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# MICROGRAVIMETRIC APPARATUS FOR SULFIDATION IN PURE SULFUR VAPOUR AT HIGH TEMPERATURES

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## Abstract

A thermobalance for studies of the high-temperature sulfidation of metals and alloys is described. This apparatus permits the determination of mass changes in a sulfidized sample as a function of temperature and sulfur vapour pressure. The main parts of this apparatus are the container with liquid sulfur and the reaction chamber with the quartz space and quartz spiral. All parts of the apparatus are equipped with thermostating furnaces. The temperature within the apparatus is controlled with an accuracy of 0.5 K. The quartz spiral (diameter 0.2 mm), consisting of 50 coils (diameter 30 mm), permits the recording of mass changes in the sample (about 200 mg) with an accuracy of $10^{-5}$ g.

Besides heterogeneous kinetics measurements, it has been shown that the self- and chemical diffusion coefficients or the deviation from stoichiometry of the metal sulfides can also be studied as functions of temperature and sulfur pressure by means of equilibration measurements.

**Keywords:** chemical diffusion, kinetics of heterogeneous reactions, measurements, sulfidation of manganese, thermobalance

## Introduction

The high-temperature corrosion of metallic materials in sulfur-containing atmospheres is well known to be much more severe than in purely oxidizing environments [1]. All conventional oxidation-resistant alloys undergo very rapid, often catastrophic degradation under these conditions [1–4]. The main reason why oxidation-resistant alloys are rapidly attacked by sulfur is the poor protective properties of sulfide scales. For the development of new materials resistant to sulfur corrosion at high temperatures, a better understanding of their sulfidation kinetics and mechanism is urgently needed. However, in consequence of the considerable experimental difficulties, the available literature data concerning this problem are fragmentary and often controversial. Because of the serious corrosion problems in atmospheres containing sulfur, there is still interest in thermogravimetry for studies of the physico-chemical properties of solids and the kinetics and mechanisms of sulfidation reactions [5, 6]. Unfortunately, sulfur ex-

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ists in the condensed state under normal conditions, and this, together with the very aggressive nature of the vapour, precludes thermogravimetric measurements in standard equipment. Thus, intensive attempts are being made to adapt thermogravimetry for studies on the kinetics of metal sulfidation and on defect structures and diffusion in metal sulfides.

The kinetics of high-temperature sulfidation of metals, and also of other reactions (e.g. $MS+1/2S_2 \rightarrow MS_2$), can be measured either in sulfur vapour or in $H_2$–$H_2S$ gas mixtures. In experiments in $H_2$–$H_2S$, the sulfur partial pressure is relatively low and does not exceed $10^{-3}$ atm at high temperatures. Measurements at higher sulfur vapour pressures require pure sulfur vapour at appropriate pressure. In contrast with $H_2$–$H_2S$ gas mixtures, where the measurements are relatively simple, in an atmosphere of sulfur vapour the situation is much more complicated, due to the possibility of the condensation of sulfur on the cool parts of the equipment. In the case of microthermogravimetric apparatus for sulfidation in pure sulfur vapour at high temperatures, all parts of the apparatus have to be equipped with thermostating furnaces. Further, the mass changes can only be measured by using a balance made of highly corrosion-resistant materials.

## Apparatus for sulfidation in pure sulfur vapour

The present paper describes a simpler version of a microthermobalance for the study of high-temperature reactions in pure sulfur vapour [7]. The scheme of the microthermobalance is shown in Fig. 1. The main parts of this apparatus are as follows: the container with liquid sulfur and the reaction chamber with the quartz spiral space. All parts of the apparatus are made of quartz and are equipped with thermostating furnaces. The upper part containing the spiral and the reaction chamber is thermostated with an accuracy of ±0.5 K. The temperature of the liquid sulfur is controlled with an accuracy of ±0.3 K in order to avoid sulfur vapour pressure fluctuations. The quartz spiral (diameter 0.2 mm), consisting of 50 coils (diameter 30 mm), permits the recording of mass changes in the sample (about 200 mg) with an accuracy of $10^{-5}$ g. The quartz spiral is suspended in the reaction tube on a special arrangement allowing its vertical movement. This makes it possible to suspend and remove the specimen from the apparatus after the reaction tube has been opened from the bottom. After the specimen has been suspended and the reaction tube closed, the system is evacuated and filled with high-purity argon three times, in order to remove oxygen traces from the reaction chamber. The reaction chamber is then heated to the appropriate temperature. When the temperature reaches the required constant value, the sulfur container is heated to the appropriate temperature to attain the necessary sulfur vapour pressure. Depending on its value, the constant pressure in the reaction chamber is reached in 3–5 min. The quartz spiral elongation during the reaction is recorded with a cathetometer with an accuracy of ±0.001 cm. The value of the spiral constant ($k_s$=1.69 mg mm$^{-1}$) is used to calculate the mass changes of the sample as a function of time.

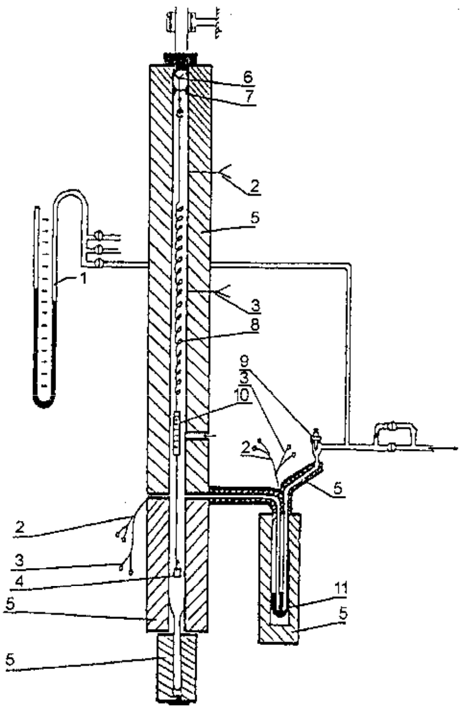

**Fig. 1** Scheme of the microthermobalance for the study of high-temperature heterogeneous reactions in pure sulfur vapour; 1 – mercury manometer, 2 – regulating thermoelement, 3 – controlling thermoelement, 4 – sample, 5 – furnace, 6 – quartz pole, 7 – suspension of spiral, 8 – spiral, 9 – teflon valve, 10 – scale for reading elongation of spiral, 11 – sulfur

One negative feature of the described apparatus is the non-automatic method of recording mass changes. Moreover, air diffuses through the teflon valve and heated pyrex glass (at about 673 K) into the reaction chamber, and during long experiments (more than 100 h) oxygen can affect the sulfidation process.

In order to illustrate the applicability of the apparatus described above, results on the kinetics of manganese sulfidation, and on the self-diffusion and chemical diffusion of manganese in manganese(II) sulfide are presented. The possibility of measurement of the deviation from stoichiometry as a function of temperature and sulfur pressure for iron sulfide is demonstrated.

## Experimental results

The rate of sulfidation of manganese was studied in the temperature range 673–1373 K at pressures ranging from 10 up to $8\cdot10^4$ Pa [8]. The longest reaction time under constant isothermal-isobaric conditions was 150 h. In agreement with previous investigations [8–10], it was found that manganese sulfidation follows a parabolic rate law.

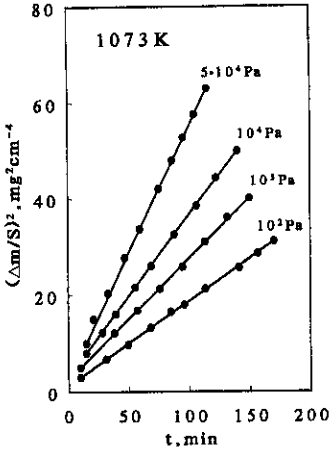

**Fig. 2** Parabolic plots for manganese sulfidation kinetics at 1073 K

Figure 2 depicts typical sulfidation runs at 1073 K for various sulfur pressures. It can be seen that these plots follow the parabolic rate law from the very beginning of the reaction, which means that the rate-determining step of the overall reaction is the outward diffusion of manganese.

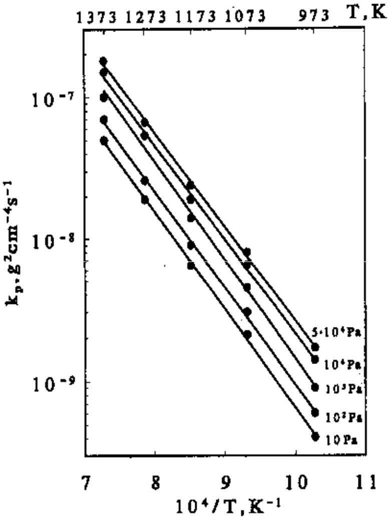

**Fig. 3** Temperature dependence of manganese sulfidation rate for several sulfur pressures

Figures 3 and 4 present the temperature and pressure dependences of the parabolic rate constants of manganese sulfidation. It follows from these plots that the above apparatus permits determination of the influence of both these pa-

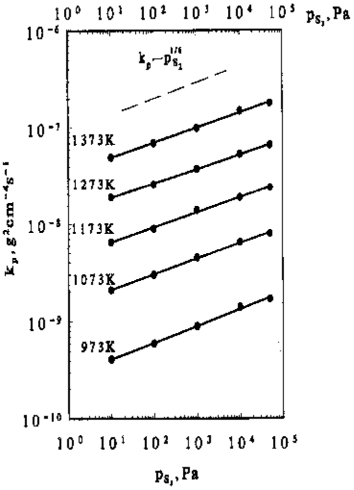

**Fig. 4** Pressure dependence of manganese sulfidation rate for several temperatures

rameters on the sulfidation kinetics. The kinetics of manganese sulfidation in the investigated ranges of temperature and sulfur pressure can be described by the following empirical equation:

$$k_p = 7.23 \cdot 10^{-3} p_{S_2}^{1/6} \exp\left(-\frac{120\ \text{kJ mol}^{-1}}{RT}\right)$$

The pressure dependence of the parabolic rate constant of manganese sulfidation (Fig. 4) is typical for a metal-deficient, $p$-type semiconductor, in which double-ionized cation vacancies, $V''_{Mn}$, are the predominant point defects [11]. Thus, the concentration of these defects is the following function of sulfur pressure:

$$[V''_{Mn}] = \text{const}\ p_{S_2}^{1/6}$$

Since the concentration of cation vacancies in $Mn_{1-y}S$ is very low ($y \le 10^{-3}$ [12]), it can be assumed that the mobility of these defects is virtually independent of their concentration. Thus, the self-diffusion coefficient of manganese in manganese(II) sulfide, and consequently the parabolic rate constant of sulfidation, should be the same function of sulfur pressure as for the defect concentration. The identical pressure dependence of the parabolic rate constant and the manganese vacancies at high temperatures proves that at high sulfur partial pressure the manganese sulfidation rate is controlled by volume diffusion and that $Mn^{2+}$ diffuses through double ionized cation vacancies. As the diffusivity of sulfur in manganese(II) sulfide is very small in comparison with that of manganese [13], then, according to Wagner's theory, the kinetic results can be used for calculation of the self-diffusion coefficient of manganese in $Mn_{1-y}S$ [14]:

$$k'_{\mathrm{p}} = \int_{p_{\mathrm{S_2}}(\mathrm{Mn|MnS})}^{p_{\mathrm{S_2}}(\mathrm{MnS|S_2})} D_{\mathrm{Mn}} \mathrm{d}\ln p_{\mathrm{S_2}}$$

By differentiation of the above equation, the manganese diffusion coefficient can be expressed in the following form:

$$D_{\mathrm{Mn}} = \left(\frac{\mathrm{d}k'_{\mathrm{p}}}{\mathrm{d}\ln p_{\mathrm{S_2}}(\mathrm{MnS|S_2})}\right)_{p_{\mathrm{S_2}}}$$

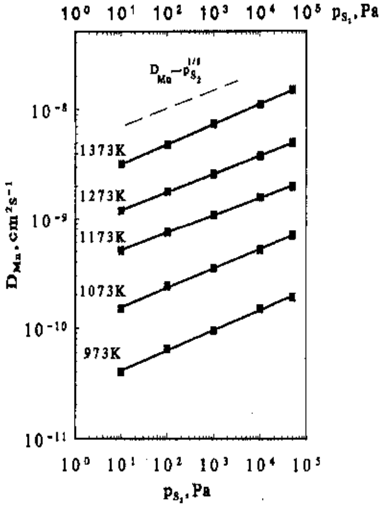

**Fig. 5** Pressure dependence of self-diffusion coefficient of manganese in $Mn_{1-y}S$

The technique of calculation of the self-diffusion coefficient by using the above equation is known as the Feueki-Wagner method [15]. On the basis of the kinetic data presented in this work, the self-diffusion coefficient of manganese in manganese(II) sulfide was calculated. Figure 5 presents the pressure dependence of the self-diffusion coefficient of manganese in $Mn_{1-y}S$ for several temperatures. The dependence of the manganese self-diffusion on temperature and sulfur pressure can be described by the following empirical equation:

$$D_{\mathrm{Mn}} = 6.7\cdot 10^{-4} p_{\mathrm{S_2}}^{1/6} \exp\left(-\frac{121\ \mathrm{kJ\ mol^{-1}}}{RT}\right)$$

The independence of the diffusion coefficient of the defects on their concentration confirms the defect model of $Mn_{1-y}S$, according to which the double ionized cation vacancies constituting the predominant disorder in this compound do not interact and are randomly distributed in the crystal lattice.

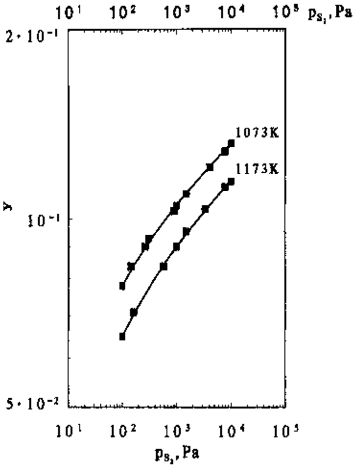

**Fig. 6** Dependence of non-stoichiometry in $Fe_{1-y}S$ on sulfur vapour pressure

As the diffusion coefficient of the defects is a direct measure of their mobility, it can be stated further that the diffusional transport of the cations in $Mn_{1-y}S$ is effected by a simple vacancy mechanism, consisting in the jumping of $Mn^{2+}$ from the lattice sites into the neighbouring cation vacancies.

The apparatus applied for sulfidation at high temperatures also allows determination of the deviation from stoichiometry and the chemical diffusion coefficients. Unfortunately, because of the sensitivity of the microthermobalance and its construction, such experiments can be performed only for sulfides that exhibit

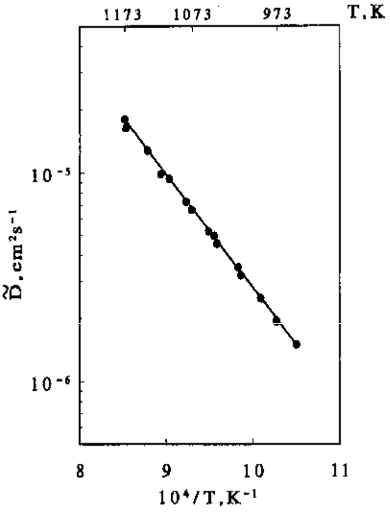

**Fig. 7** Temperature dependence of chemical diffusion coefficient in $Fe_{1-y}S$, for a sulfur vapour pressure of 1 kPa

large deviations from stoichiometry and large diffusion coefficients. As an example of such measurements, the results of studies of the non-stoichiometry and chemical diffusion coefficient in iron sulfide are presented [16] (Figs 6 and 7).

## Conclusions

The results presented above illustrate the applicability of microthermogravimetry for study of the kinetics and mechanisms of the high-temperature heterogeneous reactions of metallic materials in sulfur vapour, and of the defect structures and diffusion processes in metal sulfides.

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