DETERMINATION OF BINDING ENERGIES OF HYDROGEN IN DIFFERENT MATERIALS FROM ABSOLUTE MEASUREMENTS OF ITS CONCENTRATION IN SOLID PROBES

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Introduction

A method for analysis of experimental dynamical curves of high-temperature vacuum-extraction is developed, which allows determining the binding energy and diffusion constants of hydrogen in the probe under study.

The experimental data have been obtained using the measuring complex [1], which allows conducting the absolute measurements of the dynamical curves of high-temperature vacuum- extraction of hydrogen from a solid probe.

Main results

The developed method is based on mathematical modeling of time-dependent hydrogen diffusion in the solid probe in its slow heating up to a certain temperature below the melting point.

The probes have been studied having a form of cylinder and parallelepiped.

The probe heating occurs in a pumped extractor made of quartz glass, walls of which are kept at a constant temperature T_0. The probe heating takes place due to heat radiation of the extractor walls. The time dependence of the probe temperature is shown in Fig.1. for a cylindrical probe of standard form [2] (the probe mass is 2g). The heating time is about 40 min. The time dependence during the heating time is almost linear.

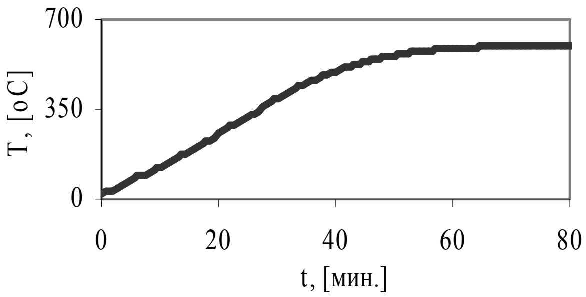

Figure 1: Probe temperature as a function of heating time

The time-dependent diffusion of hydrogen in a probe is described by the equation

$$\Delta C = \frac{1}{D}\frac{\partial C}{\partial t}, \quad C|_S = 0, \quad C|_{t=0} = C_0, \qquad (1)$$

where C - is the hydrogen concentration in the probe, $D = D_0 \cdot \exp(-\frac{u}{kT})$ is the diffusion coefficient for hydrogen in metal, u is the binding energy, D_0 is the diffusion constant, k is the Boltzmann constant.

Taking into account the form of the probe, and given initial conditions, the first term of Fourier expansion of the solution of equation (1) can be written as

$$C(x,y,z,t) = \frac{C_0\pi^3}{8}\sin\frac{\pi x}{a}\cdot\sin\frac{\pi y}{b}\cdot\sin\frac{\pi z}{l}\cdot f_1 \qquad (2)$$

where *l, a* and *b* are the height, width and depth of the probe, respectively, and the function $f_1(t,u,D_0)$ is the solution of the equation:

$$\dot{f_1} + D_0\cdot\exp(-\frac{u}{kT})(\frac{\pi^2}{a^2}+\frac{\pi^2}{b^2}+\frac{\pi^2}{l^2})f_1 = 0 \qquad (3)$$
$$f_1(0,u,D_0) = 1$$

In performing the analysis, the apparatus registers the total hydrogen flux *q(t)* through the surface of probe. According to the Fick low, this flux is

$$q(t) = -\int_S D\frac{dC}{dn}dS, \qquad (4)$$

Using the expression (2) for *C*, we obtain the following result

$$q(t) = \frac{16C_0}{\pi^2}\cdot\left[\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{l^2}\right]\cdot D_0\cdot\exp(-\frac{u}{kT})\cdot f_1. \quad (5)$$

In the case of existence of hydrogen with different binding energies in a probe the superposition principle can be used.

The results of the mathematical modeling for diffusion-movable hydrogen in the stainless steel (a) and for hydrogen in aluminum alloy (b) are given in Fig. 2.

a)

b)

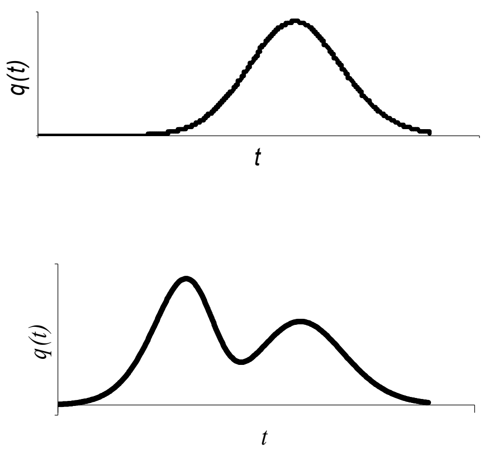

Figure 2: Results of the mathematical modeling for probes of stainless steel (a) and aluminum alloy (b)

Approximation of the experimental extraction curves by calculated ones allows one to obtain the values of binding energy u and the diffusion constant D_0 for hydrogen contained inside the probe.

The heart of the measuring complex used for measurements of extraction curves is hydrogen analyzer AV-1 and a new standard of flux for absolute calibration of the analyzer.

The analyzer AV-1 included in the State List of means of measurements, it is produced serially. The analyzer is used in laboratory of the Metallurgic Plant in Kamensk-Uralsk (during 5 years). In the laboratory of our firm the methods for measurements are developed and analyses made for great variety of alloys of aluminum, titanium, magnesium and steels. Also performed are the analyses for semiconductor materials: crystalline silicon, amorphous silicon and carbon, carbon nana-structures.

High accuracy of measurements is achieved. The statistics for each curve includes about 30 thousand points.

Mathematical treatment of the curves is made by the system of digital registration of analyzer.

The area under each peak of the extraction curve determines the hydrogen content with a given binding energy in the solid. The position and width of the maximum determine the binding energy and the diffusion constant of hydrogen.

The following values of binding energies have been obtained: u=0,2 – 0,8 eV for aluminum alloys; u=0,4-1,5 eV for titanium alloys.

A new standard of hydrogen flux in vacuum has been used for calibration of the analyzer. Fig.3. shows the hydrogen flux from the standard as a function of time.

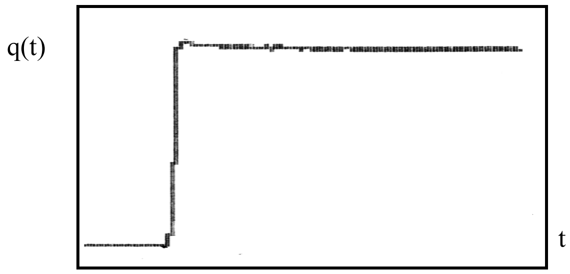

Figure 3: Oscillogram of the hydrogen flux from the standard

The stability of hydrogen flux is better than 2%. In 2004-2005 the standard testing was made in the Mendeleyev Institute. The stability of hydrogen flux during 8 month was about 1%. The certified value of molecular hydrogen was $(7,7\pm0,1)\cdot10^{-7}$ m^3Pa/c at 90% confidence.

The absolute uncertainly of the whole measuring complex on the basis of AV-1 does not exceed 6%.

Known the mean dimensions of grains of the probe material and absolute value of the hydrogen content, one can estimate the defect concentrations of various types, which in many cases are filled with hydrogen. We have found for pure aluminum that hydrogen fills all cavities along grain boundaries at atmospheric pressure.

The developed method for analysis and the measuring complex were used in studying the probes subject to thermo-mechanical loads and having fatigue cracks.

It is established that in the destruction zone the hydrogen concentration is several times higher than the mean value for the probe.

References

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