Proceedings for the Joint U.S. Russia Conference on Advances in Materials Science

The Determination of the Small Hydrogen Traps as Nucleus of Fatigue and Destruction

V. A. Polyanskiy,[*1] A. M. Polyanskiy,[†] A. K. Belyaev,[‡] Yu. A. Yakovlev,[*]

* St.-Petersburg State Polytechnic University, Polytekhnicheskaya, 29, St.-Petersburg, 195251, Russia

† RDC Electronbeamtech, St.-Petersburg, Bronevaya 6, 198188, Russia

‡ Institute of Problems in Mechanical Engineering of the Russian Academy of Sciences, Bolshoy pr. V.O. 61, St.-Petersburg, 199178, Russia

The method of investigation of the materials fatigue and destruction is suggested. This method is based on the influence of the small hydrogen concentration on materials properties. The measurement of the hydrogen concentration and its binding energy enables one to determine the fatigue and destruction zones in the materials after the mechanical, fatigue and thermo-mechanical loading.

Introduction

Considerable concentrations of hydrogen contained in metals and non-metals 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 the influx from outside and redistribution of natural hydrogen inside the material. For practically all the structural materials, the concentration of natural hydrogen is from decimal ppm to several ppm, and there have been very few works on its influence on the mechanical properties.

It is known that the hydrogen in materials is found in the 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. diffusive hydrogen. In the aluminum alloys the entire hydrogen diluted in the metal has a low binding energy which is 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 also about decimal ppm. In the aluminum alloys it includes the entire diluted hydrogen, while in steels it is up to 5-10% of the total amount of diluted hydrogen. So the volume of the hydrogen traps with low binding energy is very small.

Measuring such a low hydrogen concentration in the specimens of the mass of 1-3g presents a challenging scientific and engineering problem. Therefore, as a rule, any information on the relation between the hydrogen concentrations and the mechanical state of the metals was obtained after a preliminary saturation of the specimens by hydrogen.

[1] vapol@electronbeamtech.com

Such a saturation results in a distortion of the natural picture of hydrogen distribution over the traps with different binding energies, and thus the experimentally established laws do not always work in the case of pure mechanical loading.

We have developed a precision analyzer (AV-1) that makes possible an accurate measurement of low natural concentrations. The analyzer is so sensitive that we can measure the amount of hydrogen in the traps whose volume is thousands times smaller than the total amount of hydrogen extracted from the specimen.

The method of high-temperature vacuum extraction by analyzer AV-1 was applied for investigating the defective structure of materials for fatigue failure and destruction under the uniaxial tension.

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 the various nature, as well as the constants of hydrogen diffusion in the specimen under examination.

Method of investigation

Measurement

The precision hydrogen analyzer AV-1 is developed for determining the hydrogen content in metals and alloys under the laboratory conditions and used for output control of alloys castings.

The analyzer 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 extraction curve for specimen of AMg-5 aluminum – magnesium alloy is displayed in Figure 1.

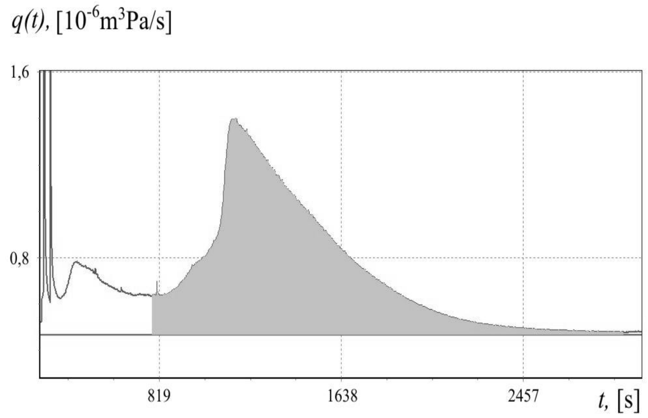

Figure 1. The extraction curve for aluminum magnesium alloy AlMg5

Estimation of the hydrogen binding energy in metal and the diffusion constants

The high sensitivity of AV-1 enables observing a number of maxima on the extraction curve. Analysing the position of the maximum and its shape, one can determine the binding energy, diffusion constants and cumulative volume of the flow with the corresponding separate peaks, cf. [1].

Figure 2 shows the experimental curve for the monocrystal silicon. The hydrogen binding energy is indicated near the corresponding peak.

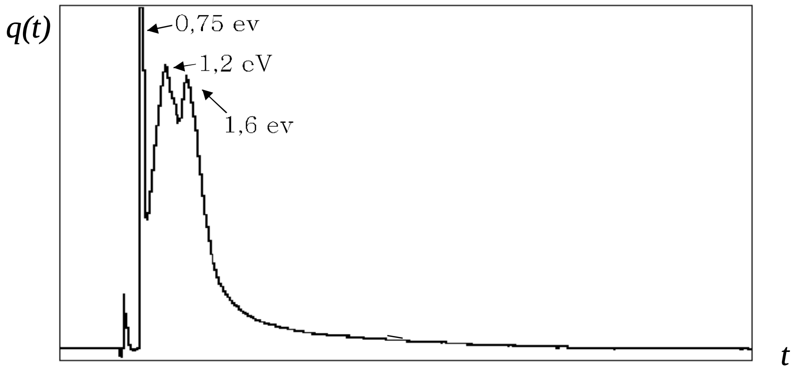

Figure 2. Extraction curve for the monocrystal silicon indicating the binding energies that correspond to the certain peaks of the curve

The result of many tests confirms that the hydrogen inside metals and semiconductor materials has discrete energy levels. E.g. for the aluminum alloys, two-four levels are observed within the range 0.2 to 0.8 eV.

Results and Discussion

For our analysis we took the titanium tubes of a steam generator (diameter 22 mm, thickness 2.6 mm) which had been subjected to cyclic non-uniform heating. The temperature of the cold part of the tube was 100 ^{o}C and that of the hot part was 300 ^{o}C. The temperature drop within the 15 cm length was about 200 ^{o}C. The ends of the tube were fixed which results in the thermal strains. After approximately 15,000 loading cycles, the fatigue cracks formed at the point with minimum temperature.

In order to analyze the hydrogen content the tube was cut into small specimens. The schematic of the specimens' positions relative to the crack is shown in Figure 3.

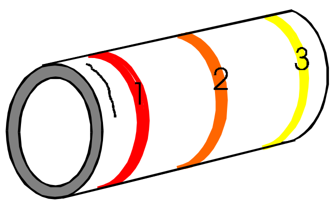

Figure 3. Schematic of the titanium tube with the crack and the specimens' positions relative to the crack. The red denotes the hydrogen concentration values of 498 [ppm] while the orange and yellow ones stand for 329 [ppm] and 186 [ppm], respectively.

The hydrogen content in the tubes was controlled before the steam generator started. The initial content was 20 [ppm]. In the process of operation, the hydrogen content in the tube went up more than by 10 times, while that in the destruction zone increased by 25 times. In the destruction zone, the hydrogen concentration is 2.5 times higher than that in the other parts of the tube. Therefore one observes the absorption of hydrogen from the outside and its redistribution into the fatigue destruction zone.

The full concentration of hydrogen is not the only indicator of accumulation of the defects. The shape of the extraction curve on the fatigue crack zone is of special interest. The experimental curves in Figures 4 and 5 show that the last peak area in the specimens after loading is the largest one if we compare it with the unloaded specimen.

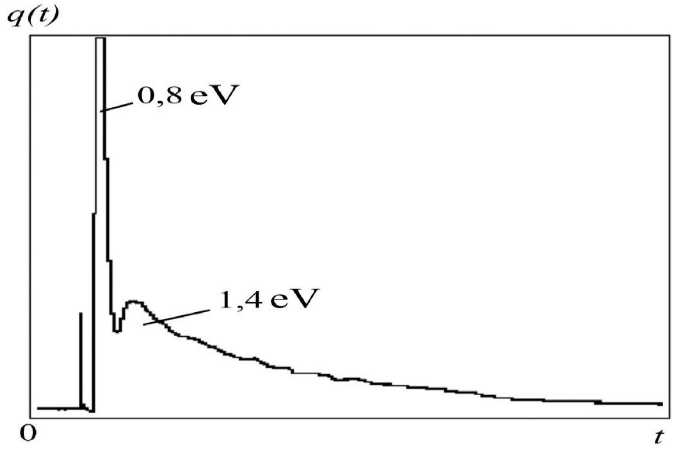

Figure 4. Experimental extraction curve of the unloaded specimen

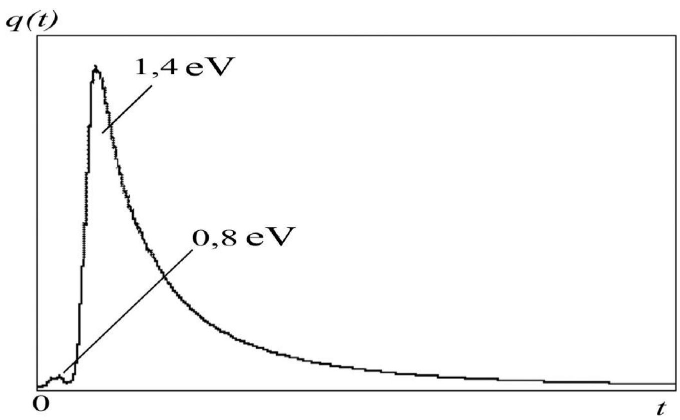

Figure 5. Experimental extraction curve of the specimen after loading

The gases are known to dilute in metals [2]. In many cases the gases which do not form stable chemical compounds with the alloy components are accumulated on the grain boundaries in the traps of various natures. There exists a 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 specimens the dynamics of gas release is studied. The dynamic curves of the gas release – extraction curves – are used for determining the dislocation density and the rate of change in the dislocation density. It was experimentally discovered that the adsorption of gas molecules with a very high binding energy was possible in the 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 [3].

In many cases it is impossible to explain the increased concentrations by hydrogen diffusion from the environment as the natural hydrogen concentration in the air is 0.5 ppmv. The literature provides descriptions of two mechanisms of hydrogen accumulation, which are the transfer by micro-defects inside the material and the release of hydrogen from water under 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 is accompanied by accumulation of the 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, due to the strains, the hydrogen is bound with free surfaces and it causies 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 of the opinion that the hydrogen has the discrete 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 correct then the prevention of hydrogen diffusion in materials serves to substantially increase in its fatigue strength and the 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

- 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 specimen 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 the fatigue phenomena and the destruction of structural materials are accompanied by increased concentration of bound hydrogen in the destruction zone.

- It was first time detected that the mechanical loads result in a substantial redistribution of hydrogen according to the binding energies inside metals.
- 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 specimens. The natural hydrogen in the metals contains the information on the past history of the material, which, once the methods have been developed, will make it possible to obtain more detailed information from the measured extraction curves.
- The metrological setup consisting of a hydrogen analyzer and the calibration standards enables implementing the principle of a single measurement utility for analysis of various metals and alloys and obtaining additional information on the volume and structure of the internal and surface mechanical defects.

Acknowledgements

- The financial support of the Sandia Corporation, contract 891092, and the Russian Foundation for Basic Research, grants 08-08-00737 and 08-01-12017, is acknowledged.

References

[1] A.M. Polyanskiy, V.A. Polyanskiy, D.B. Popov-Diumin, Diagnostics of mechanical condition of materials by method of high-temperature hydrogen vacuum-extraction", In: Proceedings of the Sixth International Congress on Thermal Stresses, vol. 2, pp. 589-592, Vienna, Austria, 2005.

[2] B.A. Kolachev, Hydrogen brittleness of metals (in Russian), Metallurgy, Moscow, 1985.

[3] O.V. Klyavin, Dislocation dynamic diffusion in crystal bodies (in Russian), FTT, vol. 35, No. 3, 1993, pp. 513-541.