Simulation of Thermostimulated Hydrogen Release from Ti, Zr, Pd, Ni

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Introduction

Thermo-stimulated hydrogen release (TSHR) at linear heating (1 °C s-1) from Ti, Zr, Pd, Ni with various thicknesses (0.05÷1 mm) was investigated. The models of hydrogen release were considering, taking into account the diffusion of hydrogen atoms to the surface and the formation and desorption of hydrogen molecules from the surface. Based on the models and experimental TSHR spectra, a program for simulating the hydrogen release process was developed.

Materials and Methods

The samples selected from transition metals Ti, Zr, Ni, Pd and Pt in the form of plane-parallel plates with various thicknesses. Electrolytic saturation was carried out in 0.1–1.0 M H_2SO_4 solution for 0.5–72 h at current density 20–200 mA/cm^2 at room temperature.

Experimental parameters:

To study the processes of diffusion release of hydrogen from flat metal plates, experiments were carried out on thermally stimulated gas release (TSGR) of hydrogen from samples of various thicknesses into vacuum with heating rate β = 1 °C/s.

Experimental results & Discussion

Fig. 1 shows the experimental and calculated dependences for thermostimulated hydrogen release (TSHR) from titanium and zirconium plates with various thicknesses, saturated in the electrochemical cell with a H_2SO_4 solution. In Fig. 1a can be see that as the thickness of the sample increases, the position desorption peak moves toward the high temperature region. In Fig. 1a, the solid line of curves 1–3 is the experimental results and the dashed line is the calculated results.

With prolonged (24 h) cathode saturation of the titanium plate, a second high-temperature (>600 °C) peak appears in the TSHR spectrum associated with the formation of hydride phase in zirconium (Fig. 1b). If the samples contain hydrides, the model should additionally take into account the possibility of their decomposition during linear heating (Section Contribution from the decomposition of hydride phases).

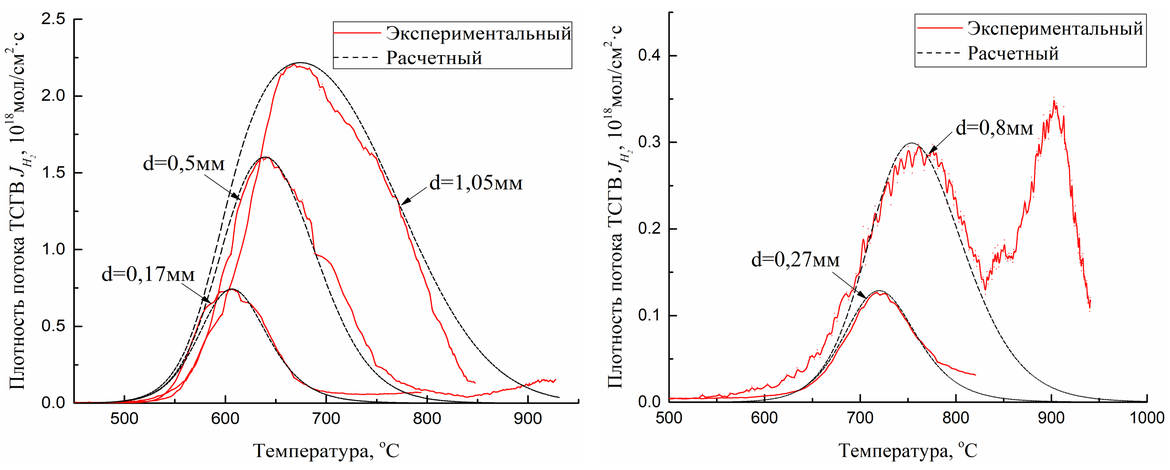


Fig. 1 – Experimental (solid) and simulated (dashed) TSHR spectra from Ti (VT 1-0) and Zr (E110) at heating rate of 1 °C/s with various thicknesses (cathodic saturated): a – Ti: d = 0.17-1.05 mm, t = 6 h, I = 0.2 A, H_2O+ H_2SO_4 (1M); b – Zr: d = 0.27 mm, t = 24 h, j = 100 mA/cm^2, H_2O+ H_2SO_4 (0.5M); d = 0.8 mm, t = 21 h, j = 100 mA/cm^2, H_2O+ H_2SO_4 (1M).

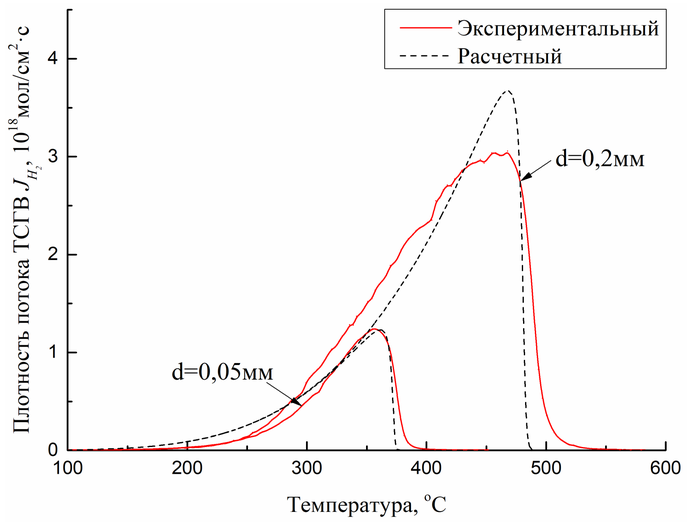


Fig. 2 – Experimental (solid) and simulated (dashed) TSHR spectra from Pd at heating rate of 1 °C/s with various thicknesses (cathodic saturated): d = 0.05 mm, t = 0.5 h, j = 100 mA/cm^2, H_2O+ H_2SO_4 (0.5M); d = 0.2 mm, t = 20 h, j = 90 mA/cm^2, H_2O+ H_2SO_4 (0.1M).

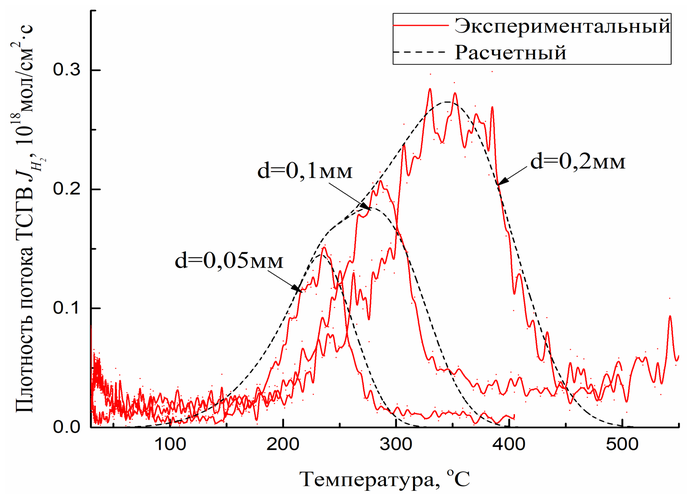


Fig. 3 – Experimental (solid) and simulated (dashed) TSHR spectra from Ni at heating rate of 1 °C/s with various thicknesses (cathodic saturated): d = 0.05-0.2 mm, t = 20 h, j = 120 mA/cm^2, H_2O+ H_2SO_4 (1M).

The experimental TSHR results for Pd, Ni are shown in Fig. 2, 3. In these of transition metals samples (4–6 periods of group VIIIB), hydrogen can accumulate in noticeable amounts in the form of solid solutions, but the second high-temperature peak associated with hydride decomposition is not observed even at significant times of hydrogen saturation.

Model of hydrogen migration

1. Diffusion of hydrogen in the sample:

$$\frac{\partial n(x,t)}{\partial t} = D(t)\frac{\partial^2 n(x,t)}{\partial x^2}, \qquad D(t) = D_0 \exp\left[-\frac{E_a}{k(T_0+\beta t)}\right]$$

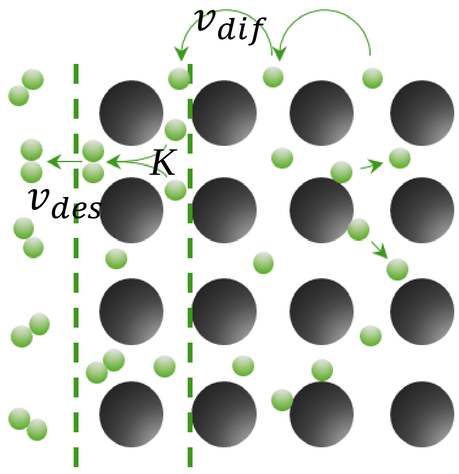
2. Recombination and desorption of hydrogen on the surface:

Ti and Zr:

$$\pm D\left.\frac{\partial n}{\partial x}\right|_{x=\pm\frac{d}{2}} = \mp K_0 \exp\left(-\frac{E_K}{kT}\right) N_1^2(t) = \mp K_0' \exp\left(-\frac{E_K'}{kT}\right) n_H^2\left(\pm\frac{d}{2},t\right).$$

Pd and Ni:

$$\begin{cases} \pm D\left.\frac{\partial n}{\partial x}\right|_{x=\pm\frac{d}{2}} = \mp J_H\left(\pm\frac{d}{2},t\right)\sigma_1 N \\ \frac{dN_1}{dt} = -J_H\left(\pm\frac{d}{2},t\right)\sigma_1 N - 2kN_1^2(t) \\ \frac{dN_2}{dt} = kN_1^2(t) - \nu_{-3}N_2(t) \\ N + N_1 + N_2 = N_0 \end{cases}$$



Conclusion

Relations between the activation energies and preexponential factors of the diffusion and the hydride decomposition processes with the temperature position of the maximum intensity in TSHR spectrum, and the relation of these values with sample thickness, heating rate, spectrum width and position of inflection points on the TSHR curves are obtained. The kinetic features of the processes of the release and accumulation of hydrogen atoms on the surface, the formation of hydrogen molecules and it desorption are taken into account at the description of the experimental TSHR curves.

It has been shown that the programmable TSHR method is a convenient tool for determining the activation energies, the pre-exponential factors for diffusion, desorption and hydride decomposition processes in case of thin samples.

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