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Abstract

Full Text

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EXTRACTION OF SULFIDE INCLUSIONS FROM MOLTEN SLAGS BY MEANS OF AN ELECTRIC FIELD

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In the present work we give the results of our investigation on the use of the electrocapillary motion of liquid metallic drops ([1]) for extracting sulfide inclusions from molten slags.

The experiments were carried out at a temperature of about 1400° in corundum or porcelain boats filled with molten dump-furnace slags of the following composition (in percent): CaO 15; Al_2O_3 10; SiO_2 43; Fe_{total} 20; MgO 10; Ni 0.1–0.2; Co 0.02 and S 0.15–0.2. The greater part of the nickel and cobalt is present in them in the form of matte inclusions: Ni 15; Co 0.5–0.6; S 16–17 and Fe 65, with sizes from 10^{-4} mm to 0.2 mm (white points in Fig. 1a). Carborundum rods served as current leads; they reduced iron oxides only in small volumes of slag immediately adjacent to them.

Fig. 1. Microsections of dump slag before passage of current (*a*) and after passage of a current of 0.05 A for 5 min (*b*). White spots are matte inclusions; dark areas are pores. 340×

In preliminary experiments, a matte drop of larger radius $r = 0.9 \div 1.3$ mm was immersed in the slag and, for a time from 2 to 10 min, a constant electric field of strength $E = 5 \div 7$ V/cm was switched on. Then the cell was rapidly cooled, broken, and the distance traveled by the drop was determined. It was found

that the inclusions move toward the cathode with velocities $u = 7 \div 10 \cdot 10^{-3}$ cm/sec, corresponding to mobilities $v = u/Er = 1.0 \div 1.5 \cdot 10^{-2}$ cm/sec · V.

To clarify why the direction of motion proved to be opposite to that observed earlier ([1]), while the mobilities were substantially smaller, we

Table 1

Mobility of Ni_3S_2 drops in iron-free slags

CaO	SiO_2	Al_2O_3	η, poise ([2])	r, cm	E, V/cm	u, cm/sec	v, cm/sec · V	Direction of motion
48	42	10	6	0.11	2.55	2.8	10	toward the anode
41	47	12	18	0.12	2.55	0.95	3.1	toward the anode
36	51	13	30	0.10	2.55	0.5	1.95	toward the anode
30	56	14	75	0.11	2.55	0.25	0.9	toward the anode

Table 2

Effect of the FeO content in the slag on the motion of drops

CaO	Al_2O_3	SiO_2	FeO	r, cm	E, V/cm	u, cm/sec	v, cm/sec · V	Direction of motion
52	41	7	—	0.1	2.2	4.5	20	toward the anode

CaO	Al_2O_3	SiO_2	FeO	r, cm	E, V/cm	u, cm/sec	v, cm/sec · V	Direction of motion
50.5	40	7	2.2	0.1	2.2	4.5	20	toward the anode
49.5	39.1	7.15	4.25	0.09	2.2	2.7	13.5	toward the anode
47.2	37.3	7.3	8.2	0.1	2.2	$1.3 \cdot 10^{-2}$	$6 \cdot 10^{-2}$	toward the cathode
39.5	31.2	7.7	21.4	0.11	2.2	$3.6 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	toward the cathode

we studied the influence of the slag composition. The results of experiments with Ni_3S_2 drops in iron-free slags of various compositions are given in Table 1. They show that the mobility of the drops is inversely proportional to the viscosity (η) of the slag. In accordance with this, the surface charge density of the drops (ϵ), calculated by formula ([3])

$$\varepsilon = v \cdot 2\eta, \tag{1}$$

was in all cases practically the same, namely: $12 \div 13.5 \cdot 10^{-6}$ coul/cm^2.

The data obtained with different contents of iron oxides in the slag are presented in Table 2. An increase in the FeO concentration initially lowers the mobility of the drops, and, beginning with 8% FeO, changes the direction of their motion to the opposite one. In other words, the charge of the sulfide, negative in an iron-free slag, decreases with the addition of FeO, passes through zero, and becomes positive. Apparently, as the FeO concentration increases, the transfer of iron ions from the slag into the sulfide begins to play an increasingly important role in the formation of the double layer:

$$Fe^{2+}_{(slag)} \rightarrow Fe_{(sulf.)} - 2e, \tag{2}$$

and not the reverse displacement of nickel ions:

$$\mathrm{Ni}_{(\mathrm{sulf.})} \rightarrow \mathrm{Ni}^{2+}_{(\mathrm{slag})} + 2e. \qquad (3)$$

Upon reaching 8% FeO, process (2) becomes predominant. However, a further increase in the FeO concentration leads not to an increase but to a decrease in the mobility of the drops, despite the growth of their positive charge and the decrease in the viscosity of the slag. In this connection the simplest formula (1) proves unacceptable.

Indeed, the large magnitude of the exchange current ([4]) at the boundary between the metal and the slag containing appreciable FeO concentrations, as well as the high limiting diffusion currents (i_l) ([5]), indicate that the concepts of an ideally polarizable drop are completely inapplicable in the considered–

Table 3

Mobility of sulfide drops in slags with 23% FeO

Slag composition, %	Slag composition, %	Slag composition, %	η, poise ([8])	r, cm	E, V/cm	u, cm/sec	v, cm/sec· V	Direction of motion
FeO	CaO	SiO_2						
23	43	34	1	0.1	3	$6{\cdot}10^{-3}$	$20 \cdot 10^{-3}$	toward the cathode
23	37	40	1.5	0.09	3	$6.1 \cdot 10^{-3}$	$22 \cdot 10^{-3}$	toward the cathode
23	35	42	2	0.1	3	$5.9 \cdot 10^{-3}$	$19.7 \cdot 10^{-3}$	toward the cathode
23	31	46	4	0.08	3	$5.8 \cdot 10^{-3}$	$24 \cdot 10^{-3}$	toward the cathode
23	31	46	4	0.1	3	$5.9 \cdot 10^{-3}$	$18 \cdot 10^{-3}$	toward the cathode

Slag composition, %	Slag composition, %	Slag composition, %	η, poise ([8])	r, cm	E, V/cm	u, cm/sec	v, cm/sec· V	Direction of motion
23	31	46	4	0.135	3	$6 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	toward the cathode
23	31	46	4	0.135	9	$17 \cdot 10^{-3}$	$14 \cdot 10^{-3}$	toward the cathode

in the case under consideration by us. The equation determining the mobility of a partially polarizable drop ([6]):

$$v = \frac{\varepsilon r}{2\eta(1 + r/2\varkappa w)} \tag{4}$$

contains the depolarization coefficient (k) (the expression in parentheses), in which $\varkappa$ is the electrical conductivity of the electrolyte, and

$$w = \frac{RT}{nFi_{\text{p}}}, \tag{5}$$

where n is the number of charges of the ion, and F is the Faraday constant. In particular, assuming that the polarization is of a concentration character ([4,5,7]) and taking $i_{\text{p}} = 0.5$ (% FeO) A/cm^2, and $\varkappa = 0.3$ ohm^{-1}·cm^{-1}, we obtain, for a drop with $r = 0.1$ cm in slag with 20% FeO, a rather large depolarization coefficient $k = 25$. The decrease in the polarizability of the drop is probably the main cause of the reduction of its mobility in slags containing iron oxides.

An additional confirmation of what has been said is provided by the results of experiments with a constant FeO concentration (23%) and a variable ratio of CaO and SiO_2 contents (Table 3). It turned out that in this case the mobilities of the drops hardly depend on the viscosity of the slag, despite a fourfold increase in the latter. Obviously, the retarding effect of the increase in viscosity is here compensated by an increase in the force moving the drop. This can hardly be attributed to an increase in the charge of the drop, since in iron-free slags this was not observed when CaO was replaced by SiO_2. Most likely, the compensation is connected with a decrease in the limiting diffusion current and the consequent decrease in the depolarization coefficient.

It is interesting to note that the direction of motion of the nickel sulfide drops coincides, and the mobilities differ little from those observed for matte in dump slag. It is possible that this is caused by the convergence of the compositions of the surface layers of both types of drops, due to the reaction:

$$\mathrm{Ni}_{(\mathrm{sulf})} + \mathrm{Fe}^{2+}_{(\mathrm{slag})} = \mathrm{Fe}_{(\mathrm{sulf})} + \mathrm{Ni}^{2+}_{(\mathrm{slag})}. \tag{6}$$

To extract matte drops from molten (1400°) dump slag, a current of 0.05–0.1 A was passed through the latter at a voltage gradient of 7–15 V/cm. The cell was then rapidly cooled and polished sections were made at different places along the length of the boat. Their examination under a microscope showed that in the surface layer of slag up to 0.1 mm thick the number of beads did not change noticeably. Probably, the presence in this layer of a very viscous film rich in Fe_2O_3 paralyzed the motion of the inclusions. On the contrary, in the bulk of the slag the number of drops decreased sharply (cf. Figs. 1b and 1a), and increased near the cathode.

Thus, the experiments carried out fully confirmed the possibility of extracting valuable sulfide inclusions from waste molten slags by means of electrocapillary motions.

In these experiments two interesting features were observed. At the cathode, a considerable number of droplets was found whose size (up to 1–1.5 mm) greatly exceeded the initial size. In addition, the actual mobility of small droplets proved to be many times greater than that estimated from equation (4). For example, after a 10-minute passage of a current of 0.05 a ($E = 12$ V/cm), no inclusions even as small as $3 \cdot 10^{-5}$ cm remained in the middle part of the cell, 6 cm long. In other words, globules of this size traveled a distance of not less than 3 cm. Therefore their mobility ($vr = 4 \cdot 10^{-4}$ cm/sec per V/cm) exceeds by more than 100 times the value calculated ($vr = 3.3 \cdot 10^{-6}$ cm/sec per V/cm) from formula (4). Apparently, both features are a consequence of the mutual entrainment of droplets during their motion. It is known that the layers of electrolyte adjacent to a droplet undergo tangential motion in an electric field, terminating in its rear part (^3). This motion, more powerful near large droplets, can entrain smaller droplets located nearby and cause the latter to merge with the former. Visual observations of mercury droplets in a solution of KCl in glycerin confirm what has been said. Small Hg droplets located near a large one (2 mm) rapidly merged with it after the current was switched on.

Such coalescence increases the rate at which inclusions are removed from the slag. In particular, the observed mobility ($4 \cdot 10^{-4}$) of matte droplets, according to formula (4), corresponds to a radius of 10^{-3} cm. The number of globules of this size in the slag is fairly large. The rate of their motion, apparently, is also the determining factor in extracting finer matte inclusions.

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