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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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EVAPORATION OF SULFUR FROM SULFIDE SCALE SEPARATED FROM COPPER

In the course of reaction with liquid or vaporous sulfur, metallic copper becomes covered with the reaction product in the form of a sulfide scale. The scale consists of two layers—an outer dense layer and an inner porous layer ([1,2]). The formation of the porous layer, located between the dense layer of scale and the metal, indicates the arrival of sulfur in this region from the side of the dense scale layer. For such arrival there are two possibilities: decomposition of the dense layer with formation of free sulfur ([3,4]), and diffusion (penetration) of sulfur through the dense layer along grain boundaries and macrodefects ([5,6]). In both cases, the transport of sulfur to the unreacted copper can take place through the gas phase ([2,4]) in the pores of the inner porous layer. In order to assess the role of vaporous sulfur in the formation of the inner porous layer, we studied the evaporation of sulfur in vacuum from the dense layer of the scale. In this case the outer side of the dense scale layer, just as during its formation on copper, was in contact with liquid sulfur or its vapors. The inner side, corresponding to the interface between the dense and porous layers of the scale, bordered on the vacuum.

Fig. 1. *a*—tube with sulfur (1) and copper rod (2) before reaction; *b*—the same tube after reaction; 3—dense layer and 4—porous layer of the scale; *v*—sample prepared for the experiments

These conditions were ensured by the following arrangement of the experiment. The reaction between copper and sulfur was carried out in glass tubes. One end of the tube was sealed and sulfur was placed on the bottom. A copper rod, fitted to the diameter of the tube and polished with emery paper, was inserted into the free end of the tube. The inner diameter of the tubes was from 2.5 to

Fig. 2

Figure 2: Fig. 2

5 mm. The copper and sulfur had the same purity as in the preceding work ([7]). The tubes were suspended inside a vertically arranged quartz reactor, the upper part of which was provided with a refrigerator for trapping sulfur vapors. The lower part of the reactor was in a furnace. A vacuum of approximately $5 \cdot 10^{-4}$ mm Hg was created in the system. The tubes were slowly heated to the specified temperature, at which they were held for a definite time under continuous pumping. Carrying out the reaction in tubes restricted the propagation of the reaction front between copper and sulfur practically only by the dimensions of the cross section of the copper rod. It is clear that at the beginning of the reaction, owing to the gaps that inevitably existed between the rod and the walls of the tube, part of the sulfur escaped from the tube; however, in the course of the reaction the scale, growing on the copper, isolated the sulfur in a closed space. As before ([1–3]), the scale consisted of dense and porous layers. The boundary between them was clearly visible and approximately corresponded to the position of the lower base of the copper rod before the reaction. The tubes were cut along this boundary, and their lower parts with sulfur and the dense scale layer were used for studying evaporation. The preparation of the samples is explained in Fig. 1.

The evaporation of sulfur from the scale was studied by the weight method in the same reactor and at the same temperatures at which the scale had formed on copper*. The evaporation rate was determined from the loss in weight of the tube with sulfur and the "plug" of scale after heating in vacuum. The loss in weight of the samples due to

* Here and in the subsequent exposition, for brevity, the outer dense layer of the scale is called simply the scale.

the evaporation of sulfur, referred to a unit surface area of the scale, is shown in Fig. 2a. As follows from Fig. 2a, the rate of sulfur evaporation is constant at a constant temperature. The results obtained at 445°C for specimens with different cross-sectional areas agree satisfactorily with one another*.

It was noted, however, that the rate of evaporation depends on the thickness of the scale. As can be seen from Fig. 3a, with increasing scale thickness it rapidly decreases.

Fig. 2. Evaporation of sulfur from sulfide scales: *a*—loss of weight of specimens; *b*—movement of the scale-sulfur boundary. 1—445°, specimens with different cross-sectional areas (*I*—4.75, *II*—5.00, *III*—7.23, *IV*—18.75, *V*—19.26 $\cdot 10^{-2}$ cm^2); 2—400°; 3, 4—370°; 5—344°.

decreases. Observations of the scale-sulfur boundary showed that, during the process of sulfur evaporation from the scale, this boundary moves in the direc-

Fig. 3

Figure 3: Fig. 3

Figure 4: plots of evaporation rate versus x_0 and x_0^{-1}. Legend: 1 measured from weight loss; 2 calculated from displacement of the scale–sulfur boundary.

Figure 4: Figure 4: plots of evaporation rate versus x_0 and x_0^{-1}. Legend: 1 measured from weight loss; 2 calculated from displacement of the scale–sulfur boundary.

tion of the sulfur. Simultaneously, on the opposite side of the scale, bordering on the vacuum, a porous zone develops, consisting of separate sulfide crystals poorly bonded to one another. The movement of the scale-sulfur boundary was measured with a cathetometer. The results obtained are presented in Figs. 2b and 3b. From these figures it is seen that the rate of movement of this boundary, like the rate of evaporation of sulfur into the vacuum from the opposite side of the scale, is constant and does not change with time. Knowing the composition of the scale near the boundary with the sulfur and its density, one can calculate the amount of sulfur that has joined the scale at this boundary per unit time. The rates of sulfur addition to the scale calculated in this way are given in Table 1. There, for comparison,

Fig. 3. Evaporation of sulfur from sulfide scales of different thicknesses: 1–0.65; 2–0.85; 3–0.95; 4–1.30; 5–2.10 cm. Temperature 434°. *a*–loss of weight of specimens; *b*–movement of the scale-sulfur boundary.

* Experiments with specimens turned upside down showed that the evaporation rate at constant temperature also did not depend on whether the scale was in contact with liquid sulfur or with its vapors.

the rates of sulfur evaporation, measured from the loss of weight of the specimens, are given. The composition of the scale near its boundary with sulfur was determined by chemical analysis. The density of the sulfide scale formed on copper at 445°, equal to 5.60 $g \cdot cm^{-3}$ (1). We used this value for the calculations.

Fig. 4. 1 –measured from weight loss; 2 –calculated from displacement of the scale–sulfur boundary

As follows from the data of Table 1, the rate of sulfur evaporation from the scale–vacuum boundary agrees, with an accuracy of about 5%, with the rate of sulfur addition to the scale at the scale–sulfur boundary.

The sulfide scale on copper at 445° consists mainly of the high-temperature modification of monovalent copper sulfide, $Cu_{2-x}S$, with considerable deviations from stoichiometric composition $(0 \leq x \leq 0.25)^{(8,9)*}$. Sulfides of this composition are *p*-type semiconductors with a high concentration of defects in the cation part of the crystal lattice ([11]). The anion part of the lattice contains no noticeable disturbances. The self-diffusion coefficients of sulfur in Cu_2S are several orders

of magnitude lower than those of copper ([12]). The movement of sulfur through the scale may also occur by diffusion along grain boundaries and macrodefects ([5,6]); however, the amount of sulfur transported by this path is apparently small. Consequently, it must be assumed that the evaporation of sulfur from the scale is not determined by sulfur diffusion. On the other hand, the displacement of the scale–sulfur boundary and the formation of a porous zone at the scale–vacuum boundary indicate that, in the course of evaporation, copper diffuses through the scale in the direction toward the sulfur.

The agreement of the rates of evaporation and addition of sulfur at the opposite boundaries of the scale corresponds to the occurrence of the process under stationary conditions, in which an amount of copper equivalent to the evaporated sulfur is transported by diffusion through the scale. This feature of the process was already used by Rickert in studying the evaporation of sulfur, iodine, and selenium from Ag_2S ([13]), CuJ ([14]), and Ag_2Se ([15]) by the electrochemical method. Evaporation of sulfur from the scale may consist of the following successive stages: removal of copper ions from the scale–vacuum boundary by diffusion through the scale; chemical reactions at the scale–vacuum boundary (in the adsorbed layer ([18])), leading to the formation of sulfur molecules S_x, where $x = 2, 4, 6$, and 8 ($S^{-2} \rightarrow 2e + S(\text{ad.})$; $xS(\text{ad.}) \rightarrow S_x(\text{ad.})$); and, finally, the phase transition adsorbed layer–vapor ($S_x(\text{ad.}) \rightarrow S_x$). The electrons released in the formation of sulfur molecules from its ions at the scale–vacuum boundary are transported together with copper ions to the scale–sulfur boundary, where the reactions given above proceed in the reverse direction. The overall rate will be determined by the rate of the slowest of these stages.

The diffusion flux in the stationary state through a layer of constant thickness x_0 is expressed by the equation ([16])

$$j_1 = \frac{D(C_1 - C_0)}{x_0}, \tag{1}$$

* Copper sulfide of composition $Cu_{1.8}S$ is known under the name digenite ([10]).

where D is the diffusion coefficient, and C_1 and C_2 are the concentrations of the diffusing substance at the two boundaries. In deriving equation (1) it is assumed that D does not depend on concentration. The amount of substance Δm that has diffused through a unit cross section S in time t is equal to:

$$\left(\frac{\Delta m}{S}\right) = \frac{D(C_1 - C_2)}{x_0}\, t. \tag{1a}$$

Calculations show that the product of the rate of evaporation of sulfur from the scale by its thickness at 434° is a quantity that is approximately constant and does not depend on the magnitude of the evaporation rate. Figure 4 shows the dependence of the evaporation rate on the thickness of the scale at this same temperature. It follows from Fig. 4 that the evaporation rate is inversely

proportional to the thickness of the scale. Hence it may be concluded that evaporation of sulfur from the scale is limited by the diffusion stage. It should be borne in mind, however, that at small scale thicknesses this stage may not be the slowest one limiting the rate of the entire process (17-19).

Table 1

Temp., °C	Thickness of sulfide scale, cm	Rate of sulfur evaporation $\cdot 10^3$, $g \cdot cm^{-2} \cdot min^{-1}$	Rate of sulfur attachment at the scale-sulfur boundary $\cdot 10^3$, $g \cdot cm^{-2} \cdot min^{-1}$
445	1.03	2.35	2.37
445	1.03	2.35	2.25
434	0.65	2.80	2.63
434	0.85	1.95	1.98
434	0.95	1.75	1.73
434	1.30	1.29	1.21
434	2.10	0.90	0.78
400	0.90	1.42	1.42
370	0.55	1.00	1.02
370	0.75	0.80	0.78
344	0.60	0.51	–

In conclusion we note that the mechanism described above for the evaporation of sulfur from a dense layer of sulfide scale may occur in the process of formation of a two-layer sulfide scale on copper.

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