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# Determining the bound energies of dissolved hydrogen on the basis of a multichannel diffusion model in a solid☆

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**Abstract**

A hypothesis of the multichannel character of hydrogen diffusion in solids has been substantiated in the paper. Based on this hypothesis, a mathematical model of hydrogen diffusion in the crystalline lattice was constructed. The model allowed determining the dissolved hydrogen binding energies using an extraction curve. The curve is measured by an industrial vacuum-extraction procedure with mass-spectrometric detection of hydrogen streams. The paper presents various experimental data that supports the validity of the multichannel model and discusses the advantages and disadvantages of the proposed approach in comparison with the well-known method of thermal desorption spectra (TDS) that is recognized as the classical way of experimentally determining dissolved hydrogen binding energy in solids.



*Keywords:* Hydrogen binding energy; Hydrogen diffusion; TDS; Hydrogen analyzer; Vacuum hot extraction; Standard.

## 1. Introduction

The research of hydrogen diffusion in solids is of great practical value. The phenomena of hydrogen embrittlement and casting cracking during cooling and crystallization occur as a result of hydrogen diffusion. Gorsky proved in Refs. [1,2] that crystalline matrix deformations occurring due to mechanical stresses affect, aside from the temperature and the concentration gradient, atomic diffusion in solids. This allowed to explain the mechanisms by which hydrogen embrittlement gradually evolves in mechanical details and cold cracks form in weld joints. Hydrogen diffusion plays an important role in the processes of corrosion, cracking and brittle fracture of materials. Hydrogen also has a notable effect on the electric properties of semiconductors [3–8].

Industrial plants control hydrogen concentrations in metals and semiconductors [9–11]. Thousands of experiments on measuring hydrogen concentrations and the parameters of the interaction of hydrogen with the solid matrix are conducted daily all over the world.

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Hydrogen diffusion is used to extract hydrogen from a solid body during the analysis while the samples are heated. Hydrogen flow is measured in such experiments. Interpreting the dependences of these flows on analysis duration and sample temperature allows to estimate the energy of the interaction of hydrogen with the solid body matrix and its defects. The studies of diffuse hydrogen flows have revealed that the state of hydrogen in a solid body is characterized by certain energy levels of hydrogen's bonding with the crystalline lattice, grain surface, various structural defects and inclusions. According to the obtained results, the hydrogen with binding energies in the range of 0.2–0.4 eV significantly affects steel plasticity and strength.

Thermal desorption spectroscopy (TDS) is a commonly used method of experimentally estimating binding energies; it is substantiated in Ref. [12]. Extracting hydrogen from a sample is regarded as a first-order chemical reaction with the activation energy equal to the binding one. Thus, hydrogen diffusion within the studied sample is considered insignificant.

On one hand, this contradicts the experimental data, as even for relatively small sample sizes taking diffusion into account significantly alters the binding energy values [13]. On the other hand, this approach is insufficiently precise, as evidenced by the attempts to mathematically simulate the experimentally measured thermal desorption spectra (TDS) [14]. In these simulations, binding energies of around 0.2 eV produce, as a rule, noticeable hydrogen flows under normal conditions, which is not observed experimentally.

It is possible to estimate the binding energies through using other methods, for example, the spectral method [15], but this only works well for thin samples in the form of films and membranes.

Due to the significant effect of hydrogen with different binding energies on the structure and strength of materials, it is necessary to develop approaches that would be suitable not only for scientific research but also for industrial experiments.

### *2.1. Measuring hydrogen concentration by the vacuum-heating method*

The vacuum-heating method [15–18] is one of the ways for measuring hydrogen concentrations in solid samples; it is used in research as well as in the industrial monitoring. For our experiments we used an industrial AB-1 hydrogen analyzer with mass-spectrometric monitoring of the time dependence of hydrogen flow from a sample heated in vacuum.

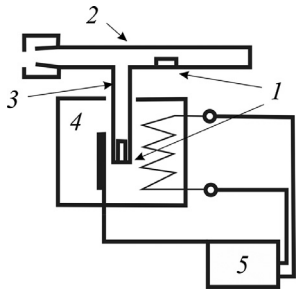


Fig. 1. The extraction system of a hydrogen analyzer: cylindrical samples (*1*), extractor (*2*), analytical branch (*3*), radiation-heated furnace with a thermocouple (*4*), furnace temperature controller (*5*).

Fig. 1 shows the system of sample preparation consisting of an extraction system *2*, *3* (made of quartz glass) and a radiation furnace *4* whose temperature is kept constant during the analysis. Cylindrical samples *1* are placed into a non-heated extractor branch *2* made of thin quartz glass.

During the analysis the sample *1* is discharged without breaking the vacuum into the analytical branch *3*. The latter is kept at a constant extraction temperature which is automatically maintained by the heater *4* fitted over the branch. A functional scheme of the analyzer is shown in Fig. 2.

For most alloys the extraction temperature lies within the range of 400–800 °C. The extractor volume is continuously vacuum-pumped to an operating pressure of 100 μPa. The analyzed sample is slowly heated to the extraction temperature. The hydrogen flow discharged from the sample is measured by a mass analyzer pre-calibrated by samples with the standard hydrogen content. A time dependence of hydrogen flow from the extraction system (i.e., the extraction curve) is obtained as a result of analyzing a sample. The integral of the extraction curve is proportional to the quantity of hydrogen extracted from the sample.

Curve shapes are characteristically different for aluminum, magnesium and titanium alloys, and various steel grades. In order to find the diffusion parameters, we have compared the experimental and the calculated extraction curves (the latter is obtained through mathematically modeling the transient hydrogen diffusion in the studied sample.

### *2.2. Modeling the hydrogen diffusion process in the sample*

Let us examine the process of heating the sample in vacuum on the example of titanium samples used in the experiments. The shape of the sample is close