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Experimental determination of parameters of multichannel hydrogen diffusion in solid probe

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ABSTRACT

The multi-channel diffusion mechanism is modeled by diffusion equations.

The method for analysis of experimental dynamical curves of vacuum hot extraction (VHE) is developed, which allows to determine the binding energy and diffusion constants of hydrogen in the probe under study.

The experimental data have been obtained using industrial hydrogen analyzer, which allows to carry out the absolute measurements of the dynamical curves vacuum hot extraction of the hydrogen from a solid probe. Experimental verification of mathematical models gives adequate results.

The differences of the proposed approach with the method of TDS are discussed.

Introduction

The study of hydrogen diffusion in solids has a great practical importance. The phenomenon of hydrogen fragility and cracking castings in the process of cooling and crystallization occurs as a result of the hydrogen diffusion.

Gorsky [1,2] has proved that apart from temperature and concentration gradient, mechanical tensions arising in deformation of crystal matrix influence diffusion of atoms in solids. This has made it possible to explain the mechanism of the gradual evolution of hydrogen embrittlement in metallic parts, elements and the formation of cold cracks in welds. The hydrogen diffusion plays an important role in the processes of corrosion, cracking and brittle failure [3–8]. The influence of hydrogen on electric properties of semiconductors is also essential [9].

Control of the hydrogen concentration in metals and semiconductors is usually performed in industry [10–12]. Every day, thousands experimental determinations of hydrogen concentration and parameters of its interaction with the solid state matrix are performed in the world. During the test the sample is heated in vacuum or in the flux of an inert gas during this analyses for extraction of the hydrogen.

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The flux of hydrogen is measured in such experiments. The study of these fluxes as function of time and temperature allows one to estimate the energy of interaction of hydrogen with the solid state matrix and its defects.

It was established that hydrogen in solids occupied certain energy levels. It was established that hydrogen in solids occupied certain energy levels. It was found that hydrogen with binding energy in the range of 0.2–0.4 eV considerably influences on plasticity and strength of the steels.

Usually for determination of binding energy is used the method of thermo-desorption spectra (TDS). This method is given in Ref. [13]. Extraction of hydrogen from a sample is considered as a chemical reaction of the first order with the activation energy equal to the binding energy. Thus the effect of the hydrogen diffusion inside the studied sample is considered negligible.

On the one hand, this contradicts to the experimental data, since even at relatively small sizes of the sample account for diffusion introduces essential corrections to the values of binding energy [14]. On the other hand, mathematical modeling of the TDS measured experimentally evidences for low accuracy of such approach [15]. As a rule, the hydrogen's binding energies of about 0.2 eV should yield notable hydrogen fluxes at normal conditions, that is not observed experimentally.

It is possible to estimate the binding energy using other methods, e.g. the spectral one [9]; however this method is adequate only in the case of thin samples in the form of films and membranes.

In connection with the strong influence of hydrogen with different binding energies on the structure and strength of materials it becomes necessary to develop approaches which can be used not only in scientific experiments but also in industrial tests.

Measurement of hydrogen concentration by vacuum hot extraction method

The vacuum heating method is used both in experiments and in industrial control of hydrogen concentration in a solid probe [9,16–19] (Hydrogen Analysis by Vacuum Hot Extraction (VHE). In our experiments we used industrial hydrogen analyzer AV-1 with mass-spectrometric registration of dependence of hydrogen flux from the sample on time, in the process of the sample heating in vacuum. The exterior of the apparatus is shown in Fig. 1(a).

Fig. 1(b) shows the system of probe preparation composed of the extraction system 1, 3 (made of the fused silica) and the radiation furnace 4 whose temperature maintained constant during the analysis. The samples 2 are placed in the cold appendix of extractor 1.

In performing analysis, the sample 2 is thrown off to the analytical Fig. 1 without spoiling of vacuum. The analytical appendix 3 is maintained at a constant temperature of extraction, which is provided by the furnace 4 put on the appendix.

A schematic drawing of the AV-1 is presented in Fig. 2.

For most of the alloys the extraction temperature falls in the range 400–800 °C. The extractor volume is pumped continuously with the analyzer pump down to the working pressure of 100 μPa. The investigated sample is heated slowly up to the extractor temperature. The hydrogen flux from the sample is measured by mass-spectrometric analyzer preliminarily calibrated on the standard hydrogen containing samples or on the gas calibration. As a result, dependence of hydrogen flux from the extractor system on time (the extraction curve) is obtained. An integral of the extraction curve over time is proportional to the amount of hydrogen extracted from the sample. The shape of the curve has features typical for the aluminum, magnesium, titanium alloys and the different marks of steels. In determining the diffusion parameters, we compare the experimental extraction curve to the calculated one obtained by mathematical modeling of the time dependent hydrogen diffusion in the studied sample.

Modeling of diffusion process in sample

Consider the process of the sample heating in vacuum using the titanium samples studied experimentally as examples.

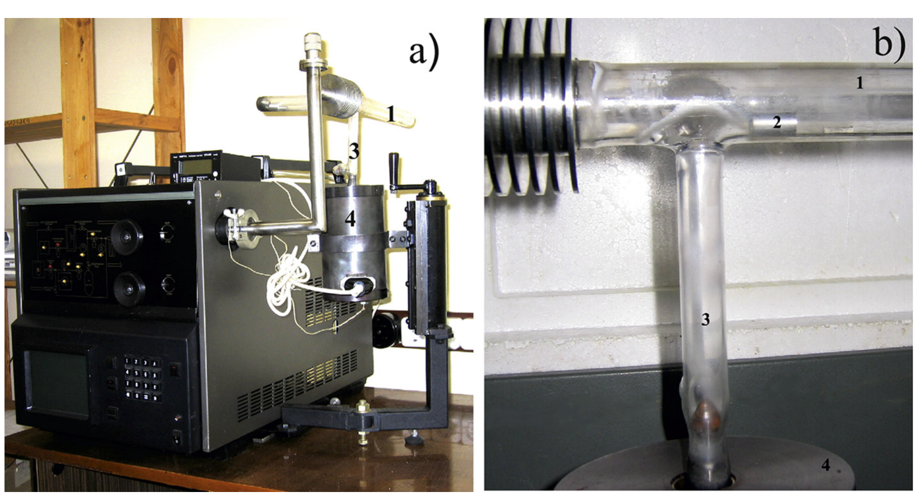

Fig. 1 – Hydrogen analyzer AV-1 (a) and its extraction system (b).