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# SPIRAL VACUUM MICROBALANCE FOR STUDIES OF REACTION KINETICS IN GAS-SOLID SYSTEMS

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The spiral vacuum microbalance for studies of the kinetics of mass changes of solids at high temperatures is described. Some novel improvements ensure high sensitivity of the balance and stability of temperature and pressure. Results of studies on the kinetics of the oxidation of copper carried out at 1000° prove the suitability of this balance in the investigation of kinetics of heterogenous reactions.

In recent years there has been a rapid development of gravimetric methods in studies of the kinetics of various high-temperature processes. One may cite here investigations of chemisorption on semiconducting oxides, measurements of the kinetics of decomposition of solids, and studies of the kinetics of oxidation of metals and alloys [1—7]. Very sensitive microbalances of an absolute sensitivity of the order of $10^{-6}$—$10^{-7}$ g at a load up to 10 g have been developed. They have been used in the study of the dependence of deviations from stoichiometry in metal oxides on the partial pressure of oxidant, and hence in the study of the thermodynamics of defects. The gravimetric method considered consists in the determination of the mass gain of the sample in the course of reaction at constant temperature and gas pressure. In measurements of this type a sample is hung on a suitably sensitive microbalance, isolated from the surrounding atmosphere which is necessary for maintaining the specified partial pressure of the oxidizing agent. The classical set-up of this type described by Gulbransen contained a quartz beam microbalance [1]. A simpler device and easier manipulation is found in McBain and Bakr microbalances with a quartz spiral [8]. Microbalances with spirals of molybdenum [9], tungsten [10] and copper-beryllium alloy [11] are also widely employed. They are easier to make, show higher tearing resistance and also possess high sensitivity.

In the present work a spiral vacuum microbalance is described containing some novel elements. It was tested by studying the kinetics of copper oxidation at 1000° at various oxygen pressures. The design is outlined in Fig. 1. The spiral was made of 0.2 mm diameter tungsten wire recrystallized in hydrogen. The spiral contained about 200 coils 10 mm in diameter. It was found that the elongation of the spiral was a linear function of load up to 700 mg. In this range the sensitivity of the balance was $376 \pm 2$ $\mu$/mg. The spiral elongation could be read with an accuracy of $\pm 2 \times 10^{-3}$ mm, and hence the weight gain could be determined with an accuracy of $\pm 5 \times 10^{-6}$ g.

The apparatus was made of quartz glass. The upper part of the apparatus containing the spiral was thermostated with water at $21 \pm 0.1°$. This was necessary

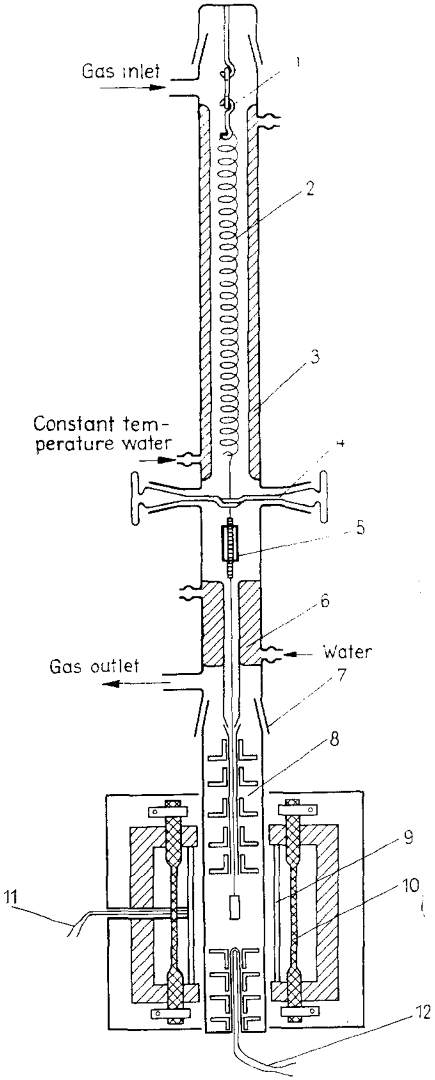

Fig. 1. Scheme of the vacuum microbalance. 1. Hooks for fixing the spiral; 2. tungsten spiral; 3. thermostating jacket; 4. arrestment of the sample; 5. window for microscopic observation; 6. water jacket; 7. connection of the ground joint of the furnace tubing to the microbalance; 8. quartz plates; 9. asbestos casing for the furnace tubing; 10. heating elements; 11. thermocouple controlling the furnace temperature; 12. measuring thermocouple

since the elongation of the spiral depended considerably on temperature. The microbalance was equipped with arrestment, which facilitated hanging and replacing of the samples and prevented vibrations of the spiral during admission of the gases. The elongation of the spiral was measured using a microscope with micrometric ocular by observing the scale (5) which was fixed to a thin quartz thread. The thread at the same time held a sample. The scale was made of 1 mm diameter glass tubing coated with a silver mirror which was marked at 1 mm intervals. The distances between the marks were measured with an Abbe comparator with an accuracy of $\pm 1 \times 10^{-3}$ mm. The scale was observed through a flat window made of optical quartz. To minimize the effect of thermal radiation and thermodiffusion on the microbalance readings and to ensure constant temperature in the reaction region, a number of auxiliary devices were applied. Between the space occupied by the spiral and the furnace was a narrowing surrounded by a water cooler (6). From the bottom part of the cooler a quartz tube led out. This tube constituted at the same time a holder for quartz plates (7) placed coaxially in the upper part of the heating system. The same number of quartz plates were

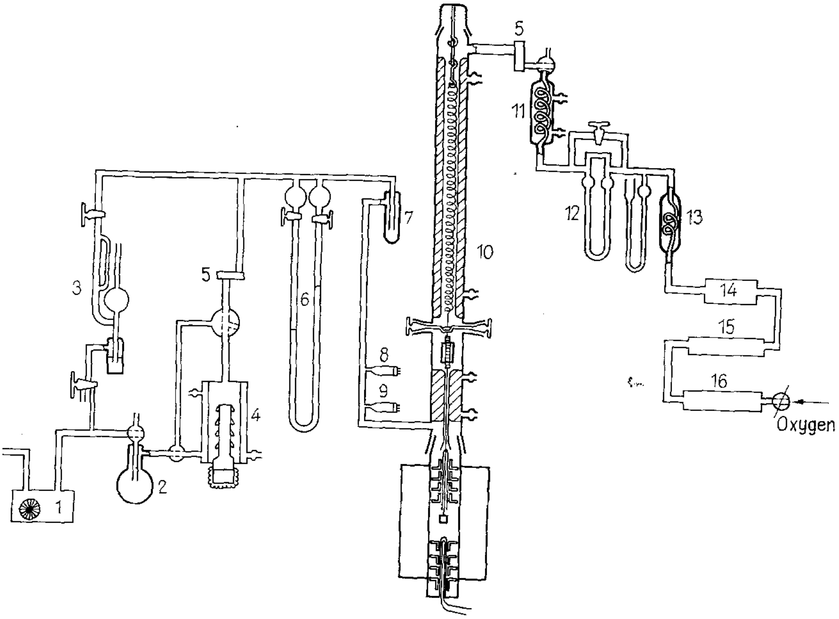

Fig. 2. Scheme of the thermogravimetric apparatus for studies of the kinetics of metal oxidation under flow conditions. 1. Rotary pump; 2. low vacuum container; 3. MacLeod gauge; 4. diffusion pump; 5. metal valve of "Alpert" type; 6. oil manometer; 7. liquid nitrogen trap; 8. 9. heads of the resistance and ionization manometers; 10. microbalance; 11. cooler, thermostating the gas introduced; 12. flowmeter; 13. manometer; 14. 15. 16. system for purification of the gas

placed on the thermocouple casing in the lower part of the furnace. The furnace tube was made of quartz glass which allowed the measurements to be carried out at temperatures up to 1200°. To obtain higher temperatures ceramic tubes (alundum or other) may be employed. The reaction space was heated by a furnace containing six silite heating elements of size 8 × 180 × 150 mm fitted in the ceramic casing. In order to reduce light radiation and to ensure the uniform heating of the sample an asbestos screen was fixed between the quartz tube and the heating elements. The temperature of the furnace was kept constant by a compensating regulator connected to a thermocouple (11). The temperature of the reaction space was measured with another thermocouple (12) connected to a high precision compensator. It was proved that variations in the reaction space did not exceed 0.5% within 10 cm during several hours. The desired pressure of oxygen at constant flow rate was maintained by the vacuum system equipped with two metal membrane valves of the "Alpert" type [12, 13]. The outline of the apparatus including the dosing and pumping systems is shown in Fig. 2. The system was equipped with a number of manometers of various types which made possible the measurement of pressure over a wide pressure range. It is appropriate to apply an electronic regulator; this considerably improves the constancy of the pressure maintained in the system.

The test experiments involved oxidation of spectrally pure copper under a constant oxygen flow. The gas was introduced at the upper part of the apparatus, passed through the narrowing to the reaction space, and left the apparatus by an outlet placed below the cooler (6). This position of the gas outlet meant the rigid connection of the microbalance with the vacuum system, ensuring regular gas flow and facilitating at the same time manipulation of the furnace tube. The above-described system ensured stability of the temperature of the spiral. The system of plates acting as radiation shields also maintained constancy of the temperature in the reaction space within 10 cm, and reduced diffusion of the gas in the furnace tube. The constant downward flow of oxygen from the top of the apparatus was favourable for several reasons. First, under these conditions the flow vibrations of the spiral were considerably damped, which allowed the readings of the mass gain to be made with higher accuracy. Secondly, gas flow at a constant rate through the space occupied by the spiral contributed to the maintaining of constant temperature in this part of the apparatus. Finally, the flow of gas through the reaction space is recommended, and in the case of fast processes even necessary, for maintaining a constant and well defined pressure of oxidant in the close vicinity of the sample. It should be mentioned that the flow rate of the gas affects the magnitude of the spiral elongation. In view of this fact calibration of the spiral and measurements of the oxidation rate were carried out at oxygen flow rates at which the elongation of the spiral was not affected by this factor.

The kinetics of copper oxidation were studied at 1000°, in the pressure range $6.6 \times 10^{-3}$—0.5 atm, at a constant flow rate of oxygen of 10—15 ml/min depending on the gas pressure; the copper samples were in the form of flat plates $1.25 \times 0.75 \times 0.045$ cm. The sample surface was polished with emery paper prior to the measurement down to the grade 4/0, and washed with acetone and water. In order to hang the specimen on the spiral the lower quartz tubing was lowered and, after fixing the sample, lifted again, the two tubings being connected by a ground joint (7). The joint was cooled with a water cooler made of metal. During these operations the spiral was fixed with the arrestment (4). Before each run the apparatus was swept with purified argon, and then evacuated, a vacuum of the order of $10^{-5}$ Torr being maintained during the heating of the furnace up to the desired temperature. It was found that no oxidation of copper occurs under these conditions (the weight of the sample remained constant during the heating of the furnace). This was in agreement with expectation since the dissociation pressure of $Cu_2O$ calculated from thermodynamic data for 1000° amounts to about $10^{-7}$ atm [14], whereas the partial pressure of oxygen in the apparatus could be estimated as $10^{-8}$ atm.

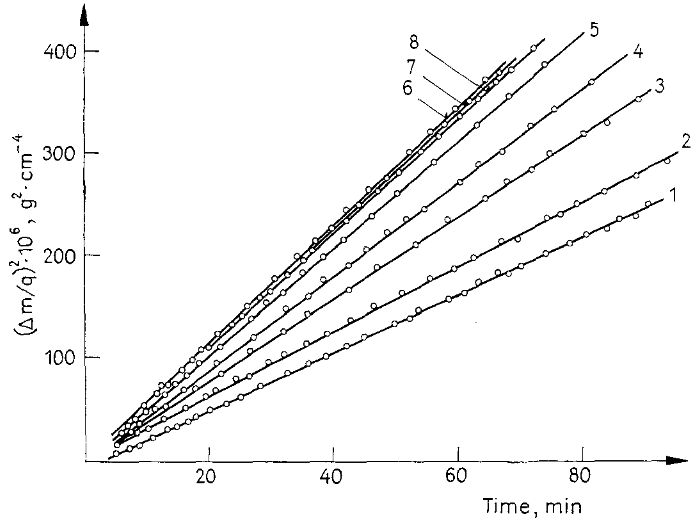

Fig. 3. Kinetics of copper oxidation at 1000° at different oxygen pressures. Curves 1—8 correspond to the following oxygen pressures: $6.6 \times 10^{-3}$ atm, $1.32 \times 10^{-2}$ atm, $2.63 \times 10^{-2}$ atm, $5.7 \times 10^{-2}$ atm, $7.9 \times 10^{-2}$ atm, $1.05 \times 10^{-1}$ atm, $1.95 \times 10^{-1}$ atm, $3.3 \times 10^{-1}$ atm

After establishment of the desired temperature in the reaction space, the sample was heated for about 20 min, after which oxygen was admitted. Its pressure and flow rate were controlled by membrane valves.

It was found in accordance with the results reported by other authors [15, 16] that the oxidation of copper follows a parabolic rate law

$$\left(\frac{\Delta m}{q}\right)^2 = k_p'' \cdot t + C \tag{1}$$

where $\Delta m$ is the mass gain, $q$ the sample surface, $k_p''$ a parabolic rate constant of oxidation, $t$ the oxidation time, and $C$ a constant resulting from the fact that the reaction course is unestablished. In Fig. 3 the kinetics of copper oxidation at several pressures of oxygen are plotted with a parabolic system of co-ordinates. In Fig. 4 the dependence of the parabolic rate constant on the oxygen pressure is given with the double-logarithmic system. As seen from the Figure, the rate of copper oxidation increases with the increase in oxygen pressure up to a value of $1.0 \times 10^{-2}$ atm, remaining practically constant above this pressure. This result is in agreement with theoretical suppositions. The dissociation pressure of CuO at 1000° is $1.2 \times 10^{-2}$ atm; hence, at pressures lower than this value a mono-phase layer of cuprous oxide is formed. Since $Cu_2O$ is a metal-deficient, $p$-type semiconductor, the rate of growth of this oxide layer should increase with increase of oxygen pressure [17—19]. At pressures higher than $1 \times 10^{-2}$ atm a thin layer of CuO is formed on the surface of the $Cu_2O$ layer and the rate of the layer growth becomes independent of the oxygen pressure. The dependence of the rate of copper oxidation on the oxygen pressure in the pressure range of $6.6 \times 10^{-3}$—$1.2 \times 10^{-1}$ atm can be described by the following empirical equation:

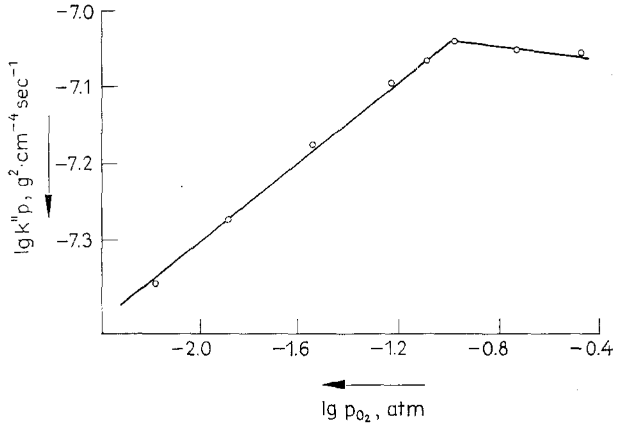

Fig. 4. Dependence of the rate of copper oxidation on the oxygen pressure at 1000°

$$k_p'' = (2.39 \pm 0.05) \times 10^{-7} \cdot p_{O_2}^{(0.25 \pm 0.005)} \tag{2}$$

The dependence obtained is in good agreement with the results of O'Keeffe and Moore [20] concerning the dependence of deviations from stoichiometry in cuprous oxide on oxygen pressure:

$$y = \text{const}\ p_{O_2}^{(0.27 \pm 0.015)} \tag{3}$$

The practically identical values of the exponents in Eqs (2) and (3) confirm the mechanistic model proposed for copper oxidation by Moore.

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Résumé — On décrit une microbalance spirale à ressort fonctionnant sous vide servant aux examinations des cinétiques de changement de masse des corps solides aux hautes températures. Certains perfectionnements nouveaux procurent une grande sensibilité et une stabilité de la température et de la pression. Les résultats de l'étude de la cinétique de l'oxydation de cuivre à 1000° prouve l'utilité de cette balance dans le cas des réactions hétérogènes.

Zusammenfassung — Es wurde eine Spiralvakuumwaage zur Untersuchung der Kinetik von Gewichtsänderungen fester Stoffe bei hohen Temperaturen beschrieben. Verbesserungen versichern hohe Empfindlichkeit und Temperatur- und Druckstabilität. Kinetische Untersuchungen der Kupferoxydation bei 1000° bewiesen die Brauchbarkeit der Waage zum kinetischen Studium von heterogenen Vorgängen.

Резюме — Описаны спирально-вакуумные микровесы для изучения кинетики изменения массы при высокой температуре. Некоторые усовершенствования обеспечивают высокую чувствительность весов и стабильность температуры и давления. Результаты изучения кинетики окисления меди при температуре 1000°C показали применимость этих весов при исследовании кинетики гетерогенных реакций.