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KINETIC FEATURES OF NICKEL OXIDE REDUCTION BY METHANE AND HYDROGEN AT NONISOTHERMAL CONDITIONS

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In the work the results on the kinetics of NiO reduction by methane and hydrogen at nonisothermal conditions, based on *in situ* measurements of the reaction rate, as well as on periodic measurements of sample weight loss, and XRD and SEM examinations during reduction are presented. Based on the data obtained within a wide range of the heating rates (1+1000 *K/s*) and methane/hydrogen pressure (5÷300 *torr*), heating rate (V_h) - gaseous reducer's pressure (P_{gas}) diagrams of the reduction thermal regimes were constructed. According to these diagrams at low heating rates and high methane pressure the reaction occurs mainly during heating stage (nonisothermal conditions). On the other hand, at high heating rates and low methane pressure, the process fully takes place under isothermal conditions (after the maximum temperature of the sample, T_{max} , is established). In the case of hydrogen reduction, regardless of the hydrogen pressure, at low heating rates the reaction proceeds completely in the heating stage, and at high heating rates, on the contrary, the process takes place completely under isothermal conditions (at T_{max}).

Figs. 9, references 18.

1. Introduction

Kinetics of chemical reactions is often studied under the isothermal conditions, i.e. at constant temperatures in space and time. This is primarily due to the fact that the theory of kinetics of the isothermal processes is well developed for both the simple and complex reactions [1-3]. Besides, isothermal experiment seems to be simpler from the view point of data processing too. However, over the last decades, the interest in the nonisothermal methods of studying the kinetics of chemical reactions has increased [4,5]. Their necessity comes from the acquisition of kinetic data at high temperatures which are needed to solve a number of applied and scientific problems. It should be noted that obtaining of such data by

conventional isothermal methods is associated with principal difficulties. First of all, it is a certain conversion of the reaction mixture up to the reference temperature and its possible role in the follow-up process. Since the reaction time decreases with increasing temperature and can become commensurable with the duration of heating stage, the considerable amount of reaction mixture is converted at the heating stage and very often under uncertain temperature conditions, which can lead to significant errors during data processing. Obviously, the process under such conditions can not be considered as isothermal.

On the other hand, if the reaction under study is sufficiently exothermic, during the fast heating the overheating of the reactive mixture at the initial stage is inevitable. Unlike isothermal, non-isothermal experiments are more convenient and easier to carry out, since there is no need for an initial jumplike rise in temperature and, as a rule, they are more informative.

Currently the most popular method for studyng non-isothermal processes is the thermal analysis, and the most common approach is the linear heating, when the sample is placed in the furnace, the temperature of which varies linearly.

However, it should be noted that the heating rate of the sample in most setups of thermal analysis (thermography, thermogravimetry, differential scanning calorimetry, etc.) is limited to a maximum of $100\div150^{\circ}$ C/min. Meanwhile, for a number of technological processes of practical and scientific importance, the behavior of the chemical reaction is extremely interesting at high heating rates [6].

Thus, for most combustion processes, namely for self-propagating high temperature synthesis (SHS) the rate of substance heating in the combustion wave reaches to $10^2 \div 5.10^{50}$ C/s [7]: Particularly, just for the reduction of NiO under combustion mode by hydrocarbonic reducers, the heating rates in the combustion wave is about 100-500°C/s [8].

To fill this gap, two new setups: high-speed scanning electrothermography (HS SET) [9-14] and high-speed temperature scanner (HSTS) [15-17] have been developed and constructed in the laboratory of Macrokinetics of solid phase reactions of the Institute of Chemical Physics of NAS RA. They enabled to obtain new data on high-temperature kinetics for a number of solid phase reactions, including fast-heating conditions.

In [13,14] the reduction of NiO taken in the form of thin wire $100 \square n$ in diameter was performed by hydrogen [13] and methane [14] at strongly isothermal conditions utilizing electrothermographic setup. It was found that at T>800°C the rate of hydrogen reduction is practically independent of gas pressure, and the loss in the wire weight can be described by the parabolic law. In contrast to hydrogen reduction, the reduction by methane is characterized by existence of a clearly marked induction period, followed by rapid acceleration of the process. As a result, the weight loss curve has a S-

shaped form, which is specific for the topochemical reactions proceeding via stages of nucleation. Besides, the increase of methane pressure significantly reduces the induction period, and shifts the whole reduction process to the shorter time region.

In this work the results on the kinetics of NiO reduction by methane and hydrogen at nonisothermal conditions based on *in situ* measurements of the reaction rate, as well as on periodic measurements of the sample weight loss, XRD and SEM examinations during reduction are presented.

2. Materials and Methods

experiments were carried out by high-speed The scanning electrothermography setup [9-11] over a wide range of linear heating rates using nickel wire of the NP-2 trademark (99.5%) 100 µm in diameter, 8.5 cm long and the wieght of about 10^{-2} g. The electrical resistance of the wire was measured at room temperature, which usually was used to detect mechanical defects in the wire and to check that it is installed correctly. Nickel wires were preliminary oxidized in air at $T = 1300^{\circ}C$ during 150 s, yielding a NiO oxide layer of about 6 μm thick. The mass growth of the wire, Δm , in this case was about 0,2 mg. To obtain a thinner ($\delta \approx 3 \mu m$, $\Delta m \approx 0.1 mg$) or thicker $(\delta \approx 12 \ \mu m, \Delta m \approx 0.38 \cdot 0.4 \ mg)$ oxide layers, in some experiments, oxidation was performed at T=1300°C with duration t=30 and 700 seconds respectively. Fig. 1 shows XRD pattern of the oxidized nickel wire (a), its cross-section (b) and SEM image of the wire surface (c).

The oxidized nickel samples were placed into a stainless steel reactor, which was sealed, evacuated, followed by purging with reactive gas and filled to required pressure. Then samples were heated at various rates to a reference temperature, which was then kept constant. The temperature ranges of the study were 800-1300°C and 800-1050°C for reduction by hydrogen and by methane, respectively. Gas pressure was varied from 5 to 300 *Torr*, and the heating rates have changed in a wide range, from 1 to 1000 *K*/*s*. Special purity grade methane (>99.99%) was used, and high purity hydrogen was obtained from titanium hydride by heating it to T = 600-700°C.



Fig. 1. Diffractogram (a) of the NiO/Ni wire, its cross section (b) and surface microstructure (c).

The temperature of the wire was determined by optical method, based on the measurement of the light radiation intensity of the wire in the nearinfrared region (λ =0.8-1.5 μ m). Silicon solar photocells placed in front of the reactor windows (the reactor and photocells were thermostated at T=20°C) served as light radiation detectors. The relationship between the actual temperature of the sample and photosignal was obtained by means of a special calibration procedure based on the use of a reference wire (Pt, W, or Mo) with the same geometry, for which the temperature dependence of the electrical resistance is known [18]. In experiments platinum was mainly used as a reference wire.

To study the chemical, phase, and structural transformations, the process was automatically interrupted by swiching off the power after a given time and the measurements and analyses were performed on samples cooled to room temperature. Cooling rates reach up to 10,000 *K/s*. The samples obtained from this way were first weighed and then examined by SEM/EDS, (Prisma E), XRD (Dron 3.0) methods The surfaces of the wires and their cross sections were subjected to microscopic examinations. An analytical balance (KERN 220-5DNM) with an accuracy of $10^{-5} g$ was used to weigh the wires.

During experiments the temperature of the wire, T, electrical power, W, and electrical resistance, R, were continuously recorded (up to a frequency of $10 \ kHz$) by a computer connected to the setup, through which continuous, *in situ* calorimetric conductometric measurements were performed. Figure 2 shows the characteristic curves of the T, W and R values recorded during the linear heating of the NiO/Ni wire in methane atmosphere.



Fig. 2. Dependencies of temperature (T), electrical power (W) and electrical resistance (R) of NiO/Ni wire vs time at NiO reduction by methane. $V_h=50 \text{ K/s}$, $T_{max}=1050 \text{ °C}$, $P_{CH4}=50 \text{ Torr.}$

3. Results and discussion

3.1. NiO reduction by methane

The heat release rate due to NiO reduction by methane is determined on the basis of non-stationary equation of thermal balance as a difference of electrical powers, released on the wire at the first – reactive, $W_1(t)$, and the second – inert (after the reduction reaction is complete), $W_2(t)$, heating (with the same temperature-time history): $Wr(t) = [W_1(t) - W_2(t)]$ [9].

Indeed, at the first heating (with chemical heat release):

$$\frac{1}{4}\rho cd \frac{dT}{dt} = \frac{dq}{dt} + W_1(t) - h(T) .$$
 (1)

Second heating (when reaction is completed: dq/dt=0):

$$\frac{1}{4}\rho cd \frac{dT}{dt} = W_2(t) - h(T) \,. \tag{2}$$

From these equatios for the chemical heat evolution rate one can derive:

$$\frac{dq}{dt}(T,t) = W_1(t) - W_2(t) \,. \tag{3}$$

Eq. (3) is true for both the isothermal and nonisothermal interaction regimes.



Fig. 3. NiO/Ni sample temperature (T), reaction rate (W_r), and conversion degree (α) dependencies vs time at the reduction by methane. V_h=500 K/s, P_{CH4}=50 Torr.

In Fig. 3 Wr(t)=W₁(t)-W₂(t) depicts heat release rate during the reduction reaction, and the conversion degree, α , is defined as:

$$\alpha(t) = \frac{Q(t)}{Q_{tot}} = \frac{\int_{0}^{0} W_r(t)dt}{\int_{0}^{\infty} W_r(t)dt} = \frac{\int_{0}^{0} [W_1(t) - W_2(t)]dt}{\int_{0}^{\infty} [W_1(t) - W_2(t)]dt}$$

As shown in Figure 3, the nonisothermal reaction of NiO reduction with methane, similar to the isothermal one [14], is characterized by a well-defined induction period followed by a sharp self-acceleration of the process. As a result, the $\alpha(t)$ curve obtained from both the *in situ* measurements of the electrical power (solid line) and gravimetric measurements (round dots on the $\alpha(t)$ curve) has S-shape form for both the isothermal and nonisothermal regimes, and is described by the well-known Avrami equation [1]:

$$\alpha = 1 - \exp(-kt^n).$$



Fig. 4. SEM images of NiO/Ni wire surfaces at various stages of reduction by methane: initially oxidized Ni wire (a); t=1 s, T=900°C (b); t=2 s, T=1000°C (c); t=3 s, T=1050°C (d); t=4 s, T=1050°C (e, f). $P_{CH4}=50$ Torr, $V_h=100$ K/s, $T_{max}=1050°C$.

In parallel with the kinetic measurements, XRD and SEM examinations of the samples at different stages of the process were performed to reveal the reason of the specific shape of the kinetic curve. It has been established, that in the induction period, before intensive chemical interaction, nickel nuclei are formed on the surface of the nickel oxide, which subsequently extend and grow into the volume of the oxide, forming highly porous nickel layer (see SEM images of NiO/Ni sample surfaces at various stages of reduction, Fig. 4). Thus, appearance of the S-shaped kinetic curve and presence of the induction period are caused just by the nucleation and further growth of the formed nuclei.

As it follows from the data presented in Fig. 5, increasing the heating rate moves the reaction from the heating stage (nonisothermal interaction) to the isothermal region. Thus, at $V_h=50 \text{ K/s}$ (Fig. 5a), the reduction occurs and finished at during the heating stage. At $V_h=100 \text{ K/s}$ (Fig. 5b) the reduction proceeds at transition from the nonisothermal to isothermal period, while at $V_h=200 \text{ K/s}$ (Fig. 5c) the reaction completely occurs at the reference temperature.



Fig. 5. Dependencies of the sample temperature, T, and the reaction rate, W_r , vs. time at reduction of NiO by methane at various heating rates: V_h =50 (a), 100 (B) and 200 (c) K/s. P_{CH4} =50 torr.

It was shown that the increase of methane pressure significantly reduces the induction period and moves the whole reduction process to the shorter time region (Fig. 6 a-c). At that, in the case of linear heating up to certain reference temperature, depending of methane pressure and heating rate, the reduction occurs either at heating stage or fully at the reference temperature, i.e. at isothermal conditions.



Fig. 6. Dependencies of the sample temperature, T, and reaction rate, W_r , vs. time at reduction of NiO by methane at various pressures: $P_{CH4}=10$ (a); 50 (b) and 100 (c) *Torr*. $V_h=100$ K/s.



Fig. 7. $P_{\text{CH4}}\text{--}V_{h}$ diagram of NiO reduction regimes by methane.

Based on the data obtained at various heating rates and methane pressures, a heating rate – methane pressure diagram of NiO reduction regimes was constructed (Fig. 7), according to the which at low heating rates and high pressures the reaction occurs mainly at heating stage. On the other hand, at high heating rates and low methane pressures, vice-versa, the process fully takes place at isothermal conditions.





Fig. 8. Time dependencies of the NiO/Ni sample temperature (T) and conversion degree (α)at reduction by hydrogen. V_h=5 (a), 200 (b) *K/s*; T_{max}=1230°C.

The reduction of NiO/Ni wires with hydrogen was performed from $T_0=800^{\circ}C$ to $T_{max}=1300^{\circ}C$, and the heating rates were changed in the range from 1 to 1000 *K/s*. Because no changes in electrical power related to the process kinetics were observed in NiO reduction experiments, unlike methane reduction, we followed the reduction kinetics based only on mass loss measurements. On the other hand, based on our previous results that the rate of nickel oxide reduction with hydrogen at T> 800°C doesn't dependent on hydrogen pressure [13], all experiments were performed at hydrogen pressure value of 10 *Torr*.



Fig. 9. P_{H2} - V_h diagram of NiO reduction regimes by hydrogen.

According to the data shown in Fig. 8, in the first case, the reduction process completely takes place during the heating stage, while in the second case, it begins after the reference temperature was reached.

The simplest diagram V_h-P_{H2} obtained for different heating (Fig. 9) demonstrates that regardless of the hydrogen pressure, at low heating rates ($V_h \le 100 \text{ K/s}$) the reaction proceeds completely in the heating stage, and at high heating rates ($V_h > 150 \text{ K/s}$), on the contrary, the process takes place completely under isothermal conditions (at T_{max}).

Conclusion

Data obtained at various heating rates of the partially oxidized nickel wires in the methane and hydrogen atmospheres at various gas pressures testify that heating rate of the sample plays crucial role in the mechanism of reduction processes. For both the reducing gases heating rate (V_h) - gas pressure (P_{gas}) diagrams of reduction regimes were constructed, demonstrating that depending on the heating rate value two extreme regimes of the reduction may be realized, when practically complete reduction of the oxide takes place under isothermal (low heating rates) or nonisothermal (high heating rates) conditions.

ՄԵԹԱՆՈՎ ԵՎ ՋՐԱԾՆՈՎ ՆԻԿԵԼԻ ՕՔՍԻԴԻ ՎԵՐԱԿԱՆԳՆՄԱՆ ԿԻՆԵՏԻԿԱՅԻ ԱՌԱՆՁՆԱ՜ԱՏԿՈԻԹՅՈԻՆՆԵՐԸ ՈՉ ԻԶՈԹԵՐՄ ՊԱՅՄԱՆՆԵՐՈԻՄ

Վ. Ս. ՎԱՐԴԱՆՅԱՆ, Ղ. Ա. ՉԱՏԻԼՅԱՆ և Ս. Լ. ԽԱՌԱՏՅԱՆ

Աշխատանքում ներկայացված են մեԹանով և ջրածնով նիկելի օքսիդի վերականգնման կինետիկայի արդյունքները ոչ իզոԹերմ պայմաններում, Հիմնված փոխազդեցու-Թյան արադուԹյան անմիջական չափումների, ինչպես նաև նմուշների զանգվածի կորստի պարբերական չափումների, ռենադենա ֆաղային անալիզի ու լուսածրային էլեկտրոնային մանրազննու[ժյան Հետազոտու[ժյունների Հիման վրա: Նմուչների տաքացման տարբեր արադու[ժյունների ու դագի տարբեր ճնչման արժեքների Համար ստացված տվյալների Հիման վրա կառուցվել են տաքացման աարադու[ժյուն (Vh) – դագի ճնչում (Pgas) դիադրամները, Համաձայն որոնց տաքացման փոքր արադու[ժյունների և մե[ժանի ճնչման մեծ արժեքների դեպքում վերականդնման ռեակցիան ընխանում է Հիմնականում տաքացման փուլում (ոչ իզո[ժերմ պայմաններ]: Մյուս կողմից, տաքացման մեծ արադու[ժյունների դեպքում, ընդՀակառակը, պրոցեսն ամբողջու[ժյամբ ընխանում է իզո[ժերմ պայմաններում: Ի տարբերու[ժյուն մե[ժանի, ջրածնով վերականդնման դեպքում, անկախ դագի ճնչումից, տաքացման փոքր արադու[ժյունների դեպքում վերականդնումն ամբողջապես ընխանում է տաքացման փուլում, իսկ արադ տաքացման դեպքում` իզո[ժերմ պայմաններում (Tumax ջերմաստիճանում):

КИНЕТИЧСКИЕ ОСОБЕННОСТИ ВОССТАНОВЛЕНИЯ ОКСИДА НИКЕЛЯ МЕТАНОМ И ВОДОРОДОМ В НЕИЗОТЕРМИЧЕСКИХ УСЛОВИЯХ

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В работе представлены результаты кинетики восстановления NiO метаном и водородом в неизотермических условиях, основанные на *in situ* измерении скорости реакции, а также периодическом взвешивании образцов и исследовании последних методами рентгенофазового анализа и сканирующей электронной микроскопии. На основе данных, полученных при различных скоростях нагрева и давлении газа, построены диаграммы режимов восстановления в координатах скорость нагрева (V_h) – давление газа (P_{gas}), согласно которым при низких скоростях нагрева и высоких давлениях метана реакция востановления протекает преимущественно на стадии нагрева (неизотермические условия). С другой стороны, при высоких скоростях нагрева и низких давлениях метана, наоборот, процесс полностью протекает в изотермических условиях. В случае восстановления водородом, независимо от давления газа, при низких скоростях нагрева реакция полностью протекает на стадии нагрева, а при высоких скоростях нагрева, наоборот – полностью протекает в изотермических условиях (при T_{max}).

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