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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE KINETICS OF THE PROCESSES OF FORMATION OF OXIDE FILMS ON TUNGSTEN AND MOLYBDENUM

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In studying the kinetics of the oxidation processes of tungsten and molybdenum by using a method that makes it possible to determine the change in weight with high accuracy, along with obtaining data characterizing the process of oxidation of these metals, facts were revealed whose consideration is of interest in interpreting data on the oxidation kinetics of any metals.

The apparatus used made it possible to carry out continuous observations of the process of growth of oxide films over a wide range of oxygen pressures and temperatures by the weight method.

Fig. 1. Schematic of the apparatus: **1** —balance, **2** —tubular furnace, **3** —recording circuit, **4** —recording galvanometer

Weighing was carried out with specially constructed vacuum quartz microbalances of the beam type (see Fig. 1). The sensitivity of the balance was $5 \cdot 10^{-7}$ g per division of the microscale (equal to 0.001 mm) with a load of up to 7 g. The oscillation period of the balance was 5 sec. Along with visual observations, an automatic recording of the change in weight was made with the aid of the corresponding electronic circuit and a recording galvanometer.

The specimen, suspended on a long platinum thread from the balance beam, was heated in a tubular furnace, which was constructed in two variants—for high temperatures with a vacuum jacket and for medium temperatures without one. This furnace design made it possible to obtain temperatures up to 1050° at a vacuum down to $1 \cdot 10^{-7}$ mm Hg (the furnace windings were made bifilarly). The temperature was measured by a thermocouple located in the immediate vicinity (1-2 mm) of the specimen, and was maintained constant with an accu-

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

racy of ±2°. Oxygen, obtained by decomposition of chemically pure potassium permanganate, was purified by passage through granular chemically pure KOH and traps cooled with liquid oxygen. Specimens made from tungsten or molybdenum sheet of 99.95% purity, with a surface area of 8 to 30 cm^2 and a weight of up to 5 g, were subjected to various—

preliminary treatment. The samples of the first series, immediately after grinding, were degreased by treatment in a KOH solution. The samples of the second series, after grinding, were subjected to additional electrolytic polishing, followed by thorough washing in distilled water. In the third series, after the treatment indicated above, the samples were oxidized, and the oxide that formed was either reduced in hydrogen at a temperature of 600° and $P_{\mathrm{H2}} = 20$ mm Hg, or completely evaporated in vacuum ($\sim 10^{-7}$ mm Hg) at temperatures of 600 and 1050°, respectively, for molybdenum and tungsten.

Fig. 2. Oxidation of tungsten and molybdenum. $P_{\mathrm{O2}} = 100$ mm Hg. *I*—W; *II* —Mo

The surface preparation described, and the high sensitivity of the balance, made it possible for the first time to observe quantitatively the process of oxidation of tungsten and molybdenum at temperatures close to room temperature (Fig. 2), which had not been achieved even in such a carefully executed work as the study by Gulbransen and Wysong [1]; the latter did not detect the formation of an oxide film on Mo at room temperature.

Fig. 3. Oxidation of tungsten at $P_{\mathrm{O2}} = 24$ mm Hg. 1—ground; 2—electrolytically polished

With increasing temperature, the amount of oxygen reacting with both molybdenum and tungsten increases noticeably; at the same time the rate of the very process of growth of the oxide film on these metals increases considerably. At temperatures above 300°, the growth of oxide films on both tungsten and molybdenum is satisfactorily described by an equation of parabolic type:

$$X^2 = kt + C.$$

In the investigation it was found that the value of k—the oxidation-rate constant—in the case of oxide films of considerable thickness depends little on the magnitude of the initial (specific) surface. Thus, for molybdenum samples with identical visible surfaces but with greatly differing true surfaces (some samples after electrolytic polishing, and others after reduction in a hydrogen atmosphere of a previously formed oxide film MoO_2), the rate constants at the same temperature proved to be equal, while the values of the constant C in the equation differed severalfold. For polished samples C was close to zero, while for reduced samples the value of C proved to be close to the amount of oxygen consumed in the process of preliminary formation of the oxide film.

If the increase in specific surface due to loosening of the surface layers of the metal during reduction of the oxide has little effect on the value of the rate constant k, then the difference in the surface condition of the samples,

subjected only to grinding or, after grinding, to electrolytic polishing, is reflected to a greater extent precisely in the values of the rate constant k and even in the activation energy than in the value of the constant C. The effect of differences in surface treatment on the course of the kinetic curves is well illustrated by Fig. 3.

Table 1

Experimental conditions	Temperature range in °C	E, kcal/mol
Tungsten		
Electrolytically polished, $P_{O2} = 24$ mm	360—500	46.5
Ground, $P_{O2} = 24$ mm	390—500	41.0
Ground, $P_{O2} = 100$ mm	360—550	43
Ground, $P_{O2} = 100$ mm, thin films	200—360	22
Molybdenum		
Ground, $P_{O2} = 100$ mm	360—500	36.0
Ground, $P_{O2} = 100$ mm, thin films	320—360	25

The temperature dependence of the oxidation-rate constants of tungsten and molybdenum for specimens with different preliminary surface treatments is presented in Fig. 4. The values of the activation energy are given in Table 1.

The difference in the activation energies for electrolytically polished and ground tungsten specimens is probably due to the fact that grinding produces strong mechanical deformation of the surface layer, with the appearance of residual stresses. In the case of specimens subsequently subjected to electrolytic polishing, the stressed surface layer dissolves. Indeed, in electron-diffraction examination in the latter case a clear pattern characteristic of rolled tungsten with

Fig. 4

Figure 4: Fig. 4

the texture axis [001] is observed. In the case of oxidation of ground metal, the activation energy decreases, apparently owing to the stresses arising during grinding.

At temperatures below 360°, both for tungsten and for molybdenum, the course of the straight line $\lg k—1/T$ changes; its slope indicates that in this temperature region the process proceeds with a lower activation energy, namely with a value almost 2 times smaller than the values corresponding to higher temperatures.

The data on oxidation kinetics obtained for various temperatures, both on different specimens and under conditions in which, on the same specimens, the oxidation process was carried out by successively changing one temperature regime to another, showed that the rate constants depend strongly on the thickness of the oxide film. At small thickness the rate constant has the greatest value; with increasing thickness, the rate constant for the same temperature decreases severalfold. These relationships are evident from the data in Fig. 4.

Fig. 4. Temperature dependence of the oxidation-rate constants of tungsten and molybdenum: a—molybdenum; —ground tungsten, $P_{\mathrm{O2}} = 100$ mm Hg; —ground tungsten, $P_{\mathrm{O2}} = 24$ mm Hg; —electrolytically polished tungsten, $P_{\mathrm{O2}} = 24$ mm Hg.

Such a dependence of the rate constants on the thickness of the oxide film can apparently be explained by the fact that scale growth is determined by the process of diffusion of the components through the oxide film, which, as is known—

may proceed both along grain boundaries and within the crystal lattice. At lower temperatures, when, owing to the slow course of the process, the thickness of the oxide film under the experimental conditions does not reach significant values and proves to be commensurate with the dimensions of the crystallites in it, the decisive role in the transfer of the reacting components should be played by diffusion along grain boundaries (or blocks arising in individual grains as a result of the disordered formation and development of oxide nuclei), characterized by a smaller activation energy. As the thickness of the oxide layer increases to values far exceeding the dimensions of individual oxide grains, the oxidation rate begins to be determined by diffusion of the components in the bulk of the crystal lattice, which is associated with a larger activation energy. The role of temperature in this case is reduced to its influence on the rate of transition from the region of small oxide thicknesses (with intercrystalline diffusion determining the process) to the region of large oxide thicknesses, with bulk diffusion being decisive.

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