# INVESTIGATION OF HYDROGEN INDICATORS OF THE MATERIALS BRITTLENESS, FATIGUE AND DESTRUCTION

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*In this paper we describe the equipment that makes it possible to obtain information on the structure of hydrogen bonds within the material according to the hydrogen extraction curve at heating a sample in vacuum.*
*The experiments we conducted have confirmed that fatigue phenomena and destruction of structural materials are accompanied by increased concentration of lightly bound hydrogen in the destruction zone. This concentration may be considered as an indicator of the materials brittleness, fatigue and destruction.*

**Keywords:** hydrogen brittleness, diffusely hydrogen, brittleness, fatigue and destruction

## Introduction

Hydrogen that is contained in the structural flaws of constructional materials is an indicator of their presence and accumulation in the process of operation. It is known that, at application of mechanical loads, hydrogen inside the metal is concentrated in the areas of tensile mechanical stresses (Gorsky effect [1]).
On the other hand, elevated hydrogen concentrations are often one of the causes of destruction. Saturation with hydrogen from the outside ultimately leads to hydrogen brittleness.
Accumulation of hydrogen in the destruction zone occurs both by ingress from outside and by redistribution of natural hydrogen inside the material.
For practically all the structural materials, natural hydrogen concentrations are as low as decimal ppm fractions to ppm units, and there have been very few studies of their effect on the mechanical properties.
It is known that, inside the materials, hydrogen is found in traps with different binding energies. In steels the total hydrogen content is 0.1-6 $n.cm^3/100g$, while

it is only hydrogen with a low binding energy that affects the strength, i.e. diffusively mobile hydrogen. In aluminum alloys the entire hydrogen diluted in the metal has a low binding energy – about 0.2-0.8 eV. The concentrations that are critical for the mechanical strength of weakly bound hydrogen in steels and aluminum alloys are similar – they are decimal ppm fractions. In aluminum alloys it includes the entire diluted hydrogen, while in steels it amounts to 5-10% of the total amount of diluted hydrogen.

Measuring such low hydrogen concentrations at a mass of the examined sample of 1-3 g presents a scientific and engineering problem. Therefore, as a rule, all the information on the connection between hydrogen concentrations and the mechanical state of the metals was obtained after preliminary saturation of the samples with hydrogen. Saturation from the outside results in a disturbance of the natural picture of hydrogen distribution in accordance with binding energies, and thus the laws established experimentally do not always work in case of usual mechanical loading.

We have developed a precision analyzer (AV-1) that makes it possible to accurately measure natural concentrations. The sensitivity of the analyzer is such that it is possible to measure the amount of hydrogen in the traps whose volume is thousands of times lower than the total amount of hydrogen extracted from the sample.

The method of high-temperature vacuum extraction using analyzer AV-1 was applied for investigating the defective structure of materials subjected to fatigue failure and to destruction at uniaxial tension. When this method is applied, the sample does not heat up to a melting temperature; consequently «natural» hydrogen must carry the information on the status of the crystal lattice of the metal after its manufacture and operation.

The method developed for analysis of the dynamic curves of vacuum extraction enables us to determine the binding energy and the volumes of traps of various nature, and the constants of hydrogen diffusion in the sample under examination.

We've the instrument for correlation investigation between the binding energy and the volumes of traps and mechanical conditions of the materials.

## 1 Experimental equipment

The precision hydrogen analyzer AV-1 was developed for determination of hydrogen content in metals and alloys under plant laboratory conditions and used for output control of castings from different alloys.

The analyzer operates on the mass-spectrometric principle. The sample preparation includes the application of a vacuum extractor and an oven. In the process of analysis the metal sample inside the metal extractor gradually heats up to an extraction temperature of 400-800 $^{o}$C. The temperature of the analysis is below the melting temperature of the sample. The gases released at heating in vacuum are analyzed by the mass-spectrometer. The time dependence of the hydrogen flow $q(t)$ is registered by the digital registration system in the form of an extraction curve. The extraction curve for aluminum alloy AMg-6 is shown in fig. 1.

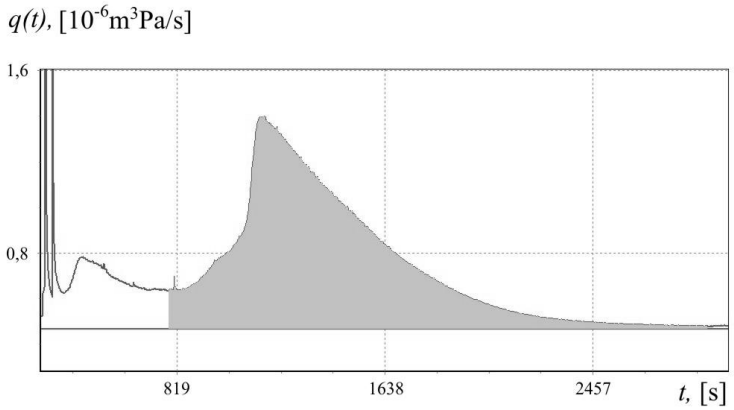


**Figure 1:** The extraction curve for simple aluminum alloy AMg-6

In order to determine the content of hydrogen in solid samples from alloys of titanium, copper, magnesium and in steels, it is common practice to use two rapid methods: spectral and that of melting in the flow of the inert carrier gas. These rapid methods require regular (once a shift, or even once an hour) calibration by using hydrogen content standards - the State standard samples (SSS). The SSS certificate shows the attested value of hydrogen content in the standard sample and the admissible discrepancy at a confidence probability of 0.95. For aluminum alloys the relative admissible discrepancy value is from 6 to 30%.

When using absolute methods to determine hydrogen content, the sample is heated in vacuum. The gas released from it is accumulated in the calibrated volume. Once the extraction is over, the pressure within that volume is measured. On the basis of the pressure, the total amount of the extracted hydrogen and its content in the sample can be calculated. The hydrogen adsorbed on the surface of the sample is subtracted from the total amount as a predetermined correction. This approach can result in a considerable systematic error. In fig. 1 the peaks that correspond to the surface and diluted hydrogen are divided by color. The amount of the surface hydrogen (white square under extraction curve) exceeds the amount of the diluted (grey square under extraction curve) by 0.3 times.

We have developed the measure of the molecular flow of hydrogen in vacuum for calibration of the mass-spectrometer.

Independent tests of the standard were carried out at D.I. Mendeleev VNIIM (St. Petersburg) over a period of 8 months in 2004-2005.

The average hydrogen flow value is 7.70·10-7 $m^3$Pa/s, the relative root-mean-square error value of the random component of measurements is ±1%. The relative value of the admissible discrepancy at a confidence probability of 0.9 is 1.7%.

Thus we have developed a highly measurement complex for absolute measurement of hydrogen content in a solid sample of practically any composition.

The high sensitivity of AV-1 and representative statistical data (about 30,000 points per curve) make it possible to see a number of maxima on the extraction

curve. By the position of the maximum and by its shape, one can determine the binding energy, diffusion constants and cumulative volume of the flaws, to which separate peaks correspond.
Fig. 2 shows the experimental curve for titanium alloy PT-7M. Opposite the peaks, one can see the hydrogen binding energies that correspond to them.

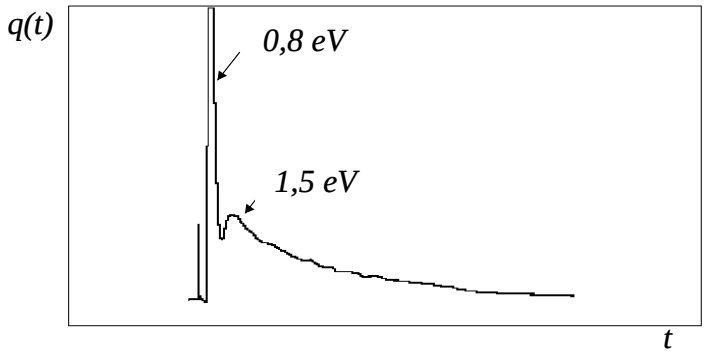


**Figure 2:** Extraction curve for titanium alloy PT-7M indicating the binding energies that correspond to separate peaks of the curve.

As a result of numerous tests it was possible to establish that hydrogen inside metals and semiconductor materials occupies discrete energy levels. E.g., for aluminum alloys, 2-4 levels can be observed within the 0.2 to 0.8 eV range.

## 2 Accumulation and redistribution of hydrogen in the process of operation of structural materials

By using the AV-1 analyzer, a study was made of 4 mm-thick plates from aluminum-magnesium alloy (h=4 mm). Fatigue cracks were formed in the plates at cyclic loading. After the plates were cut into samples 7 mm wide and 15 mm long, the hydrogen content in these samples was determined. The map of hydrogen distribution relative to the crack is shown in fig. 3.

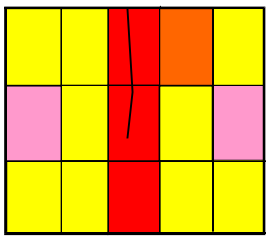

**Figure 3:** Map of hydrogen distribution in the plate.
In red are shown the hydrogen concentration values of 1.9-2.0 [n.cm$^3$/100g],
In orange - 0.00017 [mass%], in yellow – 1.3-1.6 [n.cm$^3$/100g],
In violet – 1.2-1.3 [n.cm$^3$/100g]

The zone on the crack formation line has a hydrogen content that is 1.5 times higher than the background value. The distance at which the gradient of hydrogen concentration is observed is about 3h (i.e. three thicknesses of the plate). An elevated hydrogen content is observed on the crack line and its continuation where it is not visible.

Full concentration of hydrogen is not the only indicator of accumulation of flaws. The shape of the extraction curve on the fatigue crack line has its special features. It is clearly seen on the experimental curves in fig. 4 and fig. 5 that in the samples from the destruction zone the first peak area is four times larger, while the other peaks are smaller, than in the background samples. Our equipment enables separating various binding energies, even those of weakly bound diffusively mobile hydrogen, and register redistribution of hydrogen among the traps at destruction.

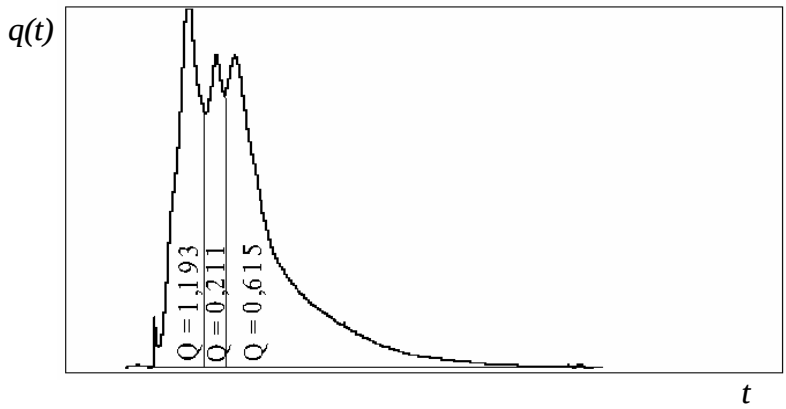


**Figure 4:** Experimental extraction curve of the sample on the fatigue crack line

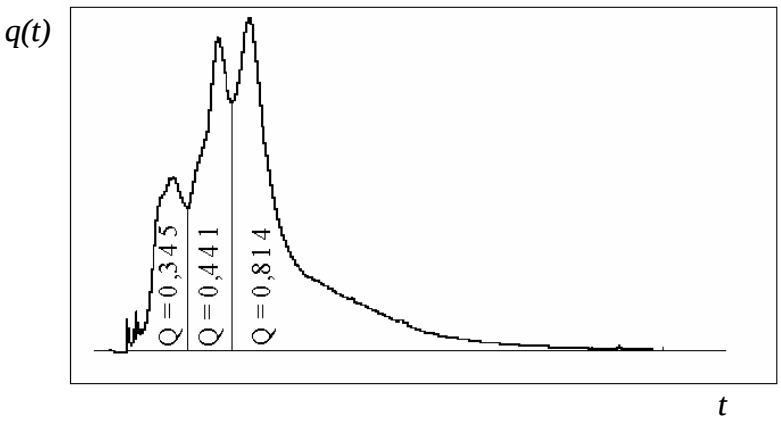


**Figure 5:** Experimental extraction curve of the background sample

Thus, at fatigue destruction, the distribution of hydrogen according to binding energies in the destruction zone radically changes. The total amount of the diluted hydrogen also increases, but not so significantly.

The samples (about 5 mm in dia., 5mm high) used for determination of hydrogen content were fashioned out of a previously torn St3 steel sample. A photo of the sample after application of a mechanical load is shown in Fig. 6. The same photo shows the cutting scheme with the ordinal numbers of the samples for hydrogen content determination. It is clearly seen that that the initially cylindrical part of the sample has been subjected to plastic flow at stretching. Therefore the average diameter and masses of samples №№ 3, 4, 5, 7 are different. On the contrary, sample № 6 was machined on a lathe out of a practically non-deformed part.

In the destruction zone (sample № 3) mechanical strains were at a maximum.

In samples №№ 4, 5, 7 they monotonously decreased but were clearly above the yield point.

In sample № 6 fashioned out of a fastened part of the sample the strains were minimal.

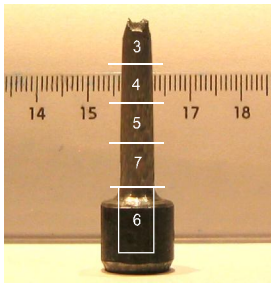


**Figure 6:** The St 3 sample destroyed at axial tension with a scheme for cutting testing samples. The upper part is the destruction zone; the lower part is the zone of fastening the sample in the tensile-testing machine.

The diagram of distribution of diffusively mobile hydrogen along the sample length is given in Fig. 7.

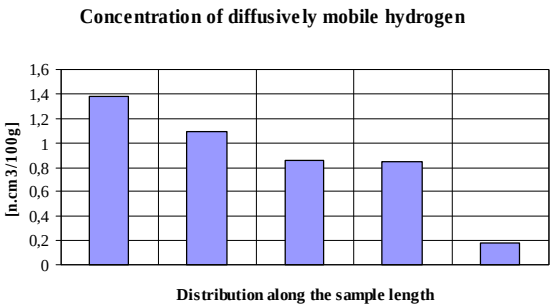


**Figure 7:** Distribution of diffusively mobile hydrogen. On the left is the destruction points, on the right – the sample machined from a non-deformed section.

In the same way as in the previous case, strongly bound hydrogen has much larger concentrations in the non-deformed area. Fig. 8 shows a distribution diagram for concentrations of strongly bound and diffusively mobile hydrogen along the sample.

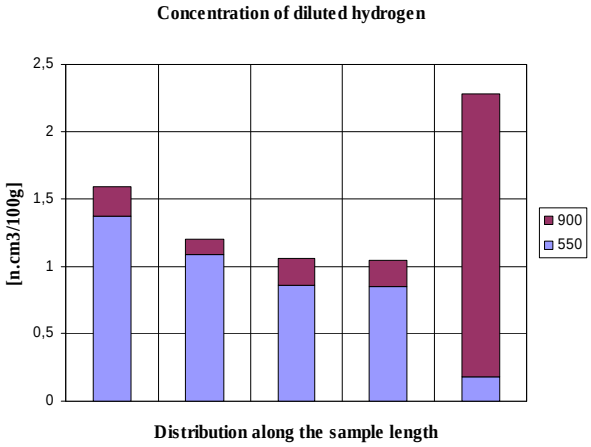


**Figure 8:** Distribution of concentrations of diffusively mobile (550) and strongly bound (900) hydrogen along the sample. The upper level of the columns represents the cumulative concentration of hydrogen in the sample. On the left is the destruction point, on the right is the sample machined from a non-deformed section.

Analysis of the experimental data shows that full concentration of hydrogen is approximately equal everywhere. In the destruction zone, practically all the hydrogen is in the diffusively mobile state, and on the contrary - in the zone not subjected to plastic flow it is in the strongly bound state.

## 3 Discussion of the results

The capability of gases for dilution in metals is known [3]. In many cases gases that do not form stable chemical compounds with alloy components are accumulated along the grain boundaries in traps of various nature.

There is a known method of examining the dislocation structure of solids by low-temperature saturation of metals with inert gases (helium, argon etc.). Upon subsequent heating of the samples up to various temperatures, the dynamic of gas release was studied. Determined by using the dynamic curves of gas release – extraction curves – were: density of dislocations and the rate of dislocation density changes. It was experimentally discovered that adsorption of gas molecules with a very high binding energy is possible in micro-defects on the free surface of the crystal. E.g., the binding energy for chemically inert helium is about 1 eV, which is close to the chemical bond energy [4].

In many cases it is impossible to explain elevated concentrations by hydrogen diffusion from the environment as the normal hydrogen concentration in the air

is 0.5 ppmv. The literature provides descriptions of two mechanisms of hydrogen accumulation – transfer by micro-defects inside the material and release of hydrogen from water at corrosion.

In our experiments we managed to study the fine structure of hydrogen bonds in metal. We studied natural concentrations and discovered that the fatigue phenomenon and simple destruction at uniaxial tension are accompanied by accumulation of weakly bound hydrogen. The accumulation itself can be explained by the processes of hydrogen transfer at formation of new structural micro-defects in the destruction zone. It is most probable that, at application of strains, hydrogen is bound with free surfaces thus causing weakening of the material due to a reduction of the free energy and fixation of the defects. After rupture, the tensile stresses disappear and the hydrogen is squeezed out into a weakly bound state.

We are in opinion that hydrogen has the discreet character of the energy levels in the solid body. Therefore each peak of the extraction curves corresponds to a different character of the hydrogen bond with the crystal lattice of the material.

If our hypotheses are true, prevention of hydrogen diffusion inside the material serves to substantially increase its fatigue strength and increases maximum deformations. The same effect can be obtained by decreasing the gas permeability of the material surface, e.g. by designing parts with an increased surface tension or by using special coatings. The absence of hydrogen inflow from the outside will increase the service life of the part.

This fact makes it possible to use the measurement results for hydrogen concentration distribution according to binding energies not only for analysis of the causes of destruction and material quality control, but also for the development of new materials with enhanced mechanical characteristics.

Application of the methods developed to non-metallic material opens yet another application area of hydrogen diagnostics.

## Conclusions

In this way,

- We have developed the equipment that makes it possible to obtain information on the structure of hydrogen bonds within the material according to the hydrogen extraction curve at heating a sample in vacuum. The accuracy of determination of the extraction curve makes it possible to obtain information on both the hydrogen binding energy in the metal and on the concentration of mechanical flaws.
- The experiments we conducted have confirmed that fatigue phenomena and destruction of structural materials are accompanied by increased concentration of lightly bound hydrogen in the destruction zone.
- Comparison of the results of our analyses made in order to determine hydrogen content with the structural investigations data enables us to conclude that hydrogen fills up all the discontinuity flaw and defects in metals reducing their surface energy. This results in reduced strength of the material.
- It was fir the first time detected that mechanical loads result in a substantial redistribution of hydrogen according to the binding energies inside metals.

- The suggested calculation methods enable us to make approximation of the experimental extraction curves and determine the diffusion constant and the activation energy for every peak of the curve.
- The energy activation values obtained as a result of processing the experimental data for aluminum alloys are within the 0.2 to 0.8 eV range, which enables us to conclude that that there is no chemically bound hydrogen in these alloys.
- This approach to investigation of the properties of materials does not require preliminary saturation of the samples under study with hydrogen. Natural hydrogen within the metal carries the information on the past history of the material, which, once the methods are further developed, will make it possible to obtain more detailed information from the measured extraction curves.
- The concentration of lightly bound hydrogen may be considered as an indicator of the materials brittleness, fatigue and destruction.
- The metrological complex that includes a hydrogen analyzer and calibration standards enables implementing the principle of unity of measurement means at analyzing various metals and alloys, and obtaining additional information on the volume and structure of the internal and surface mechanical defects.

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