Study of the kinetics of hydrogen sorption and desorption from titanium

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Abstract

A method of thermocycling in a hydrogen medium for studying the kinetics of the interaction between hydride-forming metals and hydrogen is proposed. The method is applied to the titanium powder with a grain size of 15–20 μm. Thermocycling curves were obtained in a wide range of temperatures and concentrations for α- and β-titanium. Evaluations of the kinetic parameters of absoprtion and desoprtion as well as the heat of sorption in α- and β-titanium are presented.
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1. Introduction

The kinetics of the interaction between hydride-forming metals and hydrogen may be determined in some cases by processes of absoprtion and desorption. There are numerous data concerning equilibrium thermodynamic parameters such as solubility, heat of absorption, accumulated in many reviews [1–3], but there is not enough information about kinetic parameters describing reactions of absorption and desorption. The scope of this work was to study interaction kinetics in hydrogen–titanium system in the absence of hydride formation. The choice of titanium was motivated by its very wide use as a hydrogen absorber [4,5]. Other purposes were to develop a simple method providing the reliable experimental data in a wide range of temperatures and hydrogen concentrations in a metal and to develop models, which allow for the evaluation of kinetic parameters from these data.

2. Apparatus and methods

The investigation of the hydrogen–titanium interaction kinetics was carried out in a metal high-vacuum system includ-ing a time-of-flight mass-spectrometer, a pumping system, a diffusion system of hydrogen refinement and a working cell where the samples were placed (Fig. 1). The working cell is equipped by a capacitance pressure gauge and can be connected to pumps as well as a hydrogen refinement and inlet system. The outer oven controlled by a computer heats the autoclave made of a stainless steel tube. Temperature is measured by a chromel–alumel thermocouple.

The specimen was a fine powder of titanium with a maximum grain size less than 40 μm (Fig 2). A typical amount of titanium powder in the experiments was 6–8 mg. Before each experiment the sample was annealed in vacuum at 1.3×10^{-6} Pa, 750 °C for 1 h.

The idea of the proposed method of thermocycling is to apply a periodical temperature oscillation for a sample placed into a closed cell filled with hydrogen. Only the autoclave (volume $V_{ac} \leq 1$ ml) containing the sample is heated, while the working cell (volume $V \sim 1000$ ml) is kept at room temperature. The cooling of the sample results in hydrogen absorption and, therefore, in a pressure decrease in the closed working cell, the heating of the sample results in hydrogen desorption and in a pressure increase. The amount of absorbed (desorbed) hydrogen is derived from the pressure decrease (increase) according to the gas law. For a better statistics, data of many temperature cycles were collected.
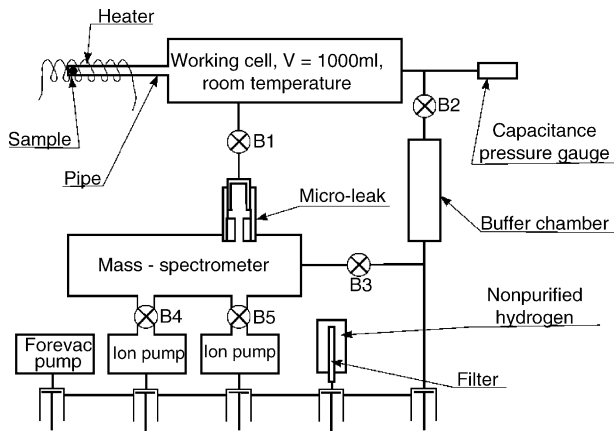
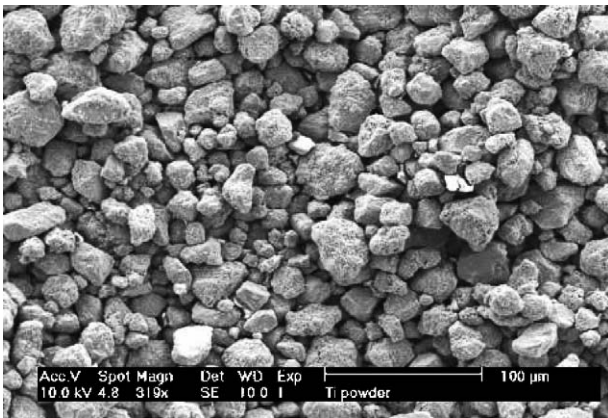Fig. 1. The vacuum part of experimental setup.

Fig. 2. The electron microscopy picture of the used titanium powder.

Such an approach gives a possibility to change the period and the amplitude of temperature oscillations, the average temperature and the initial pressure in the working cell, which influence the range of hydrogen concentrations in the sample.

The method possesses several advantages in comparison with the standard TDS method for the study of kinetics of interaction of hydride-forming metals and hydrogen. In particular, if a sample is changing during a long-time experiment (cleaving, impurities segregation), it affects the form of a thermocycling curve. Reproducibility of a curve indicates that the system behaves well and the curve may be used for the following treatment.

3. Results and discussion

The choice of the initial pressure in the cell and of the temperature range for thermocycling determines a range of attained hydrogen concentration in a material. Thus, it is possible to choose a path of reaction and to carry out the research of the kinetics of hydrogen sorption/desorption for the certain phase states of the material. It can be thermocycling either with phase transition or without. The exam-
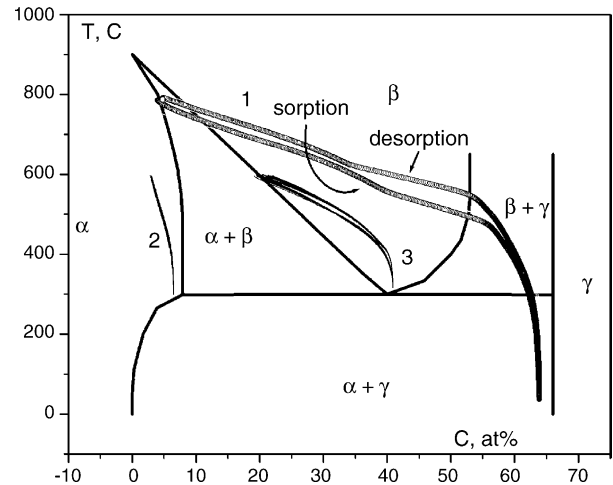

Fig. 3. The phase diagram of titanium [3] and the paths of reactions during thermocycling of titanium powder.

ple of such a research for the titanium powder is shown in Fig. 3. Here the experimental curve for thermocycling with several transitions (curve 1) is shown. The upper branch corresponds to the desorption process, the lower one is for the absorption process. The curve contains several cycles, and at the same time one can observe a very good reproducibility of these cycles. A complicated path of reaction like $\alpha + \gamma \rightarrow \beta + \gamma \rightarrow \beta \rightarrow \alpha + \beta \rightarrow \alpha$ results in many peculiarities, which are rather difficult for modelling. Besides it is necessary to take into account that the phase diagram is presented for the equilibrium system Ti–H, while in our case this system is not in equilibrium during thermocycling.

3.1. Kinetics of hydrogen absorption and desorption in α- and β-titanium

To simplify the situation, we studied the kinetics of the interaction between titanium and hydrogen separately for the α-and β-phases in the absence of phase transitions. In Fig. 3, curve 2 corresponds to thermocycling in the α-area of the phase diagram; curve 3 is the same in the β-area. To increase the accuracy of the following treatment of experimental data, we used various rates of heating/cooling of the sample.

To evaluate the kinetic parameters we consider two models with one common assumption that the entire sample is in the single-phase area during thermocycling.

3.1.1. Model 1
A gradient of concentration in the sample is negligible at elevated temperatures. In this case, the concentration of absorbed hydrogen was calculated in the following way

$$c(t) = \frac{N_h}{V_{sample}} = \frac{p_0 - p(t)}{V_{sample}} 2Vq$$

where N_h is the amount of sorbed hydrogen atoms, p_0 is the initial pressure of gas in the closed cell with the vol-

ume V (prior to the beginning of absorption of hydrogen by the sample), $p(t)$ is the current pressure, q is the quantity of hydrogen molecules in unit volume at unit pressure and room temperature. We shall designate $z \equiv 2Vq$ and express the amount of atoms of absorbed hydrogen in the sample as $c(t)V_{sample} = z(p_0 - p(t))$. Its derivative is

$$\dot{c}(t)V_{sample} = -z\dot{p}(t)$$

On the other hand, the flux of absorption rises the concentration $c(t)$ and the flux of desorption reduces it:

$$\dot{c}(t)V_{sample} = (k_a^* p(t) - b^* c^2(t))m_{sample}$$

where $k_a^* = k_{a0}^* \exp(-E_a/RT)$ and $b^* = b_0^* \exp(-E_d/RT)$ are the rate constants of absorption and desorption attributed to the unit of mass. By eliminating concentration, we obtain:

$$-z\dot{p}(t) = \left(k_a^* p(t) - b^*\left(z\frac{p_0 - p(t)}{V_{sample}}\right)^2\right)m_{sample}$$

That is a differential equation for the time dependency of the pressure in the experimental cell containing the sample. Four parameters for the rates of absorption and desorption define this dependency $-k_{a0}^*, b_0^*, E_a, E_d$. The following treatment of the data was the fitting of the experimental curve by the model one by variation of these parameters.

3.1.2. Model 2

In the second case, a gradient of concentration was taken into account. Additional assumptions were made: all the particles of the powder are balls with the same radius $R = 15\ \mu m$ (estimation is done from the micrograph in Fig. 2); the initial hydrogen concentration in all particles is equal and the initial gradient of concentration is negligible. Due to the spherical symmetry of the problem, we consider one-dimensional diffusion (along the radius of the particle r) where the concentration obeys Fick's law:

$$\frac{\partial c}{\partial t}(t,r) = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}(t,r)\right), \quad r \in (0,R),\ t > t_0$$

where $D = D_0 \exp(-E_{dif}/RT)$ is the hydrogen diffusivity. The initial and boundary conditions for Fick's equation are the following:

$$\frac{\partial c}{\partial r}(t_0,r) = 0, \quad r \in (0,R);$$
$$\frac{\partial c}{\partial r}(t,0) = 0, \quad t \geq t_0;$$
$$D\frac{\partial c}{\partial r}(t,R) = (-b^* c^2(t,R) + k_a^* p(t))m_{sample}, \quad t > t_0.$$

Here the pressure $p(t)$ depends on the amount of sorbed hydrogen as

$$p(t) = p_0 - N_{part}\int c(t,\vec{r})\,dV$$

where N_{part} is the quantity of particles of a powder. The solution of Fick's equation gives the time dependency $p(t)$. Six parameters were varied to fit the experimental curve by the model one $-k_{a0}^*, b_0^*, E_a, E_d, D_0, E_{dif}$.

3.2. Results of data processing

Thermocycling curves for α- and β-titanium have been approximated on the basis of the model 1. An example of the fitting of the curve for the α-phase is shown in Fig. 4. Here the fitting is performed in the time interval including three rates of heating/cooling. It should be noted, that the single set of parameters successfully describes absorption and desorption at all used rates. The evaluations of activation energies and pre-exponential factors of absorption and desorption in the temperature range 300–600 °C for α- and β-titanium are shown in Table 1. The heat of sorption was derived from the activation energies as $\Delta H_{est} = (1/2)(E_a - E_d)$. Numerous calculations revealed that the most stable parameter during fitting is the heat of sorption of hydrogen. The evaluated values ΔH_{est} are close to data ΔH_{ref} presented in [3]. Some discrepancy between ΔH_{est} and ΔH_{ref} may be associated with the different temperature range of 600–900 °C used in [3].

The fitting on the basis of the model 2 changes values of absorption and desorption parameters weakly. The parameters of diffusion were determined with much more inaccuracy than the parameters of absorption and desorption. In fact, the numerical simulations allow designating the area of possible values of diffusivity only. However, the discrepancy between the experimental and model curves decreases allowing for
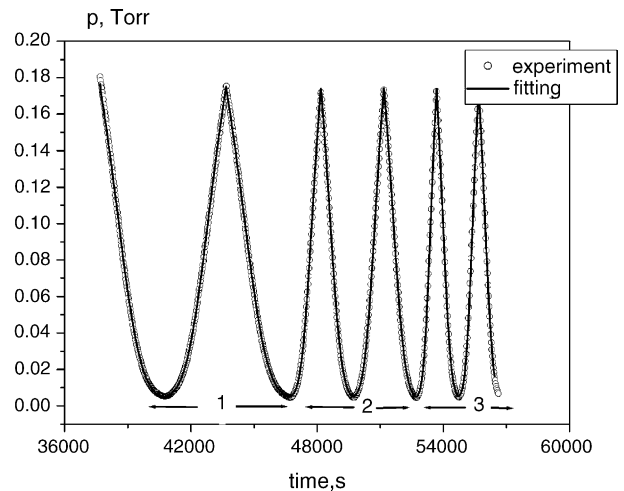

Fig. 4. Thermocycling of α-titanium: the comparison of experimental data and fitting. Rates of heating/cooling: (1) 0.1 K/s, (2) 0.2 K/s, (3) 0.3 K/s.

Table 1

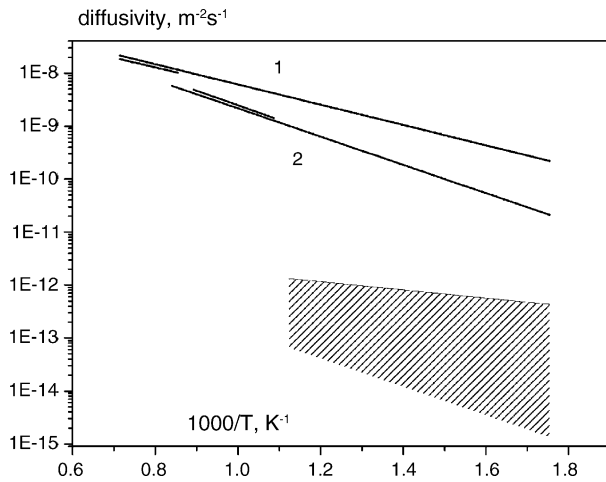|	E_a (kJ/mol)	E_d (kJ/mol)	k_{a0}^* (1/s/Pa/kg)	b_0^* (m^6/s/kg)	ΔH_{est} (kJ/mol)	ΔH_{ref} (kJ/mol) [3]
α-Phase	25–27	120–124	2.3–4.6E22	1–2E−25	−50 to −45	−45
β-Phase	38–45	128–137	4.5–45E22	1–10E−25	−50 to −42	−57

Fig. 5. The hatched area represents the evaluation of diffusivity in α- and β-titanium: (1) diffusivity in β-titanium, (2) diffusivity in α-titanium [6,7].

hydrogen diffusion. The evaluations of hydrogen diffusivity in the temperature range 300–600 °C in α- and β-titanium in comparison with [6,7] are shown in Fig. 5. We suppose that the better evaluation accuracy for the values of diffusivity in titanium could be obtained for the powders with bigger grain size.

4. Conclusion

The method of thermocycling in hydrogen medium for studying of kinetics of interaction between hydride-forming metals and hydrogen is proposed. The method is applied for the investigation of system of titanium powder and hydrogen.

Thermocycling curves were obtained in a wide range of temperatures and concentrations. It was shown that kinetics of the interaction between α- and β-titanium and hydrogen in the absence of hydride formation can be described satisfactorily well by the model involving sorption and desorption only. Kinetic parameters of absorption and desorption as well as the heat of sorption in α- and β-titanium were evaluated.

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