

In agreement with the theory, such motions were not observed at all for solidified droplets of metals or for pieces of solid magnesium oxide. This circumstance, as well as the rapidity of motion of the liquid droplets, indicates the electrocapillary, and not electrokinetic, character of the motion. The velocity of displacement (U) was directly proportional to the voltage gradient (E) and depended on the composition and size (r) of the droplet, as well as on the character of the atmosphere.

The results of experiments in an oxidizing atmosphere (air) are presented in Table 1. It also gives the values of the specific mobilities (v), i.e., the displacement velocities referred to unit voltage gradient and to unit radius.

Since metals and nickel sulfide move in opposite directions, it seemed interesting to determine the sulfur content corresponding to zero mobility. Experiments carried out at gradients $E = 5$—6 V/cm showed that a decrease in the S content in the Ni–S alloy from 26% (Ni_3S_2) to 0.4% has practically no effect on the mobility. This is probably due to the high capillary activity of sulfur, as a result of which the composition of the surface layer of the droplet remains almost constant despite considerable changes in its bulk concentration. Such behavior of sulfur is consistent with the fact of a strong lowering of the surface tension of nickel ($\sigma_{\mathrm{Ni}} = 1756$ erg/cm^2 (13)) by its addition ($\sigma_{\mathrm{Ni_3S_2}} = 452$ erg/cm^2 (14)). With a further decrease in the sulfur content, the mobility falls, at 0.15% S reaches zero, and then changes sign, i.e., the droplet moves, like the metal, toward the cathode.

Thus, at low sulfur contents the surface of Ni–S alloys is positively charged, and at high and medium contents it is negatively charged. The latter agrees with previously obtained electrocapillary curves (12) and indicates that here the double layer is formed as a result of the transition of cations from the metal into the slag:

$$\mathrm{Me} \rightarrow \mathrm{Me}^{2+} + 2e. \tag{1}$$

In a reducing atmosphere, more precisely when a mixture of nitrogen with hydrogen (72% N_2 and 28% H_2, not excluding traces of O_2) was blown over the cell, Ni_2S_3 sulfide still moved toward the anode and at the same rate. On the contrary, the mobility of metallic droplets decreased to zero for nickel, while for copper and silver it changed sign and was respectively 0.8 and 20 cm/(sec · V). This is apparently due to the following.

Table 1

Metal	$E\ \left(\frac{\text{V}}{\text{cm}}\right)$	r (cm)	$U\ \left(\frac{\text{cm}}{\text{sec}}\right)$	$v\ \left(\frac{\text{cm}}{\text{sec}\cdot\text{V}}\right)$	Direction of motion
Cu	2.3	0.07	5.8	36	Toward the cathode
Ni	2.0	0.05	2.8	28	Toward the cathode
Mn	2.8	0.075	6.3	30	Toward the cathode
Ni_3S_2	2.3	0.05	4.8	42	Toward the anode
Ni_3S_2	6.6	0.025	7.5	46	Toward the anode
Ni_3S_2	6.6	0.05	15	46	Toward the anode
Ni_3S_2	6.6	0.075	15	30	Toward the anode
Ni_3S_2	6.6	0.16	6	5.7	Toward the anode

Whereas the composition of the sulfides remains practically constant, metallic droplets may be partially oxidized or reduced depending on the composition of the atmosphere. In the presence of O_2, the layer of slag near the droplet is enriched with MeO*, and formation of the double layer may occur through the transition of Me^{2+} cations from the slag into the metal

$$\mathrm{Me}^{2+}_{(\mathrm{slag})} + 2e \to \mathrm{Me}. \tag{2}$$

It is also possible that reverse transfer of the oxygen dissolved in the droplet takes place:

$$\mathrm{O}_{(\mathrm{met})} + 2e \to \mathrm{O}^{2-}_{(\mathrm{slag})}. \tag{3}$$

Both processes lead to the appearance of a positive charge on the surface of the droplet. In an atmosphere containing hydrogen, the latter partially reduces the oxides MeO, and the more completely the nobler the metal. Therefore, in the case of silver and copper, the concentrations of oxides in the adjacent layers of slag become so small that the transition of cations from the metal into the slag (1)

* A moving droplet leaves behind a dark trace, indicating the appearance of MeO in the slag.

begins to predominate over the reversible displacement (2), while for the less noble nickel the rates of these two processes became equal.

For a quantitative comparison of the theory of electrocapillary motions with our results, the specific mobilities ($v = U/Er$) of a Ni_3S_2 drop were calculated by the formula of Frumkin and Levich (9)

$$U = \frac{\varepsilon E r}{2\eta + 3\eta' + \frac{\varepsilon^2}{\varkappa}}, \tag{4}$$

which is valid under the condition that

$$Er \ll \varepsilon / C. \tag{5}$$

Here η' and η are the viscosities of the metal and the slag, $\varkappa$ is the electrical conductivity of the latter, and ε and C are the specific charge and the capacitance of the double layer.

In the case under consideration, $\varepsilon = 15 \cdot 10^{-6}$ coul/cm^2 (12), $C = 15$ μF/cm^2 (15), $\eta \cong 1.5$ poise (16), and $\varkappa \cong 0.5$ Ω^{-1}cm^{-1} according to our approximate measurements. Since in our case $\varepsilon^2/\varkappa \ll 2\eta$ and $\eta' \ll \eta$, formula (4) gives

$$v = \frac{\varepsilon}{2\eta}. \tag{6}$$

Inequality (5) is satisfied for Ni_3S_2 drops with $r < 0.15$ cm at $E = 6.6$ V/cm. However, as is seen from Table 1, discrepancies begin at somewhat smaller* radii of the Ni_3S_2 drop. The velocities of displacement U cease to increase with increasing r at $r \cong 0.075$ cm, and at $r = 0.16$ they decrease sharply, which contradicts equation (4). In this connection, for comparison with the theory the mobilities $v_{\text{fact}} = 42$—46 cm/sec · V were taken, while calculation by formula (6) gave $v_{\text{theor}} = 50$ cm/sec · V.

The agreement in order of magnitude between v_{fact} and v_{theor} once again emphasizes that the displacements observed by us are electrocapillary motion of drops over the surface of the slag. As for their quantitative difference, it is due mainly to the simplifying assumptions made in deriving formula (4). In particular, as Frumkin and Levich (9) showed, allowance for incomplete polarizability leads to lower velocities of motion, i.e., in our case to a convergence of v_{theor} and v_{fact}.

It should also be taken into account that equation (4) and the quantities η and $\varkappa$ entering into it refer to drops moving inside a liquid, and not over its surface.

Ural Polytechnic Institute
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* Possibly this is due to the second requirement of the theory, that $R_e = Ur/\nu$ be less than unity. Here $\nu = \eta/\rho$, and ρ is the density of the slag, approximately equal to 3 g/cm^3 (17).

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

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