

NEW MICROTHERMOGRAVIMETRIC APPARATUS Kinetics of metal sulphidation and transport properties of transition metal sulphides

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Abstract

A novel microthermogravimetric apparatus to study the kinetics of metal sulphur reactions and transport properties of transition metal sulphides has been described. The main feature of this arrangement includes the application of the carrier gas for sulphur vapour transportation and the protection of the balance chamber from sulphur attack. As a consequence, the helix balance could have been replaced by an automatic electronic microbalance and the accuracy of the mass change measurements increased more than two orders of magnitude, up to 10^{-7} g. The application of two liquid sulphur reservoirs created very stable, strictly defined reaction conditions, and enabled to make rapid changes of sulphur partial pressure in the reaction chamber. It has been demonstrated that all these innovations make it possible to study not only the kinetics of very slow sulphidation processes but also to determine deviations from stoichiometry and defect mobility in transition metal sulphides.

Keywords: chemical diffusion, microthermogravimetric apparatus, $Mn_{1-y}S$

Introduction

High-temperature corrosion of metallic materials in sulphur containing atmospheres is well known to be much more severe than in purely oxidizing environments [1–4]. In fact, all conventional oxidation resistant alloys undergo under such conditions very rapid, often catastrophic degradation. This is the reason why the sulphidation of metals and physico-chemical properties of metal sulphides have been extensively studied since many years. In spite of this, however, the mechanism of sulphide corrosion, as well as the defect structure and transport properties of sulphides are still less known than the mechanism of metal oxidation and physico-chemical properties of the corresponding oxides [2–8]. Such a situation results mainly from much greater experimental difficulties in studying the high-temperature heterogeneous reactions in sulphur containing atmospheres. Sulphur is, namely, not gaseous in normal conditions and its vapours are extremely aggressive at high temperatures, attacking all the metals including gold and platinum. Consequently, all standard thermogravimetric and other

equipment commonly used in oxidation studies are not applicable under such conditions.

Thermogravimetry plays the most important role in this area of research because – like in the case of oxidation – the reaction rate in metal-sulphur system may continuously be followed as a function of temperature and sulphur activity, and valuable information on defect and transport properties of metal sulphides can also be obtained from equilibration and reequilibration kinetics [9]. Thus, during the last 40 years a number of various thermogravimetric equipments have been developed [9–21] but all of them offer much less accuracy than modern automatic microthermogravimetric devices currently used in oxidation studies. Consequently, low sulphidation rates cannot be determined with sufficient accuracy, and small deviations from stoichiometry of metal sulphides are impossible to be estimated, at all. In the present paper a novel apparatus is described, enabling not only the determination of the low sulphidation rates of metals, but also the evaluation of small defect concentrations and their mobilities in transition metal sulphides from equilibration and reequilibration kinetics, respectively.

General remarks

In all thermogravimetric equipments currently used in sulphidation studies a quartz spiral plays the role of thermobalance. In the case of H_2/H_2S gas mixtures the situation is more simple than in sulphur vapours since there is no danger of sulphur condensation on the cool parts of the apparatus and the sulphidation process can be performed under dynamic conditions i.e., with the gas stream flowing through the reaction chamber at a suitable rate, maintaining a constant sulphur pressure in the reaction zone [20, 21]. However, in this atmosphere only rather low sulphur pressures can be obtained, not exceeding 10 Pa. In addition – what is even more important – hydrogen may dissolve in the growing sulphide scale, influencing its defect structure and consequently, the kinetics and mechanism of the reaction [3, 22–24]. Thus, measurements in pure sulphur vapours are necessary. In that case the problem is more complicated because all parts of the apparatus, including the balance chamber, should be maintained at a temperature higher than that of the liquid sulphur reservoir, being its vapour source [9–12], [15–19].

It should be noted that in both types of sulphidizing atmospheres the same difficulties are encountered in measuring the sulphur vapour pressure in the reaction chamber. With respect to the H_2/H_2S gas mixtures this problem has not been solved to date, and consequently, the partial pressure of sulphur in this atmosphere can only be calculated from thermodynamic data. In the case of pure sulphur vapour its pressure in the reaction chamber may be calculated from the mass of sulphur condensed in the trap, basing on the ideal gas equation of state, as suggested by Wakihara [25] and this method is currently being used in our investigations.

As the spiral thermobalance is only used in sulphidation studies the mass of the sample is very limited and the accuracy of the mass change measurements, even in the most sophisticated arrangements, does not exceed $5 \cdot 10^{-5}$ g. In addition, the reaction course cannot be followed automatically because the elongation of the spiral may

only be recorded by cathetometer. However, one of the most important disadvantages of the discussed devices results from the fact that the sulphidation experiments are carried out in static conditions. As a consequence, the constant sulphur pressure in the reaction chamber can only be established after certain period of time, being the longer the lower is the temperature of the liquid sulphur reservoir. Thus, it is impossible to study the early stages of any solid-sulphur reaction, especially at low sulphur pressures, and equilibration kinetic measurements are entirely excluded. It should be noted, for instance, that at sulphur pressures lower than 10 Pa the evaporation rate of sulphur and its diffusional transport to the reaction chamber may be the slowest step in the overall reaction rate which precludes any reasonable kinetic conditions. These important restrictions has been partly eliminated in our last two models of thermogravimetric assemblies [9, 19] by using an inert gas for sulphur transportation in the apparatus i.e., by changing the static into dynamic conditions. However, the accuracy of the helix balance remained the same and consequently, very low reaction rates and small deviations from stoichiometry of the sulphides cannot be measured. All these disadvantages have been eliminated in our new version of microthermogravimetric apparatus described in the present paper.

Microthermobalance

The scheme of the presented assembly is shown in Fig. 1. One of the main features of this apparatus consists in the possibility of determining the mass changes of a given sample, occurring as a result of solid-sulphur interaction, with the accuracy of about two orders of magnitude higher than in all other thermogravimetric equipments, i.e., of the order of 10^{-7} g. This has been achieved owing to the replacement of the helix balance by an automatic electronic microbalance (C.I. Electronics) which is protected against sulphur attack by the stream of inert gas (helium) flowing through the balance chamber and making impossible of sulphur condensation on cool upper parts of the apparatus (Fig. 1). The second gas stream passes through one of two reservoirs with

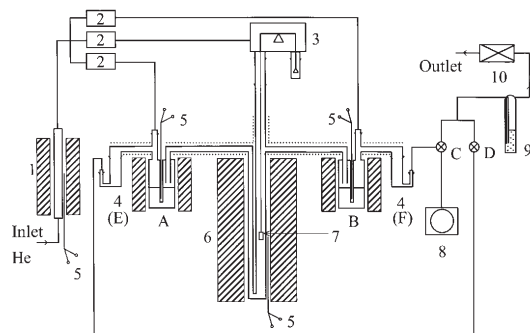


Fig. 1 The scheme of the presented apparatus; 1 – gas purifier, 2 – flowmeter, 3 – microbalance, 4 – sulphur trap, 5 – thermoelement, 6 – reaction furnace, 7 – sample, 8 – rotation pump, 9 – bulb, 10 – solid electrolyte probe; A, B – sulphur baths, C, D – valves

the liquid sulphur (A or B) carrying its vapours to the reaction chamber, where both helium fluxes join together and after having passed the apparatus leave it through one of two liquid nitrogen sulphur traps (4).

The desired partial pressure of sulphur vapour in the reaction chamber is obtained by suitable mixing of sulphur vapour with a carrier gas, the flow rate of which together with the temperature of liquid sulphur bath (A or B) determines the activity of sulphur in the He-S₂ gas mixture of the total pressure of 10⁵ Pa. This procedure ensures very stable sulphur pressure in the reaction chamber and creates vast possibilities of obtaining any desired sulphur pressure, ranging between 5·10⁴ and 10⁻² Pa.

The following, important advantage of the discussed equipment consists in the possibility of performing long-term sulphidation experiments without breaking the reaction for refilling the sulphur reservoir. If, namely, one sulphur reservoir is utilized as a sulphur vapour source, the second one acts as a sulphur trap and only very small amounts of sulphur leave the apparatus with the carrier gas. When the main part of liquid sulphur in the first bath has been evaporated, the second reservoir is heated to an appropriate temperature and in the same time the first one is cooled down and the direction of the carrier gas stream is changed. As a consequence, the second bath acts now as a liquid sulphur reservoir and the first one as the sulphur trap. This operation may be repeated several times, as a result of which the sulphur is circulating in the apparatus and only small amount of it is lost, mainly during changing the direction of He-S₂ gas stream.

Another, very important advantage of this apparatus, equipped with two sulphur reservoirs, consists in the possibility of making rapid changes of sulphur partial pressure in the reaction chamber, which is necessary in studying the reequilibration kinetics of non-stoichiometric metal sulphides.

From this short discussion it follows clearly that the apparatus described in the present paper offers novel possibilities to study the kinetics of solid-sulphur interaction at high temperatures. Some of these possibilities have been illustrated in the next section, on the example of Mn-Mn_{1-y}S-S₂ system.

Experimental

Manganese sulphidation kinetics has been extensively studied by many authors with various thermogravimetric techniques [19, 26–28]. This great interest results from the fact that manganese, besides molybdenum and niobium, is highly resistant to sulphur attack at high temperatures [3, 4, 29] and consequently, it is considered as a potential, important alloying component in designing new materials resistant to sulphide corrosion. Also, manganous sulphide itself was the subject of numerous, many-sided studies, aiming at the explanation of its defect and transport properties [30–38]. Thus, Mn-Mn_{1-y}S-S₂ system is very convenient for illustration of the quality of the described equipment.

Sulphidation kinetics

The experimental procedure in studying the kinetics of manganese sulphidation was as follows. A spectrally pure manganese plate (7) with total impurity content not exceeding 5 ppm and a surface area of about 2 cm^2 was suspended on the balance in the reaction chamber and the furnace (6) was moved down below the reaction tube. The whole apparatus was then evacuated and flushed for several h with spectrally pure helium by passing it through all three flowmeters (2) with both valves C and D open. The carrier gas, before entering the apparatus, passed through the gas purifier (1) with iron wool heated to 900 K, as a result of which the partial pressure of oxygen has been reduced from 10^{-1} down to 10^{-12} Pa. This pressure was continuously monitored in the outlet gas during the whole period of every experiment with the use of solid electrolyte probe (10). Subsequently, the valve C has been closed and the sulphur bath A was heated to the desired temperature. Simultaneously, the reaction furnace (6) was heated to the temperature at which the Mn-sample was to be sulphidized. When the desired partial pressure of sulphur vapour in He-S₂ gas mixture was reached, the furnace (6) was raised to the reaction position (Fig. 1) and the He-S₂ gas was let into the reaction chamber by appropriate changing the positions of valves C and D (C – open

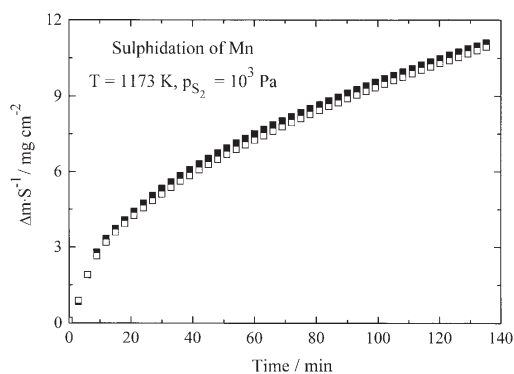


Fig. 2 The kinetics of manganese sulphidation at 1173 K and sulphur vapour pressure of 10^3 Pa, linear plot

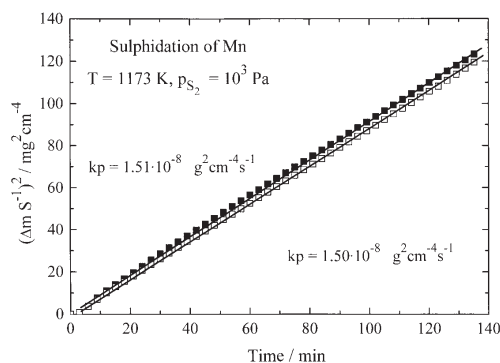


Fig. 3 The kinetics of manganese sulphidation at 1173 K and sulphur vapour pressure of 10^3 Pa, parabolic plot

and D – closed). As a result of this operation He–S₂ gas, leaving previously the apparatus through trap E, started to flow in the opposite direction, i.e., through the reaction chamber, and left the apparatus through the trap F.

It has been found, that the steady state conditions in the reaction chamber have been established during about 60 s. This rather surprisingly short time in which the sulphur pressure reached a constant value in the reaction chamber results from the laminar (without any turbulence) flow of the He–S₂ gas from the sulphur reservoir to the reaction tube. Consequently, early stages of sulphidation reaction could, for the first time, be investigated.

The rate of sulphidation was continuously followed by an automatic microbalance (3) with the accuracy of 10⁻⁷ g. Maximum fluctuations of temperature in the reaction chamber and in liquid sulphur reservoirs did not exceed ±1 K. The sulphidation rate measurements have been carried out as a function of temperature (973–1273 K) and sulphur pressure (10⁻¹–10⁴ Pa) and some of the results obtained at 1273 K and $p(\text{S}_2)=10^3$ Pa are shown, in Figs 2 and 3 in linear and parabolic plots, respectively. As can be seen, the reproducibility of the results was excellent and the sulphidation process followed strictly the parabolic rate law, in agreement with the literature data [26, 28]. Analogous results have been obtained at other temperatures and sulphur activities.

Figure 4 shows the pressure dependence of the parabolic rate constant of manga-

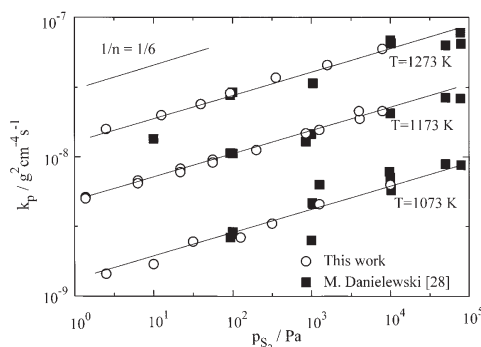


Fig. 4 The pressure dependence of the parabolic rate constant of manganese sulphidation for several temperatures

nese sulphidation for several temperatures, on the background of the most careful and accurate results obtained by Danielewski [28]. It is clearly seen, that the agreement between both series of experiments is satisfactory, but the scattering of our results, owing to much higher accuracy of mass gain measurements, as well as their automatic recording and strictly controlled thermodynamic conditions, was considerably smaller. These results may be summarized in the form of the following empirical equation:

$$k_p = 1.52 \cdot 10^{-2} p_{S_2}^{1/6} \exp\left(-\frac{127 \text{ kJ mol}^{-1}}{RT}\right) \quad (1)$$

Danielewski's data, in turn, has been presented in the following form [28]:

$$k_p = 7.23 \cdot 10^{-3} p_{S_2}^{1/6} \exp\left(-\frac{120 \text{ kJ mol}^{-1}}{RT}\right) \quad (2)$$

Reequilibration kinetics

Transport properties of transition metal oxides and sulphides are characterized by two important quantities: self-diffusion coefficient of cations, D_{Mc} , or anions, D_x (X – oxidant) depending on whether cation or anion sublattice is predominantly defected, and defect-diffusion coefficient (D_d) being the direct measure of defect mobility [6, 39]. Self-diffusion coefficient can be experimentally determined with the use of tracer method, and also may be calculated from parabolic rate constant of scale formation, using Wagner's theory of metal oxidation [2, 40]. Defect-diffusion coefficient, on the other hand, cannot be determined experimentally because it characterizes the random walk of defects in thermodynamic equilibrium [5, 6, 39, 41]. However, this most important transport property of non-stoichiometric metal oxides and sulphides can readily be calculated, if self-diffusion coefficient and defect concentration are known, because all these three transport parameters are interrelated by the following equation [5, 42]:

$$D_d C_d = D_i C_i \quad (3)$$

where C_i denotes the mole fraction of ions in the sublattice predominantly defected, D_i – self-diffusion coefficient of ions in this sublattice, and C_d – concentration of defects expressed in site fraction, which is directly related to non-stoichiometry. Thus, in the case of non-stoichiometric manganous sulphide, $Mn_{1-y}S$, in which cation vacancies are the predominant point defects, Eq. (3) assumes the following form:

$$D_v [V_{Mn}''] = D_{Mn} C_{Mn} \quad (4)$$

where V_{Mn}'' denotes doubly ionized cation vacancy and D_v – vacancy diffusion coefficient. As the defect concentration and thereby deviation from stoichiometry of $Mn_{1-y}S$ is very low ($y < 10^{-3}$) $[V_{Mn}''] = y$ and $C_{Mn} \cong 1$. Consequently, Eq. (4) may be approximated to the following form:

$$D_v y = D_{Mn} \quad (5)$$

Using this relationship and D_{Mn} values calculated from sulphidation rate measurements, as well as considering non-stoichiometry data reported by Rau [31], Danielewski and Mrowec [30] obtained the following empirical equation for the temperature dependence of vacancy diffusion coefficient in $Mn_{1-y}S$:

$$D_v = 1.41 \cdot 10^{-2} \exp\left(-\frac{79.7 \text{ kJ mol}^{-1}}{RT}\right) \quad (6)$$

It should be noted, however, that this coefficient can be much more directly calculated from chemical diffusion coefficient if only the degree of defect ionization, is known. Chemical diffusion is, namely, the process of defect migration under their concentration gradient [42–45] and consequently chemical diffusion coefficient, \tilde{D} is a direct measure of the rate of defect diffusion in a given solid under non-equilibrium conditions. Thus, the only difference between the rate of the random walk of defects and their migration rate under concentration gradient results from the accelerating effect of much more mobile electronic defects [5, 6, 39]:

$$\tilde{D} = (1 + |p|) D_d \quad (7)$$

where p denotes the degree of defect ionization. In the case under discussion $p = -2$ and consequently Eq. (7) assumes the form:

$$\tilde{D} = 3D_v \quad (8)$$

Chemical diffusion coefficient can be obtained from thermogravimetric measurements of mass changes of a given oxide or sulphide sample as a function of time, when going from one thermodynamic equilibrium state to another. $Mn_{1-y}S$ is a metal deficit p type semiconductor with doubly ionized cation vacancies and electron holes as predominant defects [31, 34, 35]. Thus, if such a compound is equilibrated at a given temperature and sulphur pressure, the concentration of defects and thereby the non-stoichiometry, y , reaches a constant value and the mass of the sample remains constant. When the sulphur pressure is suddenly changed to a lower value, the sample gradually begins to lose mass as a result of the evolution of gaseous sulphur to the environment, and liberated electrons and cations fill electron holes and cation vacancies, respectively. Consequently, the concentration of point defects and thereby the non-stoichiometry of the sulphide decreases, until a new equilibrium state is reached. Such a process is called reduction. When, on the other hand, the sulphur vapour pressure is suddenly raised to a higher value, the sulphur atoms are bonded on the sample surface with electrons and cations diffusing there from the lattice, leaving behind electron holes and cation vacancies, respectively. Thus, the mass of the sample, and thereby the concentration of point defects in the sulphide, increases. In that case the oxidation process takes place and the non-stoichiometry of the sulphide increases.

At high temperatures chemical reactions at the solid/gas interface proceed usually much faster than the solid state diffusion. Thus, the overall reduction and oxidation rates should be diffusion-controlled, and from the kinetics of mass changes of a given sample the chemical diffusion coefficient can be evaluated. The most important problem in such experiments is to verify the fundamental assumption concerning the rate-determining step of the overall reequilibration process. This can be done by making the oxidation and reduction runs under the same experimental conditions. If no hysteresis is observed and the same value of chemical diffusion coefficient is obtained from both reequilibration runs, it may be considered as experimental proof that the slowest step is the diffusion of defects. However, in the case of Mn(II) sulphide this problem remained open because deviations from stoichiometry of $Mn_{1-y}S$ were too low to be determined by TG.

It will be demonstrated below that the apparatus described in the present paper creates suitable experimental basis to solve such problems in the case of transition metal sulphides with small deviations from stoichiometry.

Reequilibration measurements have been carried out at temperatures ranging from 700 up to 1273 K and sulphur pressure interval 10^4 – 10^{-1} Pa. The experimental procedure was as follows. Both sulphur reservoirs have been heated to obtain different pressures of sulphur vapour in He–S₂ gas mixtures. When the required sulphur pressures have been reached, one of these mixtures was let into the reaction chamber to obtain manganese sulphide of a given composition, from Mn-sample suspended on the balance. After thermodynamic equilibrium had been reached, manifesting itself by the constant mass of Mn_{1-y}S sample, the sulphur pressure was suddenly changed to a lower value by appropriate switching of valves C and D, and the reequilibration kinetics was continuously followed by determining the mass losses of the specimen as a function of time, until a new equilibrium was obtained.

After this reduction run, the sulphur pressure was suddenly raised to a higher value and the kinetics of the oxidation process was followed by continuous recording of mass gains of the sample until a new equilibrium was again reached in Mn_{1-y}S–S₂ system. In order to verify the main assumption concerning the rate determining step of the overall reequilibration process as well as to prove the reproducibility of these measurements, oxidation and reduction runs have been repeated several times at a given temperature in the same sulphur pressure interval. For illustration, the results of these experiments are shown in Fig. 5. As can be seen, both the oxidation and reduction runs are fully reproducible with the maximum error not exceeding $\pm 5\%$. In addition, no hysteresis was observed between oxidation and reduction curves, clearly indicating that the reequilibration kinetics of Mn_{1-y}S was diffusion controlled. Analogous results have been obtained in other temperatures and pressure intervals.

It is interesting to note that the total mass change of Mn_{1-y}S sample during the whole oxidation and reduction runs did not exceed 45 μg , i.e., the mass change is impossible to be at least estimated in equipment with spiral balance currently used in sulphidation studies.

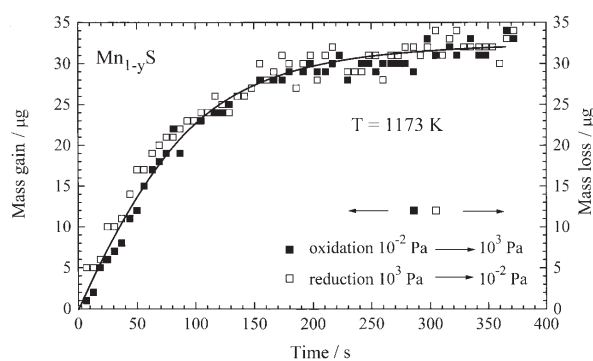


Fig. 5 The reequilibration kinetics of manganese sulphide

In order to calculate the chemical diffusion coefficient from reequilibration rate measurements, an appropriate solution of Fick's second law must be applied. For flat rectangular samples, used in these experiments, such a solution leads to the following exponential equation [43, 46]:

$$1 - \frac{\Delta m_t}{\Delta m_k} = \frac{8}{\pi^2} \exp\left(-\frac{\tilde{D}\pi^2 t}{4l^2}\right) \quad (9)$$

where Δm_t is the mass change of the sulphide sample after any time t and Δm_k is the total mass change when the new equilibrium of the specimen is established; l denotes one half of the specimen thickness, and \tilde{D} is the chemical diffusion coefficient.

It should be noted that Eq. (9) is equally valid for oxidation and reduction runs, since the boundary conditions in the solution of Fick's second law are identical for both cases. As a consequence, the same values of \tilde{D} should be obtained in both types of experiments carried out under the same reaction conditions. As already mentioned, this procedure offers an important opportunity to verify the applicability of the discussed reequilibration kinetic method.

It is convenient to express the exponential Eq. (9) in logarithmic form, so that chemical diffusion coefficient can be calculated from the slope of the straight line obtained by plotting the results of relaxation curves in semilogarithmic system of coordinates:

$$\log\left(1 - \frac{\Delta m_t}{\Delta m_k}\right) = \log\frac{8}{\pi^2} - \frac{\tilde{D}\pi^2 t}{2.303 \cdot 4l^2} \quad (10)$$

Figure 6 shows, for illustration, some experimental results obtained at 1173 K plotted in this way. In agreement with theoretical predictions, a straight line has been obtained during both the oxidation and reduction runs, clearly indicating that the overall reequilibration rates were diffusion controlled. From the slope of such straight lines the chemical diffusion coefficients have been calculated as a function of temper-

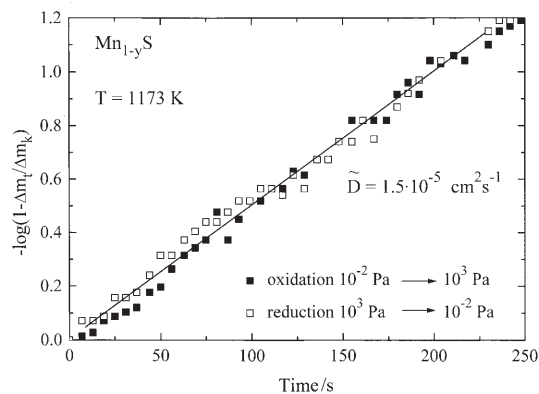


Fig. 6 The results of reequilibration measurements of Mn_{1-y}S presented in semi-logarithmic system of coordinates in agreement with Eq. (10)

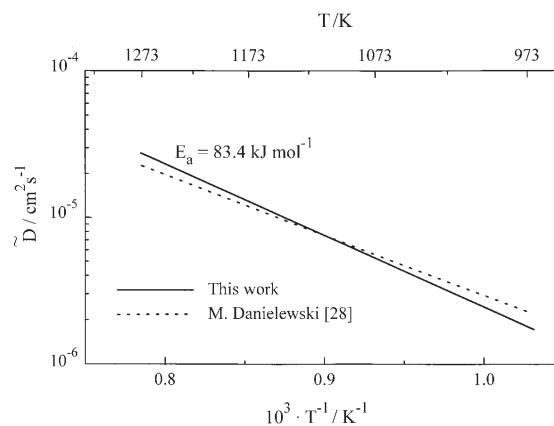


Fig. 7 The temperature dependence of chemical diffusion coefficient in Mn_{1-y}S

ature, and the results of these calculations are shown in the form of the following empirical equation:

$$\tilde{D} = 5.9 \cdot 10^{-2} \exp\left(-\frac{83.4 \text{ kJ mol}^{-1}}{RT}\right) \quad (11)$$

Introducing this empirical relationship into theoretical Eq. (8) one obtains the following semiempirical equation for the temperature dependence of defect (vacancy) diffusion coefficient in metal-deficit manganous sulphide:

$$D_v = 1.97 \cdot 10^{-2} \exp\left(-\frac{83.4 \text{ kJ mol}^{-1}}{RT}\right) \quad (12)$$

From the comparison of this relationship with that obtained by Danielewski and Mrowec [30] (Eq. (6)) it follows that the agreement between directly determined (Eq. (12)) and calculated (Eq. (6)) defect mobilities in Mn_{1-y}S is quite satisfactory. This agreement is better visible in Arrhenius plot presented in Fig. 7. Two important conclusions result from this comparison. First, it has been experimentally proved that the mobility of point defects in non-stoichiometric metal sulphides may successfully be estimated from parabolic rate constant of metal sulphidation, if the concentration of point defects in the sulphide is known. However, even a more important conclusion is, that these mobilities can directly be determined in sulphides with very small deviations from stoichiometry if the thermogravimetric apparatus meets all the requirements described in this paper.

Conclusions

The results described in the present paper allow the following conclusions to be drawn.

Microthermogravimetric apparatus developed in this laboratory offers novel possibilities to study the kinetics of very slow metal-sulphur reactions and to determine very small deviations from stoichiometry in transition metal sulphides. This became possible by introducing several important changes into the thermogravimetric equipments of previous generation currently used in sulphidation studies.

Firstly, the reaction conditions have been changed from static to dynamic ones, by introducing the inert gas for sulphur vapour transportation. This innovation, together with the application of two liquid sulphur reservoirs, created very stable, strictly defined reaction conditions, and enabled to make rapid changes of sulphur pressure in the reaction chamber.

The second important advantage, resulting from carrier gas application, consisted in the possibility of protecting the balance chamber from sulphur attack, and consequently, of maintaining the upper part of the apparatus at room temperature. The quartz spiral balance could then be replaced by an automatic electronic microthermobalance, as a result of which the accuracy of the mass change measurements increased more than two orders of magnitude, up to 10^{-7} g. It has been demonstrated that such a sensibility of the thermobalance, together with the possibility of sudden changes of sulphur pressure in the reaction chamber makes it possible to follow not only very slow sulphidation processes but also reequilibration kinetics of transition metal sulphides with very small deviations from stoichiometry.

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