

NON-ISOTHERMAL KINETICS OF HIGH TEMPERATURE OXIDATION STUDIED BY A FAST X-RAY DIFFRACTION METHOD

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Temperature resolved X-ray diffraction using a diffractometer equipped with a high temperature device was applied to the study of the oxidation of Fe-ARMCO below 570°C. The oxidation products are identified in situ and the difference method yields curves $Y(T)$ showing the global changes. These curves were calibrated to the microscopically measured end thickness of the oxide layer obtaining the growth $x(T)$. A calculated curve including the Arrhenius relation was fitted to the $x(T)$ curve yielding activation energy and values of the oxidation rate constant as a function of temperature.

Keywords: corrosion, high temperature oxidation, non-isothermal kinetics, X-ray diffraction method

Introduction

Though the high temperature corrosion of steel has been investigated extensively, the topic remains an important issue [1, 2]. Most methods do not allow in situ investigation. Generally, the samples are oxidized under specified conditions in ovens and studied after cooling. In many cases, however, phase transitions can occur on heating or cooling. Thermogravimetry (TG), one of the mostly used in situ methods, shows only weight changes, but does not identify the present phases.

The kinetics are mostly studied under isothermal conditions in various experiments at different temperatures. The temperature dependence of the oxidation rate constant is usually determined from these series [3].

Temperature and time resolved X-ray diffraction was used as an in situ method, which allows the determination of kinetic data combined with the identification of the corrosion products [4]. Series of diffraction diagrams can be re-

corded with fast detectors during a freely selectable temperature program. A numerical procedure, the difference method, applied to the series of diffraction patterns yields the activation energy and values of the oxidation rate constant as function of the temperature.

Experimental

Measuring system

The measuring system consists of an X-ray diffractometer with a high temperature device. The diffraction patterns are recorded with a position sensitive proportional counter, which allows a fast scanning of the angular range with short measuring times of 100 to 120 s, or with a scintillation counter with measuring times of 100 to 240 s.

The sample temperature can be varied stepwise or continuously between 20 and 1700°C with a freely selectable temperature program. On each temperature step or after defined time intervals diffraction pattern are recorded. Series of 300 diffraction patterns can be measured during one day.

Measurements

Bands of ARMCO-iron were heated in the high temperature device from 25 to 550°C in steps of 20 deg with an average heating rate of 4.7 deg·min⁻¹. The experiment was carried out in air. The relative moisture of the air in the laboratory was 30% at a temperature of 24°C. The diffraction patterns were recorded with a scintillation counter.

Evaluation

The evaluation of the diffraction peaks was carried out by means of a least squares fit procedure using a Gaussian curve yielding peak position, intensities and peak widths.

The kinetic parameters were obtained by the difference method [5], where two diffraction diagrams are subtracted. The sum $Y(T_j)$ of the absolute differences between each channel correlates with the changes in the diffraction diagrams.

$$Y(T_j) = \sum_{i=1}^n |Y_i(T_1) - Y_i(T_j)|$$

where j = number of the current diagram

i = number of the current channel

n = total number of channels

The difference method can be applied to the whole patterns or to selected intervals containing definite peaks, yielding separate $Y(T)$ curves for the base material and the formed oxides.

$$Y(T)_{\text{total}} = Y(T)_{\text{Fe}} + Y(T)_{\text{oxide}} + Y(T)_{\text{background}}$$

The method applied to intervals containing the peaks of the oxides yields an $Y(T)$ curve showing the relative increase of the oxide layer.

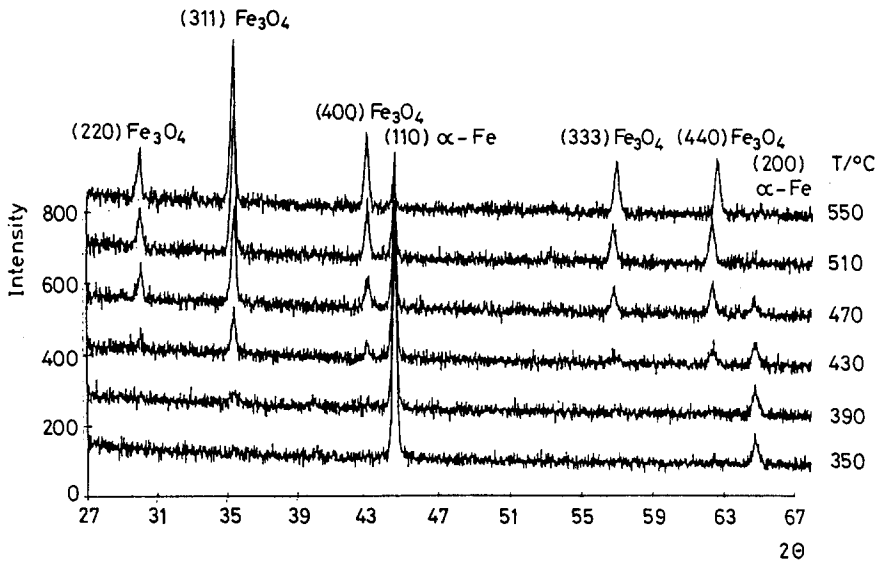


Fig. 1 Series of diffraction patterns on heating. Material: Fe-ARMCO

This $Y(T)$ curve was normalized to 1 and the $Y(t_i)$ values were multiplied by the final thickness of the oxide layer that was measured microscopically. The resulting curve $x(T)$ represents the growth of the oxide layer.

In non-isothermal experiments the growth of the oxide layer depends on two parameters: temperature and time. For obtaining the temperature dependence of the parabolic rate constant, the $x(T)$ curve must be described by a function $f = f(T, t)$ [6].

Starting with the differential equation for parabolic time dependence

$$\frac{dx}{dt} = \frac{k}{x} \quad (1)$$

and introducing the heating rate $\alpha = dT/dt$ we obtain

$$x dx = \frac{k}{\alpha} dT \quad (2)$$

The temperature dependence of reaction rates is described by the Arrhenius equation:

$$k = z e^{-E/RT} \quad (3)$$

where R is the gas constant, E activation energy and z the preexponential factor. In our case z is a normalization factor. Inserting (3) in (2) we obtain after integration the following relation for $x(T)$:

$$x(T) = \sqrt{\frac{2z}{\alpha} \int e^{-E/RT} dT} \quad (4)$$

The Eq. (4) is fitted to the measured curve $x(T)$ by means of a least squares fit procedure obtaining values for the fit parameters z and E . After the determi-

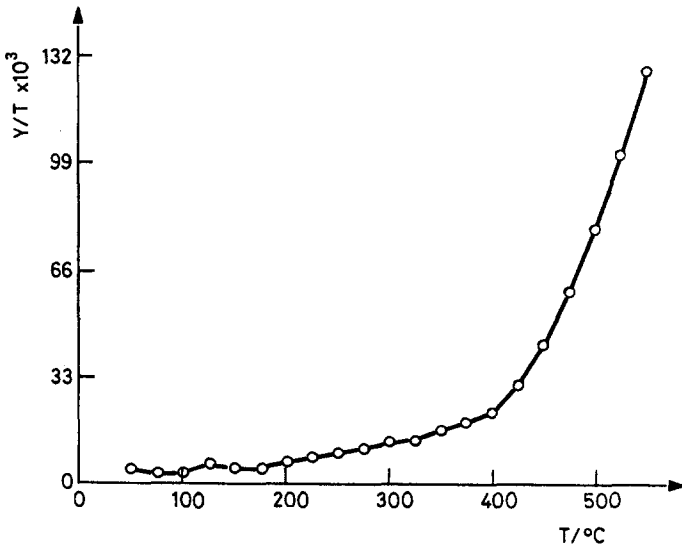


Fig. 2 Difference curve $Y(T)$

nation of these parameters, the temperature dependence of the oxidation rate constant can be described by the Eq. (3).

Results and discussion

At temperatures below 570°C Fe forms Fe₃O₄ and over long times small amounts of Fe₂O₃ [1]. On heating the formation of Fe₃O₄ was observed in situ by X-ray diffraction. The thickness of the layer is at these temperatures in an order of magnitude that can be penetrated by the X-ray beam. Selected X-ray patterns of a series are shown in Fig. 1.

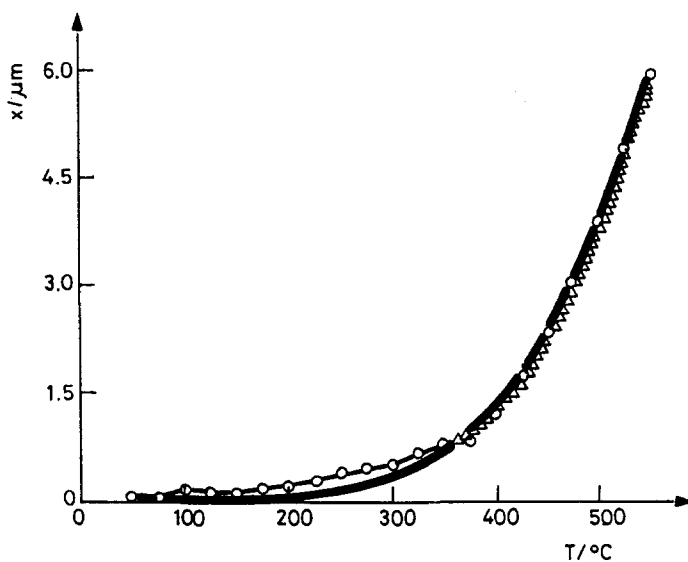


Fig.3 The measured growth of the oxide layer $x(T)$ and the fitted curve

The difference method was applied to the intervals of the diffraction patterns containing peaks of Fe₃O₄. The resulting $Y(T)$ curve (Fig. 2) was calibrated to the microscopically measured end thickness of the oxide layer, $D=6\ \mu\text{m}$, yielding the growth of the layer with temperature $x(T)$. A calculated curve (4) was fitted to the measured $x(T)$ curve yielding an activation energy of $E=80\ \text{kJ}$. Figure 3 shows the measured and the calculated $x(T)$ curve.

Inserting the obtained parameters z and E in Eq. (3) the temperature dependence of the parabolic oxidation rate constant was determined as shown in Fig. 4. These results are in agreement with literature [1].

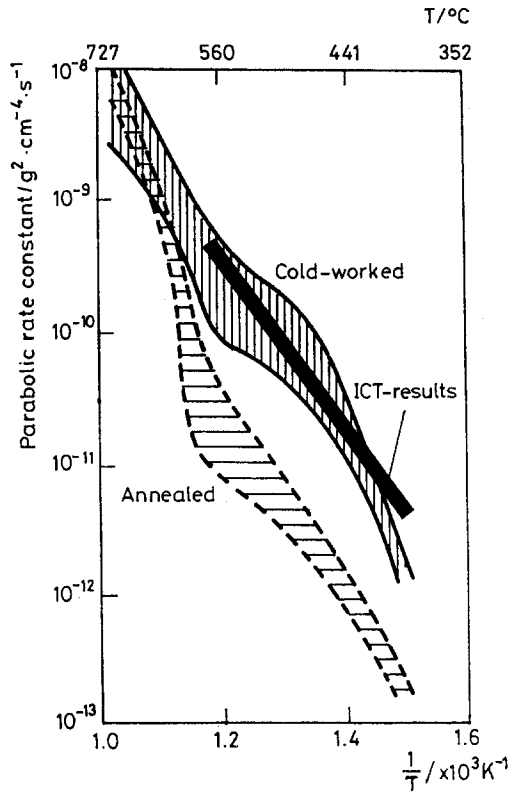


Fig.4 Temperature dependence of the oxidation rate constant in comparison with literature

The results show that X-ray diffraction is a suitable method for the investigation of the high temperature corrosion and its kinetics. The formed oxides can be identified in situ and the temperature dependence of the oxidation rate constant can be determined by means of the difference method in only one non-isothermal experiment.

References

- 1 A. Rahmel und W. Schwenk, *Korrosion und Korrosionsschutz von Stählen*, Verlag Chemie, 1977.
- 2 P. Kofstad, *High Temperature Corrosion*, Elsevier Applied Science LTD, 1988.
- 3 E. Otero, A. J. Criado, P. Hierro, A. Pardo and M. Baladia, Proc. 22nd Int. Annual Conf. of ICT, "Combustion and Reaction Kinetics", 1991, p. 114.
- 4 M. Juez-Lorenzo, V. Kolarik, N. Eisenreich, W. Engel, A. J. Criado and E. Otero, Proc. 9th European Congress on Corrosion, Royal Netherlands Industries Fair, FU-173, 1989.
- 5 N. Eisenreich and W. Engel, *J. Appl. Cryst.*, 16 (1983) 259.
- 6 N. Eisenreich, *J. Thermal Anal.*, 19 (1980) 289.

Zusammenfassung — Unter Anwendung eines Diffraktometers mit einer Hochtemperaturereinheit wurde unterhalb 570°C mittels Röntgendiffraktion die Oxidation von Fe-ARMCO untersucht. Die Oxidationsprodukte wurden in situ bestimmt und das Differenzverfahren ergab $Y(T)$ -Kurven, die die globalen Änderungen zeigen. Diese Kurven wurden anhand der mikroskopisch bestimmten resultierenden Dicken der Oxidschicht kalibriert, wobei man die Funktion $x(T)$ erhält. Dieser Kurve wurde eine berechnete, die Arrheniussche Beziehung enthaltende Funktion angepaßt, wodurch man die Aktivierungsenergie und die Oxidations-Geschwindigkeitskonstante als Funktion der Temperatur erhält.