Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1962

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1962, Volume 144, No. 5

PHYSICAL CHEMISTRY

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ON THE EFFECT OF ELECTRODE POLARIZATION ON THE PROPERTIES OF THE ELECTROLYTE-GAS INTERFACE

(Presented by Academician A. N. Frumkin, 14 II 1962)

We studied the effect of direct current on the rate of sulfur burn-off from slag (51% CaO; 41% Al_2O_3; 7.5% SiO_2 and 0.5% S) when its surface was blown with air. The experiments were carried out by the previously described method ([1]) in a graphite crucible, which served as one electrode, while the other was a silit rod. The latter was insulated from the gas phase of the furnace by a corundum tube closed at the top, whose lower end was immersed in the slag. Above the slag surface, air was blown at a constant rate; its SO_2 content was continuously monitored iodometrically.

It is seen from Fig. 1 that the rate of sulfur burn-off V (in relative units: $V = 100$ at $i = 0$) decreases with current density i when the silit rod serves as the cathode, and increases when it becomes the anode. The increase in V could, at least qualitatively, be explained by additional anodic oxidation of slag sulfur:

$$S^{2-}_{(slag)} - 2e + O_{2\,(gas)} = SO_{2\,(gas)}. \quad (1)$$

However, an attempt to relate the decrease in V to cathodic reduction of sulfur from the gas phase, i.e., to the course of process (1) in the reverse direction, was not confirmed experimentally. This is consistent with the magnitude of the equilibrium constant ([2,3]) and with the initial sulfur concentrations in our slag.

Fig. 1. Effect of cathodic (1) and anodic (2) current density on the rate of sulfur burn-off from slag at 1500°

It is also easy to show that the effect of cathodic reduction of oxygen

$$O_{2\,(gas)} + 4e = 2O^{2-}_{(slag)} \quad (2)$$

is small and cannot explain the observed decrease in the rate of sulfur burn-off. It remained to suppose that the cause of the influence of current on the burn-off

Fig. 2

Figure 1: Fig. 2

rate is depletion of the near-cathode layer in sulfur ions and enrichment of the anolyte with them, as a result of electrolytic transport.

The greatest change in the composition of the melt occurs near the silit rod, since its surface is significantly smaller than that of the crucible. Owing to the capillary activity of sulfur ions in these melts ([2]), this entails a change in its concentration in the surface layer, which affects the burn-off rate:

$$S^{2-}_{(\text{slag})} + {}^{3}\!/_{2}\, O_{2\,(\text{gas})} = SO_{2\,(\text{gas})} + O^{2-}_{(\text{slag})}. \tag{3}$$

For an experimental check of the assumption made, the surface tension of the slag (σ) was measured by the maximum-pressure method in an argon bubble. In a number of experiments, a platinum crucible and a capillary were used as electrodes; the end of the capillary was tapered to a point in order to reduce the influence of wetting. The slag surface was protected from sulfur oxidation by blowing dry argon over it. It was found that polarization of the metal-slag boundary does not affect the surface tension

Fig. 2. Effect of electrode polarization (φ) and current density (i) on the surface tension (σ) of slag.
1 –slag with 39.5% CaO, 41% SiO_2, 19% Al_2O_3, and 0.5% S; 1400°, electrodes: platinum crucible and capillary; $\sigma_{i=0} = 428$ erg/cm^2;
2 –same, but $\sigma_{i=0} = 439$ erg/cm^2;
3 –same, but with a corundum capillary near (3-5 mm) a Pt rod; $\sigma_{i=0} = 445$ erg/cm^2;
4 –same as **1**, but with 0.8% S in the slag and $\sigma_{i=0} = 450$ erg/cm^2;
5 –slag with 51% CaO, 9% SiO_2, 39.3% Al_2O_3, and 0.7% S; 1500°, electrodes: graphite crucible and SiC rods; corundum capillary near (3-5 mm) the SiC rod; $\sigma_{i=0} = 465$ erg/cm^2;
6 –same, but with an MgO capillary (5-7 mm); $\sigma_{i=0} = 460$ erg/cm^2;
7 –same, but with a Mo capillary (10-15 mm); $\sigma_{i=0} = 434$ erg/cm^2.

in the absence of sulfur and changes substantially when CaS is added to the slag. Curves **1**, **2**, and **4** in Fig. 2 show that cathodic polarization of the platinum capillary increases the value of σ, while anodic polarization decreases it; moreover, the effect is greater the higher the concentration of S^{2-} ions (see Fig. 2, **2** and **4**). In other words, cathodic polarization decreases sulfur adsorption, while anodic polarization increases it. Curve **1** is plotted in the coordinates tension–capillary potential. The potential (φ) was measured by a commutator method relative to the platinum crucible.

The observed dependence of σ on φ can be explained by the fact that the end of the capillary is not infinitely thin and the maximum pressure ($P_{\max}$) in the

bubble depends on the contact angle of wetting (θ):

$$P_{\max} = \frac{2\sigma}{r} \cos\theta. \tag{4}$$

In this case curves 1, 2, and 4 in Fig. 2 are electrocapillary and analogous to those obtained by A. N. Frumkin and co-workers (4, 5) from measurements of the contact angle of a bubble sitting on a solid metallic electrode. Later this method was used to determine the points of zero charge of a number of other solid metals (6). Under this interpretation, our measurements merely extend the indicated phenomenon also to the metal–liquid slag boundary, while the results obtained show that the potential of zero charge of the surface of a solid platinum plate in molten slag is shifted to such an extent that measurements are possible only in the region of the anodic branch.

However, the data presented do not make it possible to explain the influence of polarization on the rate of sulfur burn-off. Therefore, further measurements of σ were carried out with a capillary placed at a distance of 3-5 mm from the electrode and not connected with it in any way. Curves 3, 5-7 in Fig. 2, in the coordinates $\frac{\sigma}{\sigma_0} \cdot 100$ and i (A/cm^2), obtained in different crucibles (graphite, Pt) with different electrodes (Pt, silit) and capillaries (corundum, MgO, Mo, Pt), confirm that the surface tension of the slag decreases near the anode and increases near the cathode. In other words, electrode polarization changes the adsorption of sulfur at the slag–gas boundary. At the same time, along the surface layer a certain concentration gradient of S^{2-} ions is established. The existence of this gradient is confirmed by the fact that the effect of electric current on the value of σ decreases as the capillary is moved away from the electrode (cf. 6 and 7 in Fig. 2). However, the presence of a noticeable effect at distances of 10-15 mm from the electrode is not consistent with the small thickness of the diffusion layer, which, owing to vigorous natural convection at high temperatures, is usually about 10^{-4} cm in such cases (7). It may therefore be assumed that the adsorption of sulfur on the slag surface also changes for other reasons.

Since the reaction of sulfur burn-off is concentrated in the surface layer of the slag, a change in the concentration of sulfur ions in it is correspondingly reflected in the rate of the process.

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Received
14 II 1962

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