"SMART Hydrogen" and its determination in micro and nanostructures in materials

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Abstract

The investigation of the micro and nanostructures - hydrogen interaction gives as new information about nano, micro and meso-scale of the material properties. The presentation reports some experimental proof of this interacton on example of high-temperature extraction of hydrogen from aluminum alloys, silicon plates and nanomaterials.

1 Introduction

Hydrogen in small concentrations is containing in all materials.

In the metals, the hydrogen is contained in the traps with various bounding energies. It has been established, cf. [1], that thermo-mechanical loading results in the hydrogen redistribution over the traps. Diffuse hydrogen accumulates mostly in the aluminum alloys while strongly bounded hydrogen accumulates mostly in the titanium alloys.

The hydrogen's influence on materials' properties is of crucial importance. Even for concentrations of about 1 hydrogen atom per 10000 atoms of the matrix one can observe the hydrogen embrittlement.

This influence can not be explained by means of the hypothesis of the uniform distribution of hydrogen in the matter. Only the localization of hydrogen in microdefects, on the grains' boundaries and on the surface of nanostructures in the material can explain the considerable change in mechanical properties.

The difficulties with determination of the small volume hydrogen traps prevents the direct determination such traps in all materials. Only hydrides in titanium and zirconium alloys may be determined as small heterogeneousness during microscopic investigations.

The new highly sensitive hydrogen analyzer AV-1 allows one to observe the hydrogen emission from microcracks and dislocations on the surface of specimen.

2 Experimental Results

The high temperature vacuum-extraction method of the hydrogen content determination enables one to measure addition parameters of the hydrogen content distribution inside the materials.

The highly sensitive hydrogen analyzer AV-1 utilizes the mass-spectrometric principle. The specimen preparation requires a vacuum extractor and an oven. The specimen inside the metal extractor is heated gradually up to an extraction temperature of 400-900^{o}C. The temperature needed for analysis is below the melting temperature of the specimen. The gases released at heating in vacuum are analyzed by means of the mass-spectrometer. The time-dependence of the hydrogen flux $q(t)$ registered by means of the data acquisition system yields the so-called extraction curve.

The hydrogen bound energy levels and diffusion constant may be determined [2]. In extraction curves are well seen small peaks Fig 1.

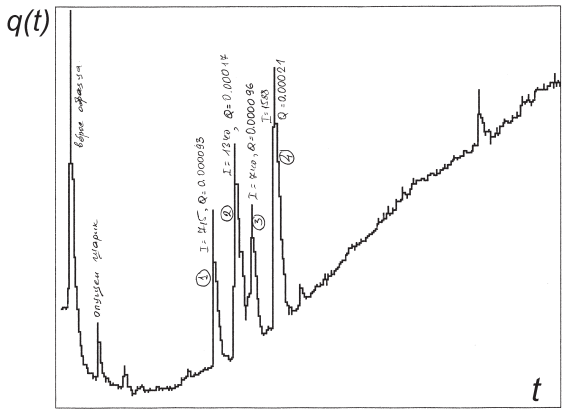

Figure 1: The part of the extraction curve for aluminum alloy D-16 with small peaks

The volume of molecular hydrogen that correspond with this peaks is approximately 10^{-8}-10^{-9} mm^3. The average size of grains in the aluminium alloy D-16 is 0.1 mm. So each small peak may correspond to one micro crack or dislocation on the surface of the the specimen.

This hypothesis has been verified. The experiments on dispersion of the hydrogen diffusion on some specially created defects of the lattice of the silicon monocrystal were carried out. The idea was to create some monocrystal internal defects of the size about 30μm and compare the results of the high-temperature vacuum extraction of hydrogen from the original monocrystal and the monocrystal with the above defects. In order to create the defects we used an infrared pulse laser with the wavelength of 1024 nanometers, the duration of the impulse of 12 nanoseconds and the energy of one impulse 2 mJ. Such a laser is usually used for creating chips in the optical glass. The coherent infrared radiation of an impulse was focused at a certain point in the glass. The size of the focused spot is about 30μm. In the focus the energy density is about $2{\cdot}10^{15}$ W/m^2. Under such energy density the substance can warm up to 1500 ^{o}K depending on the coefficient of radiation absorption. In the warming-up place one observes a visible chip.

We had used plates of monocrystal silicon of the thickness of 0.3 mm.

In order to present the experiment the plates are placed in a parallelepiped made of the optical glass.

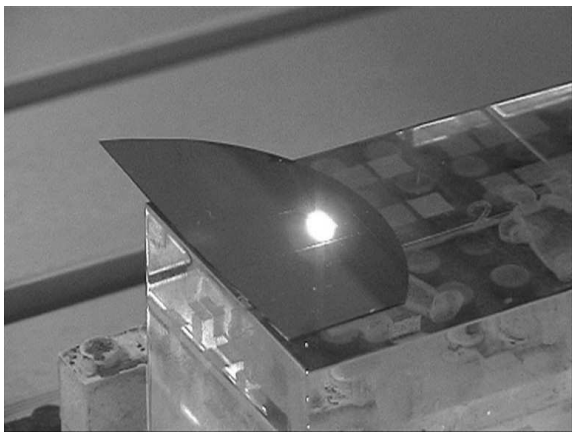

Figure 2: Tests on the silicon plates

The typical curves for the sample with and without defects are shown below. It is easy to observe that after the extraction of the main hydrogen there begins a transfer of the gas accumulated in the defects which in turn results in the noise consisting of a set of peaks. These peaks are due to the emission of hydrogen from silicon. For the regular dimples these peaks become regularised and increase their sizes, that is, the volume of the extracted hydrogen increases as well. Besides, the

temperature, at which these pulsations become considerable for the sample with chips, is 200^{o}C than that for the sample without chips. The observed effect can be interpreted as regularisation under the diffusion caused by a uniform grid of chips on the surfaces of the sample.

Some other plates (not radiated by the laser) and the plate with the chips on the surface were cut on samples of the sizes 8×15 mm^2. After that they were placed in vacuum for carrying out the experiments on the hydrogen diffusion.

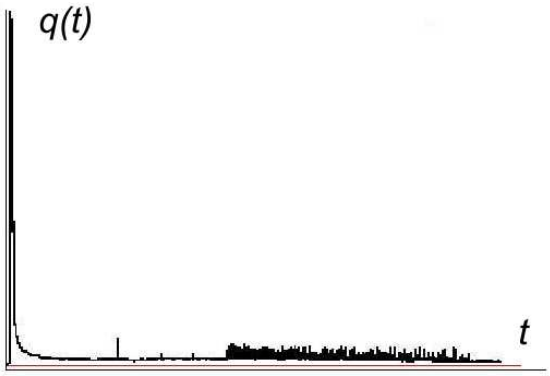

Figure 3: The extraction curve for the non-destructed silicon

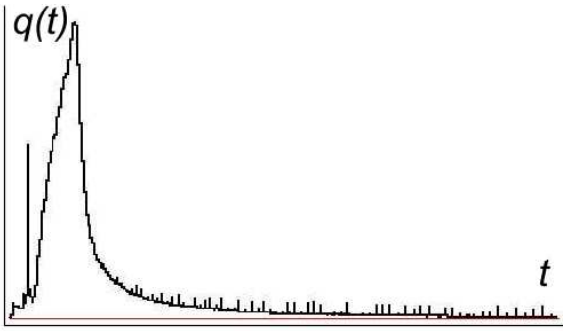

Figure 4: The extraction curve for the destructed silicon

In order to close this part of the present report it is worth mentioning that the most surprising in the results of the performed test is that the number of peaks in Fig. 4 is exactly coincident with the number of dimples in the silicon plates. The understanding of this fact remains to be tackled.

So the verification of the hypothesis gives as ability to determine the micro defects with the hydrogen analyser. We can determine both the number of the surface micro defects and their average volume.

The experiments with steels, including zinc coated steels are described in what follows. The steal plates from St 70 alloy were zincing in galvanic process. The microscopic investigations determined small spherical pores inside thin zinc layer (thickness 10 μm). This plate were cut on samples of the sizes 8×20 mm^2. After that they were analyze in AV-1 parallel with samples without zincing. The fragments of the extraction curves are shown in Fig. 5-6.

One can see that there are many small peaks in the extraction curve of the sample of St 70 with zinc layer. The small pores with diameter 0.1 μm were observed during microscopic investigations. Probably these pores are filled with hydrogen. The spherical form of the pores verifies this hypothesis. The comparison of the analyze results for samples with and without zinc layer gives the hydrogen concentration 1000 ppm in this layer.

Such concentration redistributes inside the steel owing to diffusion under mechanical loading. So the hydrogen brittleness progresses after some cycles of the bending loading.

Internal defects do not cause these small peaks because of hydrogen diffusion. But we can generalize the hypothesis about hydrogen-filled micro defects for the aluminum alloy A8.

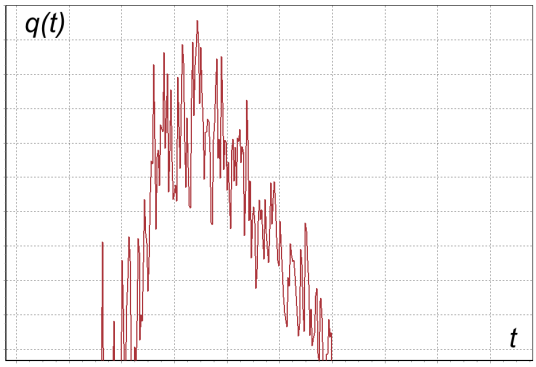

Figure 5: The fragment of the extraction curve - emission of hydrogen from sample of St 70 with zinc layer h=10 μm

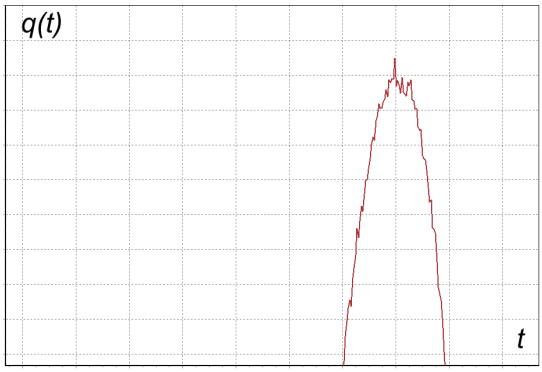

Figure 6: The fragment of the extraction curve - emission of hydrogen from sample of St 70 without zinc layer

Suppose that the structure defect has a form of tubes created the joint of three grains, as shown in Fig.7.

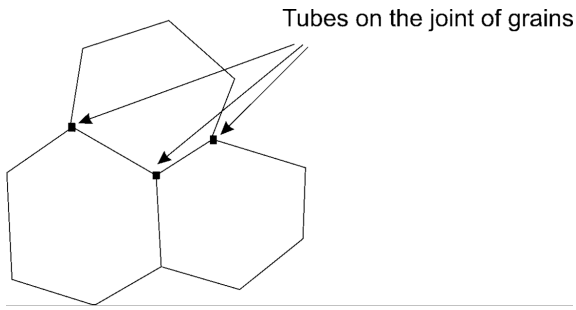

Figure 7: Scheme of the defect position on the joint grains

According to the data available in literature size of grains in technical pure, not annealed aluminum equals d=90μm. Let us take the cavities in the form of tubes. The length of the tube equals the size of the grains. The transverse dimension of the probes not undergoing loading is γ=10% of the length.

To estimate the cavity length, let us suppose that the grain has the form of a cube with length of edge b. Then from the condition of equality of the grain volumes its presentation in the form

sphere and cube one obtains:

$$b^3 = \frac{\pi d^3}{6}$$

In this approximation the volume of one cavity equals $b^3\gamma^2 = 3.8{\cdot}10^{-9}$ cm^3. The amount of hydrogen at each maximum of the extraction curves in Fig.8 is determined by integration of this maximum and equals $Q_1 = 1.18$ n.mm^3, $Q_2 = 0.82$ n.mm^3, $Q_3 = 1.8$ n.mm^3, $Q_4 = 2.7$ n.mm^3. By dividing the total amount of hydrogen by the volume of single cavity and the volume of the analyzed probe one obtains the concentration of defects corresponding to each maximum: $Z_1 = 4.2{\cdot}10^5$ cm^{-3}, $Z_2 = 3.2{\cdot}10^5$ cm^{-3}, $Z_3 = 6.4{\cdot}10^5$ cm^{-3}, $Z_4 = 9.6{\cdot}10^5$ cm^{-3}.

In the above approximation the total number of traps in 1 cm^3 of the probe, calculated from hydrogen amount, is $Z = \sum Z_i = 2.34{\cdot}10^6$ cm^{-3}, and the grain concentration is $2.58{\cdot}10^6$ cm^{-3}. The concentrations coincide within 10%.

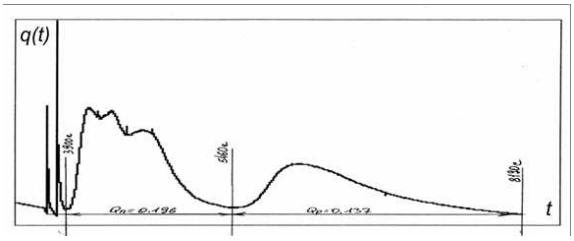

Figure 8: The extraction curve fore pure aluminum A8

Thus one can draw the conclusion that hydrogen at atmospheric pressure fills all cavities along the grain boundaries. Such cavities were discovered during microscopic investigations.

In extraction curves of Fig. 9 we indicate the temperatures of the samples during extraction of the hydrogen. These samples were made from nano-crystalline stainless steel. One can see that one peak corresponds to temperature 450 ^{o}C. This is the temperature of the nanocrystalline stainless steel recrystallization.

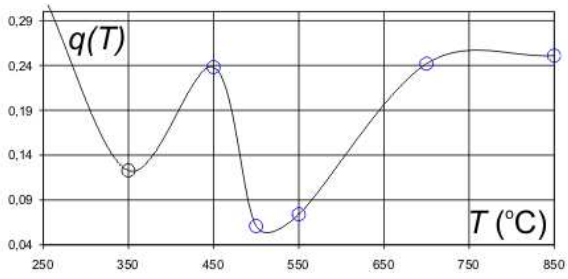

Figure 9: The extraction curve for nanocrystalline stainless steel

When microdefects and nanostructures are present, hydrogen is localized on free surface and decreases the free surface energy. This decrease results in termination of growth of micro- and nanocrystals and, on the other hand, leads to reduction of crack resistance and, in turn, to brittle destruction of the material.

It became clear that for the materials which have no stable chemical link with hydrogen, nearly whole hydrogen is concentrated in microdefects and on the surface of micro- and nanograins. Aluminum alloys, some steels, ceramic and semiconductors eject hydrogen.

Thus, the diagnostics in terms of the amount of extracted hydrogen turns out to be efficient and less effort-consuming than other methods of investigations. For instance, in order to determine an average concentration of microdefects by means of microtomography one needs to conduct measurements of about 12 hours whereas the hydrogen analysis takes 45-60 min.

3 Conclusions

The highly sensitive hydrogen analyzer AV-1 allows one to observe the hydrogen emission from microcracks and dislocations on the surface of specimen. The emission occurs during the specimen heating in vacuum and is fixed in the form of small peaks on the extraction curve.

The results of experimental investigations of aluminum alloys and steels, including zinc coated steels are shown. The size of defects determined by means of optical and probe microscopy is in a good agreement with the volume of hydrogen extracted under the atmospheric pressure. This allows us to assume that the microcracks and defects are filled by hydrogen.

These assumptions were proved on monocrystals of silicon.

Summarising we can say that we suggest a new approach to experimental investigation and diagnostics of microdefects and nanostructure in materials.

Acknowledgements

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References

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