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HYDROGEN REDUCTION OF MoO_3–Fe MIXES STUDIED BY STEPWISE DIFFERENTIAL ISOTHERMAL ANALYSIS

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The method of a stepwise differential isothermal analysis (SDIA) has been designed for studies of reduction processes in metallurgical systems. The basis of the method is in multi-parameter control of reaction rate and its use for monitoring temperature, heating rate, and gas-phase composition. In this study hydrogen reduction of MoO_3 and its mix with 30% Fe have been carried out using the SDIA technique. During the measurements, TG, DTG, DTA, EGA, and temperature control are carried out. Kinetics parameters were determined and possible reduction mechanism was suggested. The SDIA technique is well suited for these studies.

Keywords: metallurgical systems, reduction, stepwise differential isothermal analysis (SDIA)

Introduction

Reduction of metal oxides is one of the most important parts of extraction metallurgy. Carbon, hydrogen, methane, carbon monoxide are commonly used for this purpose. In particular, kinetics of reduction of metal oxides is very important in the production of complex alloyed powders and powder master alloys [1]. Thermogravimetry is widely used in chemical metallurgy, and in such applications the influence of heating rate, sample bed depth, and atmosphere must be taken into account in assessing the magnitude of the observed mass change. Therefore, kinetic data can be obtained from thermogravimetry only in favourable circumstances. In this context, care must be taken during experiments to ensure that the samples have the same composition and particle-size distribution, and they are at a uniform temperature. This can cause problems in isothermal experimental runs, and for determination of time and temperature onset points. Sometimes these factors make kinetic studies invalid [2, 3].

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In this study, hydrogen reduction processes of MoO_3 and its mix with 30% Fe have been carried out using a stepwise differential isothermal analysis (SDIA) technique [4]. These TG, DTG, DTA, EGA, and temperature measurements are allow the most probable reduction mechanism to be suggested and also permit determination of kinetic parameters. The SDIA technique has proved to be well suited for such metallurgical studies.

Theoretical background

Kinetics and mechanism of reduction are closely connected with the electronic structures of intermediate and metastable phases, but there are few reliable data on the influence of reduction parameters on electronic structure of phases. Ostrik and Gasik [5] have presented a model of reduction mechanism and also a kinetic equation for reduction of MoO_3, by hydrogen flow in a tubular thermogravimetric setup. In this model, the oxide crystal structure was represented as a combination of MoO_6 octahedra, into which hydrogen molecules and atoms are able to penetrate, leading to formation of hydrogen-molybdenum bronze, H_xMoO_3, which has a ReO_3, structure type. The electronic structure of H_xMoO_3 has been calculated using the Harrison method for perovskites. In this, the energy of covalent binding of perovskites, $W_2 = -(V_{sd\sigma} + V_{pd\sigma})/\sqrt{2}$, and energy of ionic binding, $W_3 = (\varepsilon_d - (\varepsilon_s + \varepsilon_p))/2$, are equal to 4.58 and 5.04 eV respectively, which leads to a full effective charge of oxygen in H_xMoO_3

$$Z^* = 2 - 2\left(\frac{W_2}{2W_3}\right)^2 = 1.586 \qquad (1)$$

Because (i) the energy of the 1s-state of hydrogen (–13.6 eV) is close to the energy of the 2p-state of oxygen (–14.13 eV), (ii) the hydrogen atom has a single electron, and (iii) both the energetic states are valency ones, the result is a virtual state with sp-hybridization, which leads to an abrupt change of electronic structure and decomposition of H_xMoO_3 as a metastable compound:

$$H_xMoO_3 \rightarrow \frac{x}{2}H_2O + MoO_{3-x/2}\,. \qquad (2)$$

It has been considered [5] that only activated molecules are able to take part in reaction:

$$MoO_3 + \frac{x}{2}H_2^* \rightleftarrows (H_xMoO_3) \rightleftarrows \frac{x}{2}H_2O + MoO_{3-x/2} \qquad (3)$$

Together with the initial conditions for isothermal experiment and systems of differential equations, a kinetic equation for reduction of MoO_3 by hydrogen flow has been deduced:

$$\frac{\partial x}{\partial \tau}=\frac{L_1x+L_2C^{o}_{MoO_3}}{L_1x+L_3C^{o}_{MoO_3}+L_4}\,; \tag{4}$$

$$k_1\,\alpha-\ln(1-\alpha)=k_2\,t \tag{5}$$

where α – reaction rate (degree of reduction), t – reduced time, $L_{1...4}$, k_1 and k_2 – constants, $C^{o}_{MoO_3}$ – initial MoO_3 concentration. Some simplifications have been made during development of the model, so it is unlikely that thermal analysis would be able to confirm the validity of this mechanism.

Experimental

These studies were carried out in the Dnepropetrovsk Metallurgical Institute, Ukraine. The tubular thermogravimetric setup includes a movable furnace with SiC heating elements, quartz reaction tube, inductive TG/DTA-sensor, PID temperature control, gas supply, and peripheral equipment for data acquisition (Fig. 1). Furnace and sample temperatures are measured by Pt/Pt-10%Rh thermocouples, and both temperature and weight change of the sample are recorded by strip chart recorder and X-Y-recorder. Dry electrolytic-grade hydrogen was used as a reducing agent, and pure argon was used as an inert gas. Flow rate and gas pressure were controlled throughout the experiments. Measuring and recording systems were calibrated twice a week using reference balances. Spectroscopic purity molybdenum trioxide and high-purity electrolytical iron powder were used. The SDIA method [4] used here is close to the stepwise isothermal analysis (SIA) or controlled rate thermal analysis (CRTA), of Sørensen *et al.* [6, 7], but is more stable to noise and specimen vibration. Existing SIA methods are based on controlling the heating (cooling) rate of a specimen in relation to its rate of change in weight. However, it has been shown by Husum and Sørensen [7] that separation of stages of the process depends on heating rate.

The kinetics of reduction of MoO_3 and mix MoO_3 + 30 wt% Fe in hydrogen flow (200 cm^3min^{-1}) has been studied in the range 973–1273 K. A relatively high sample mass (<1.5 g) has been used in an attempt of reproducing conditions which approach those in the technology of ferromolybdenum (60 wt% Mo) powder master alloy production.

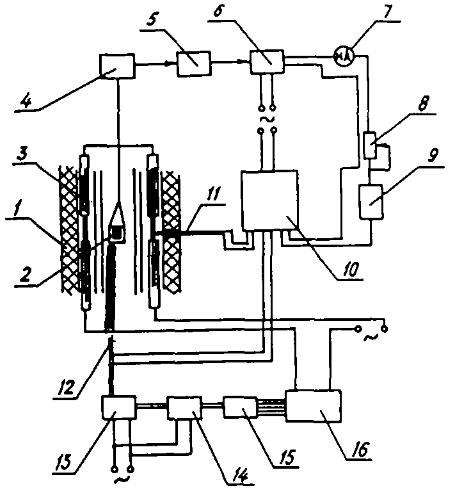

Fig. 1 Thermoanalytical setup general layout: 1 - movable furnace, 2 - specimen and crucible, 3 - heating SiC elements, 4 - TG/DTA sensor, 5 - carrying frequency measuring amplifier, 6 - AC/DC power source and hardware, 7 - µA-controller, 8 - manual adjustable resistor, 9 - e.m.f. compensation, 10 - interface/recorder, 11, 12 - thermocouples, 13 - microprocessor temperature setup/control, 14 - PID-regulator, 15 - thyristor drive unit, 16 - power supply

Result and discussion

Isothermal TG curves for MoO_3 and mix MoO_3 + 30% Fe show that iron addition does not influence weight loss at 973 K, but almost doubles reaction rate at 1073 and 1273 K. At 1173 K, the value of the isothermal kinetic curve constant k_1 (5) is 0.9969, with a relatively high correlation ($r = 0.9966$). It should be noted, however, that these experiments are not exactly isothermal. The heating rate for reduction of MoO_3 and MoO_3 + 30% Fe by hydrogen in SDIA measurements has been chosen as 11 deg·min^{-1} as in the technological production of FeMo powder master alloy [1]. The SDIA results for molybdenum trioxide and its mix with iron are shown in Fig. 2. Two stages (also confirmed by DTA) are apparent on the TG curves: $MoO_3 \rightarrow MoO_2$ (947±5 K) and $MoO_2 \rightarrow Mo$ (1078±5 K). For EGA, a thermal conductivity detector was used, and water released was transformed to acetylene by CaC_2. Two well-defined water vapour peaks are present. For pure molybdenum trioxide there is a 'leap' on the TG curve at a degree of reduction of $\alpha = 0.65$ which corresponds formally to the suboxide $MoO_{1.05}$. The presence of MoO_{1+x} suboxide has been noted previously by Solonin [8].

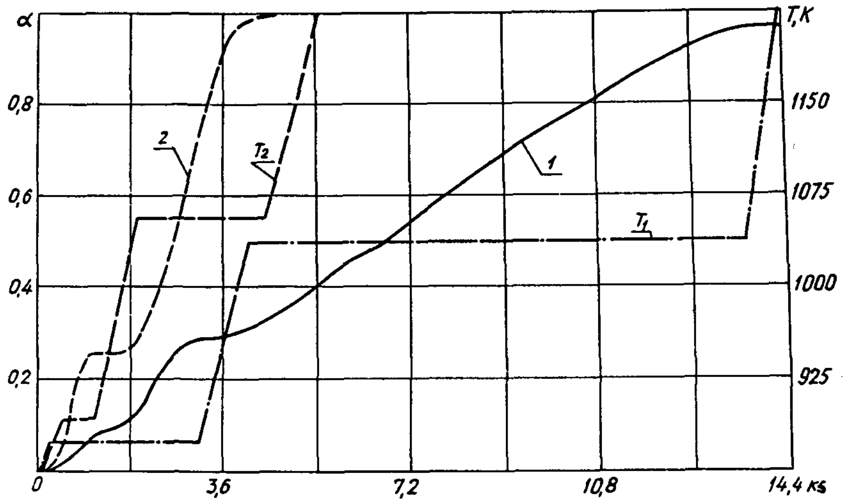

Fig. 2 Hydrogen reduction of MoO_3 (1) and MoO_3+30% Fe (2) in SDIA technique

For the mix of molybdenum trioxide with 30% Fe, SDIA gives slightly higher temperatures for both stages, 957±5 K and 1133±5 K, respectively; the reduction rate for the second stage is higher, and the reduction time is shorter. DTG curves of these runs are shown in Fig. 3 against degree of reduction α. For the case of MoO_3 + 30% Fe mix the data suggest a reaction:

$$MoO_3 + Fe \rightleftarrows MoO_2 + FeO\ ,$$

$$\Delta G^{\circ} = 97280 - 19.04T\ ,\ \mathrm{J{\cdot}mol^{-1}}\ , \qquad (6)$$

which would mean that the iron is reducing MoO_3. The difference in areas of the DTG curves is proportional to the amount of oxygen combining with iron in the first stage of reduction. Simultaneous thermal analysis (STA) was also used for calculation of activation energy of the reduction processes. In this case a simple approximation to the exponential integral was used [2, 3]:

$$\ln p(x) = -\frac{e^x}{x} + \int_{-\infty}^{x} \frac{e^u}{u}\,\mathrm{d}u \approx -a - bx\ ;\quad x = -\frac{E_k}{RT}\ ,$$

where activation energy

$$E_k \approx R\frac{T_1T_2}{T_2-T_1}\ln\left(\frac{\int_{\tau_0}^{\tau}\alpha_{T_2}(t)\,\mathrm{d}t}{\int_{\tau_0}^{\tau}\alpha_{T_1}(t)\,\mathrm{d}t}\right). \qquad (7)$$

Here, apparent activation energy of reduction (E_k) calculated after (7), equals 64.1 $\mathrm{kJ{\cdot}mol^{-1}}$ for MoO_3 and 42.9 $\mathrm{kJ{\cdot}mol^{-1}}$ for mix MoO_3 + 30% Fe. Such a decrease in activation energy could be explained by tunnelling of 3d-electrons of iron into the electronic structure of MoO_3 [1, 5].

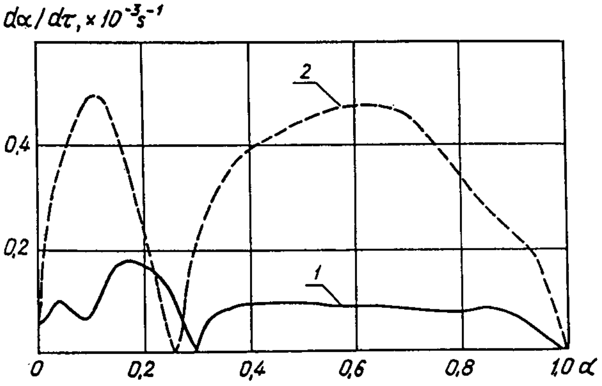

Fig. 3 Reduction rate *vs*. fractional reaction α for the TG-curves of Fig. 3

Model studies have been also carried out using a non-linear heating rate followed by a sample quenching technique. The quenched samples were X-rayed immediately in CuK_α radiation. These results enable the reduction scheme of MoO_3 and MoO_3 + 30% Fe by hydrogen to be expressed as follows:

$$MoO_3 \rightarrow Mo_{12}O_{35} \rightarrow Mo_{10}O_{29} \rightarrow MoO_{2.8} \rightarrow Mo_4O_{11} \rightarrow MoO_2 \rightarrow Mo$$

$$MoO_3 + Fe \rightarrow \begin{matrix} Mo_{12}O_{35}, \\ FeMoO_4 \end{matrix} \rightarrow \begin{matrix} MoO_2\,, Mo_2O_3, \\ Fe_2Mo_3O_8 \end{matrix} \rightarrow Mo, Fe$$

For non-isothermal runs no formation of MoO_{1+x} was detected by X-ray analysis. It is interesting that the X-ray pattern of iron disappeared when the degree of reduction reached 0.23, but after that it reappeared, confirming that iron plays an important role during this reduction process. Analysis of the final reduction product showed intermetallic phases together with free molybdenum, but no free iron. These results are difficult to explain with only conventional diffusion interaction between Mo and Fe being possible after molybdenum trioxide reduction.

Conclusions

Hydrogen reduction of molybdenum trioxide and its mix with iron has been studied using conventional and stepwise differential thermal analysis. During the measurements, TG, DTG, DTA, EGA, and temperature control have been carried out which allows the possibility of determining kinetic parameters and suggesting a reduction mechanism.

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Zusammenfassung — Zur Untersuchung der Reduktionsprozesse in metallurgischen Systemen wurde eine Methode der stufenweisen Differential-Isothermoanalyse (SDIA) entwickelt. Die Grundlage der Methode besteht in einer Vielfach-Parameterkontrolle der Reaktionsgeschwindigkeit und ihrer Anwendung zur Verfolgung der Temperatur, der Aufheizgeschwindigkeit und der Zusammensetzung der Gasphase. Unter Anwendung von SDIA wurde vorliegend die Wasserstoffreduktion von MoO_3 und von MoO_3 mit 30 % Fe untersucht. Während der Messungen werden TG, DTG, DTA, EGA und Temperaturkontrolle durchgeführt. Die kinetischen Parameter wurden bestimmt und mögliche Reduktionsmechanismen vorgeschlagen. Die SDIA-Methode eignet sich gut für derartige Untersuchungen.