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I. I. POKROVSKII and Academician of the Academy of Sciences of the BSSR M. M. PAVLYUCHENKO

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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PHYSICAL CHEMISTRY

I. I. POKROVSKII and Academician of the Academy of Sciences of the BSSR M. M. PAVLYUCHENKO

STUDY OF THE MECHANISM OF COPPER OXIDATION BY LIQUID SULFUR USING THE ISOTOPE S^{35}

The oxidation of metallic copper by liquid and gaseous sulfur is accompanied by the formation and growth, on the surface of the metal, of a sulfide scale consisting of several layers ([1,2]). The outer and middle layers are, respectively, CuS and Cu_2S and form the main dense part of the scale, with a characteristic columnar structure, while the inner layer, also consisting of Cu_2S, constitutes its porous part.

Fig. 1

Fig. 2

According to available data ([3]), the process of oxidation of copper by liquid sulfur is described by a parabolic equation and, consequently, should be limited by diffusion of one or both reactants through the sulfide scale. The existence of an inner porous layer of Cu_2S, sharply different in structure from the main part of the scale, is apparently connected with the fact that, in the oxidation process, along with diffusion of copper through the sulfide scale, counter-diffusion of sulfur takes place. At the same time, the literature indicates ([4]) that this reaction proceeds exclusively by diffusion of copper, while the formation of the porous Cu_2S layer at the boundary with copper is due to secondary processes, such, for example, as recrystallization.

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Fig. 3

Figure 3: Fig. 3

The application of the radioactive isotope S^{35} to the study of the mechanism of oxidation of copper by liquid sulfur makes it possible, in our opinion, to resolve this question unambiguously. The idea of the method we used consists in introducing the isotope S^{35} into the sulfide scale at different stages of the reaction with subsequent

with subsequent determination of its localization by means of autoradiography or layer-by-layer radiometric analysis.

Copper specimens in the form of bars measuring $7 \times 8 \times 25$ mm were prepared from a plate containing 99.9% copper. All specimens were annealed at 1000° in vacuum for 6 h. Oxidation of copper with liquid sulfur was carried out in the temperature range 270—444°.

Two series of experiments were carried out. The experiments of the first series consisted in oxidizing copper specimens with radioactive sulfur after a scale of a definite thickness had already formed on their surface. This was achieved by adding the isotope S^{35} to the liquid sulfur after a definite interval of time from the beginning of the reaction.

Fig. 3

The second series of experiments consisted in oxidizing copper specimens with liquid sulfur after a thin sulfide scale containing the isotope S^{35} had formed on their surface. This was achieved by treating the copper specimens before the beginning of the reaction with a benzene solution of S^{35} of high specific activity, followed by their oxidation with liquid sulfur. After removal from the melt, the scale-covered specimens were washed free of adhering sulfur with a ten-percent solution of sodium sulfite, rinsed with water, alcohol, and ether, dried, and cut perpendicular to the length of the specimen. The unreacted copper core was removed from inside the specimen, and the space it occupied was filled with liquid sulfur to strengthen the porous scale layer. The cross section of scale thus prepared was ground, polished, and autoradiographed in order to determine the localization of the radiosulfur.

Typical results obtained in experiments of both series are shown in Figs. 1 and 2. Fig. 1 gives an autoradiogram (positive) of a cross section of the scale formed on copper at 444° after oxidation in inactive sulfur for 17 min and then for another 43 min in the presence of the isotope S^{35}; Fig. 2 gives an autoradiogram (positive) of a cross section of the scale formed on copper at 400° after preliminary treatment of the specimen with a benzene solution of S^{35} and subsequent oxidation in inactive sulfur for 8 h.

The observed distribution of S^{35} is explained by the fact that the dense part of the sulfide scale grows outward during the reaction as a result of diffusion of

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Fig. 4

Figure 4: Fig. 4

copper from the copper core.

If the reaction proceeded only by diffusion of copper through the sulfide scale, then, obviously, the reverse side of the scale in the experiments of the first series should be nonradioactive*. Measurements showed, however, that in all experiments of this series the reverse side of the scale had appreciable radioactivity. Moreover, by means of layer-by-layer radiometric analysis, the isotope S^{35} was detected throughout the entire portion of the scale that had formed during oxidation of copper with inactive sulfur. The radiometric curve for the scale formed on copper at 444° for 96 min is shown in Fig. 3. The isotope S^{35} was introduced into the liquid sulfur 24 min after the beginning of the reaction.

* Provided that the duration of oxidation of copper in inactive sulfur is sufficient to form a scale layer ensuring complete absorption of the radiation of S^{35}. In our experiments this condition was always fulfilled.

Finally, comparison of the photomicrograph and the microautoradiogram (negative) of one and the same region of the section, parallel to the surface of the specimen and corresponding in depth to the initially inactive layer (Fig. 4), shows that the diffusion of sulfur to the copper core through the dense part of the scale occurs along individual grain boundaries, including the junctions of several columnar crystals.

Fig. 4

The results we have obtained allow us to assert that the formation of sulfide scale on copper occurs through diffusion of both reactants.

Belorussian State University
named after V. I. Lenin

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