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A NEW THERMOBALANCE FOR STUDIES OF THE HIGH-TEMPERATURE SULPHIDATION OF METALS AND ALLOYS

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A new thermogravimetric apparatus for studying the kinetics of metal sulphidation in a H_2/H_2S gas mixture is described. The main difference between this device and other equipment is the application of hydrogen to obtain a H_2/H_2S mixture at suitable sulphur partial pressures at a total mixture pressure of 1 atm.

The use of the carrier gas allows the measurement of sulphidation kinetics under dynamic conditions and consequently over a much wider pressure range of sulphur vapour, down to 10^{-12} atm.

Keywords: alloys, high-temperature sulphidation, kinetics, new thermobalance

Introduction

The mechanisms of the sulphur corrosion of metals and alloys have been studied intensively for a number of years [1, 2]. These studies provided a rational background for the design of metallic construction materials resistant to the aggressiveness of sulphur at elevated temperatures. Serious difficulties are encountered, however, which are mainly connected with the properties of such an oxidant as sulphur, and also the selection of partial pressures of sulphur which would conform with conditions existing in industrial systems.

Wide-ranging studies of the sulphidation of metals and their alloys under high pressures of sulphur vapour, i.e. under conditions which differ significantly from those existing in industry, have been conducted in many centres. The results of these investigations are often applied to the determination of defect-diffusion coefficients and defect structure, whereas the sulphidation rate constant, has a

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descriptive character, and cannot be extrapolated to the conditions encountered in industrial systems. In an atmosphere containing a low pressure of oxidant, it is important to determine the period of initial sulphidation, mainly connected with the incubation of sulphide nuclei on the metal surfaces; determination under these conditions is a good reference to industrial conditions. Such data may also be used for the determination of defect-diffusion coefficients and defect structures.

An extensive review of thermogravimetric instruments was given by Mrowec [2, 3]. Unfortunately, they all permit measurement of the sulphidation rate only in a narrow and high range of sulphur partial pressures. The application of such equipment leads to serious problems when carrying out experiments to determine sulphidation rate constants of metals and alloys in low-pressure sulphur vapour. The lack of apparatus for kinetic studies under low sulphur vapour pressure hinders practical application studies. Hence, the possibilities of construction of a system facilitating experiments on high-temperature corrosion in an atmosphere of low sulphur pressure are of interest.

The object of this paper is to report the construction of a new spiral microthermobalance for measurement of the kinetics of sulphidation of metals and alloys under dynamic gas flow and at a low sulphur partial pressure.

Description of apparatus

The scheme of the microthermobalance is shown in Fig. 1. The main difference between the apparatus presented in this paper and those already applied lies in the application of a carrier gas (hydrogen) to obtain the H_2/H_2S mixture at suitable sulphur partial pressures at a total mixture pressure of 1 atm. This mixture, in turn, is passed over the catalyst at a definite temperature. As a result, the quantitative reduction of sulphur and the formation of H_2/H_2S takes place. Such a solution provides the dynamic condition of the process (a gas flow through the reaction space) and also the possibility of a selection of low sulphur partial pressures.

Hydrogen from the bottle is passed into the deoxidation system. The yield of the hydrogen flow is determined by the flowmeter. A manostat controls the stability of the flow. The deoxidation system consists of an oxygen 'burner', a cooler and a water vapour absorber, filled with silica gel and/or molecular sieves. The purified hydrogen flows above the surface of liquid sulphur in a container, becoming saturated with its vapour. The liquid sulphur in the container is thermostated with the help of a heater coupled with a thermoelement and a thermoregulator. The temperature is set by using an additional thermometer.

The sulphur-saturated hydrogen flows out through a heated outlet, and then passes to the reaction pipe. About 80 cm of this pipe is filled with a catalyst. The

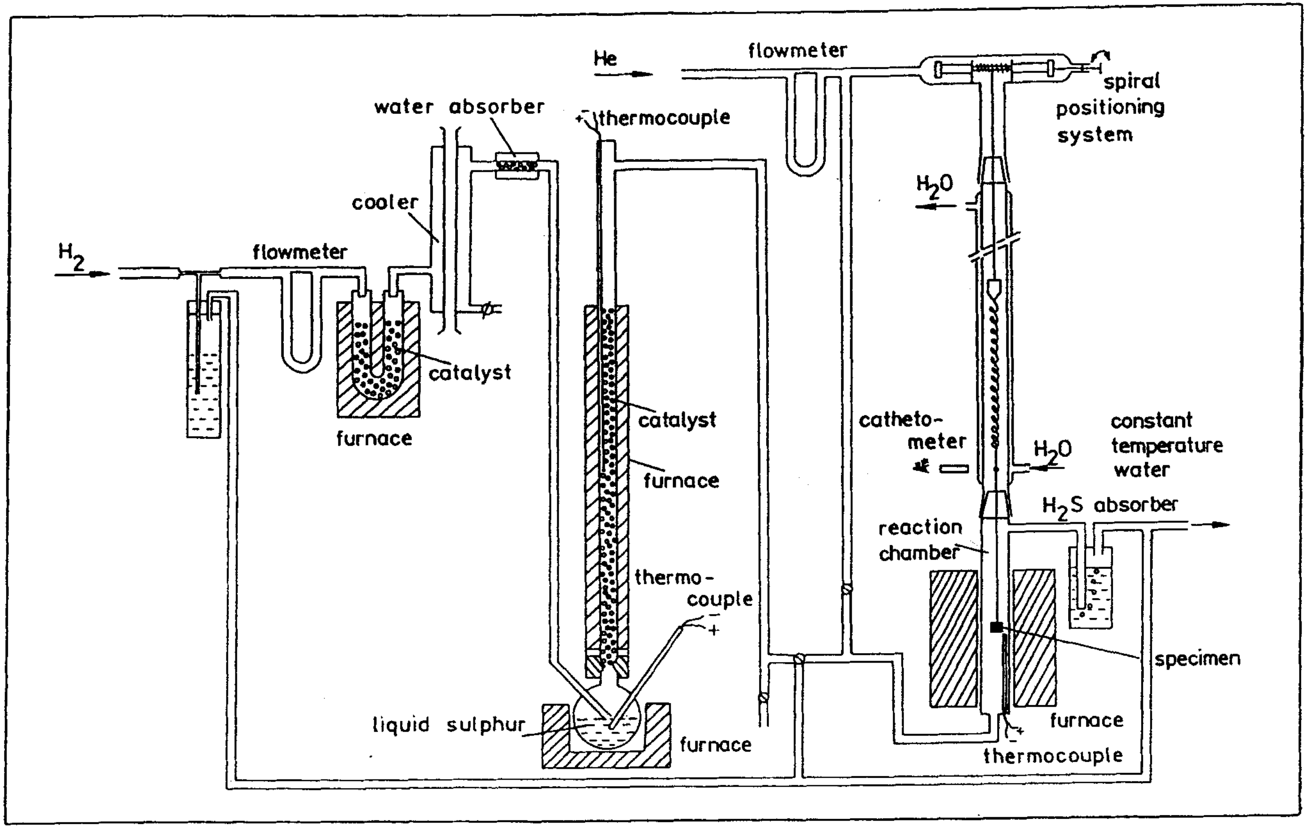

Fig. 1 Scheme of thermogravimetric apparatus for studying kinetics of metal sulphidation and defect equilibria in sulphides

temperature in this section of the pipe is maintained at 873 K by a furnace equipped with a thermoregulator. At this temperature, the following reaction takes place quantitatively:

$$2H_2 + S_2 = 2H_2S$$

The outlet gas, containing a mixture of H_2 and H_2S, is directed to the reaction furnace through a system of valves which facilitates the taking of gas for analysis, and omission of the furnace during flowing with argon.

The quartz pipe, consisting of two parts joined by ground-glass joints, is an appropriate system for measuring the kinetics of sulphidation of metals and alloys. The lower part is situated in the silite furnace, controlled by the thermoregulator. The quartz spiral is fitted in the upper part of the system. The position of the spiral can be adjusted by means of a mechanical device located at the top of the quartz pipe. It is therefore possible to introduce the specimen to the reaction zone after the assumed temperature and sulphur partial pressure are attained and also to stop the experiment by lifting the specimen up at any moment. Argon introduced from the top provides a protective atmosphere around the spiral, hindering sulphur vapour condensation in the cooler parts of the apparatus. A small argon overpressure hinders the entry of oxygen through possible leakages at the contact between the quartz pipe and the spiral suspension device. After passing through the reaction zone, the H_2/H_2S mixture is directed to the utilization system, consisting of a number of washers filled with H_2S-absorbing solutions.

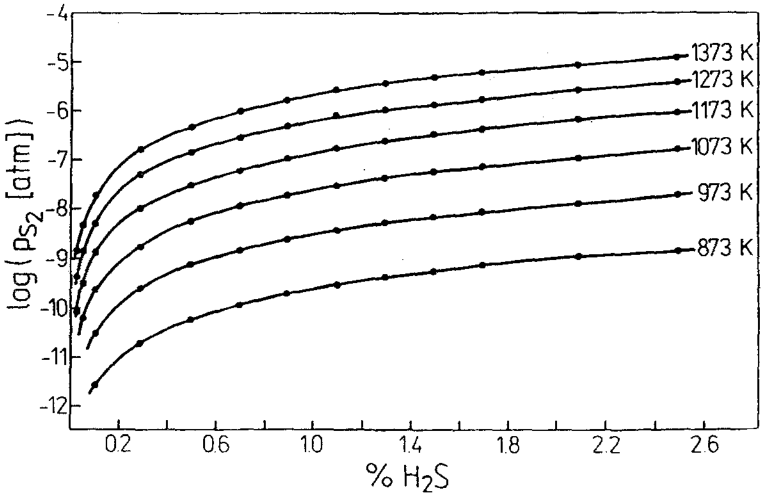

Fig. 2 Dependence of equilibrium sulphur partial pressures *versus* concentration of H_2S in H_2/H_2S gas mixture for several temperatures

Hydrogen sulphide is determined in the reaction mixture iodometrically. A well-defined volume of gas is taken through the valve. After the hydrogen sulphide content in the gas has been determined, the equilibrium sulphur pressure is read off from Fig. 2, plotted on the basis of literature data [4].

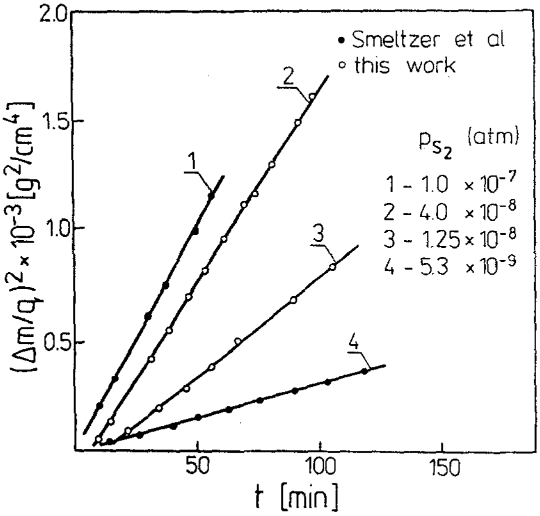

Fig. 3 Kinetics of iron sulphidation at 1073 K, for several vapour pressures

Preliminary measurements

The kinetics of iron sulphidation at 873 and 1073 K and 10^{-7} – 10^{-11} atm was measured in order to check the functionality of the described apparatus and the

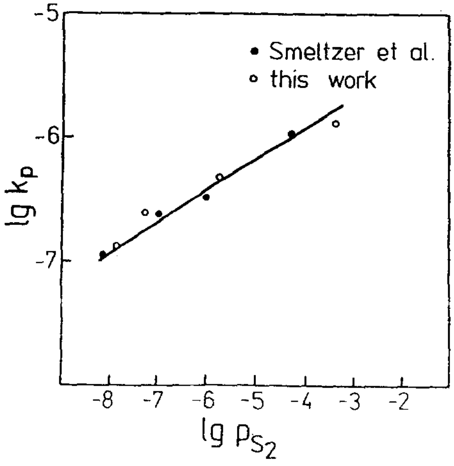

Fig. 4 Dependence of parabolic rate constant of iron sulphidation on sulphur vapour

applied measuring methods. The choice of iron metal follows from the fact that the kinetics of its sulphidation has been thoroughly studied [5].

Figure 3 presents the kinetics of iron sulphidation. It follows from the plot that deviations from the parabolic rate constant of sulphur binding are observed during the initial stage of the reaction. The origin of this is probably the process of iron sulphide nucleation. The dependence of the rate of iron sulphidation on the sulphur vapour pressure at 1073 K is presented in Fig. 4. It follows from the plot that the results obtained in this paper are in good agreement with literature data [5].

On the basis of the results presented here, we conclude that the apparatus can be used for precise measurements of the kinetics of metal and alloy sulphidation and for investigation of the deviations from stoichiometry and chemical diffusion in metal sulphides. The superiority of this design lies in the simplification of the process of H_2/H_2S mixture formation, without the use of complex and inaccurate dosing systems, and the production of a troublesome H_2/H_2S mixture. Further, with the presented apparatus it is possible to change the hydrogen sulphide concentration smoothly, which is of great importance in industry. Additionally, the samples can be removed from the reaction zone at any time and a variety of experiments can be carried out.

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Zusammenfassung —Es wird ein neue Apparat zur Untersuchung der Hochtemperatur-Sulfidierung von Metallen in H_2/H_2S Atmosphare beschrieben. Der Unterschied zwischen diesem Apparat und dem fruher benutzten, besteht im Gasdosierungsystem. Wasserstoff reagiert teilweise mit Schwefel, was eine stabile Zusammensetzung des Gasgemisches beim niedrigen Schwefeldampfdruck sichert. Gewichtsmessungen von Metallen und Legierungen konnen in diesem System bei Temperaturen von 1073 bis 1473 K mit einer Genauigkeit von 10^{-6} g ausgefuhrt werden.