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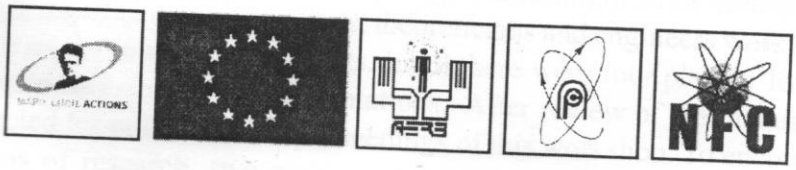

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Investigations of the Process of Material Fatigue, Embittlement and Destruction by Means of the Hydrogen Analyzer AV-1.

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ABSTRACT

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. We describe the experiments showing that mechanical loads result in substantial redistribution of hydrogen according to the binding energies inside metals.

Introduction

Hydrogen that is contained in the structural flaws of construction materials is an indicator of its 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.

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 from a mass of 1-3 g presents a scientific and engineering problem. Therefore, as a rule, all the information on the relation between hydrogen concentrations and the mechanical state of the metals was obtained after preliminary saturation of the samples with hydrogen. Saturation from 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.

Electron and Beam Technologies, Ltd has developed an AB-1 hydrogen analyzer capable of high precision measurement of natural hydrogen concentrations. The analyzer sensitivity is high enough to permit measurement of the amount of hydrogen localized in traps whose volume is thousands of times smaller than the total volume of hydrogen dissolved in 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 natures, and the constants of hydrogen diffusion in the sample under examination.

1. Experimental Equipment

1.1. Technique of Hydrogen Concentration Determination

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 °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 A8 brand of pure aluminum is shown in fig. 1.

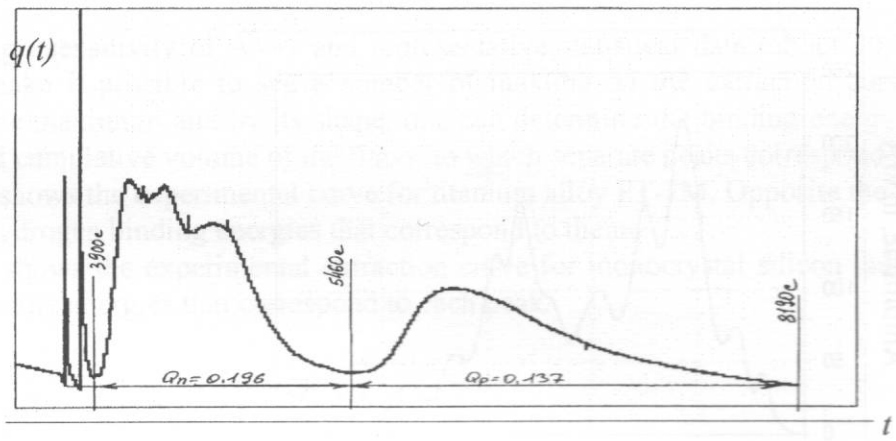

Fig 1. The extraction curve for pure aluminum of brand A8

In order to determine the content of hydrogen in solid samples from alloys of titanium, copper, magnesium and steels, it is common practice to use two rapid methods: spectral and that of melting under 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 [2]. 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 vertical lines. The amount of the surface hydrogen Qs exceeds the amount of the diluted Qd by a factor of 2.4.

The mass-spectrometric method of hydrogen registration requires calibration of the analyzer's sensitivity coefficient. We have developed a method for the measurement 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^3Pa/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 complex measurement procedure for absolute measurement of hydrogen content in a solid sample of practically any composition.

2.2. Study of the acoustic emission

The energy and spectral characteristics of the acoustic emission (AE) were studied under uniaxial tension of samples (these measurements on a sample with the working part of 50 x 10 x 6 mm at a strain rate of 1.33 10^{-3} s^{-1} were carried out on a 1231U-10 test bed at the NIKIMP pilot plant, Moscow). The mechanical to electronic AE signal conversion was achieved with a P-113 broadband piezotransducer (Volna, Chisinau, Moldova), whose frequency response is presented graphically in Fig. 2. Integral AE characteristics were determined with an AVN-3 instrument (Dal'standart, Khabarovsk) [3]. The instrument permitted measurement of AE emission intensity and of the 0.5-s averaged AE signal envelope.

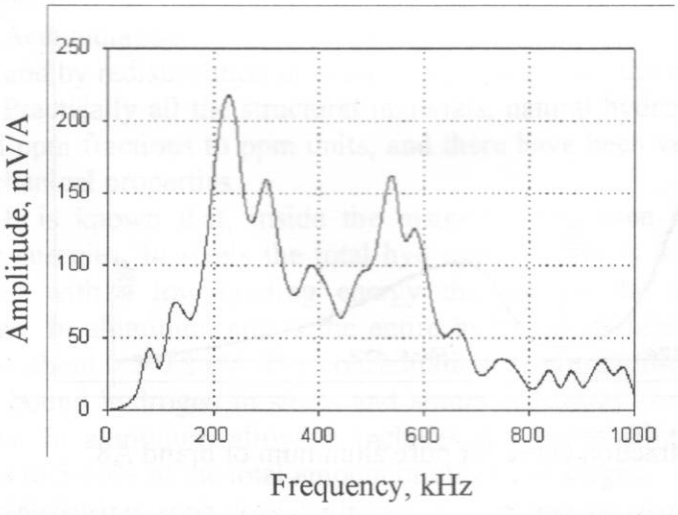

Fig 2. Frequency response of the P-113 transducer.

These measurements were paralleled by recording the loading parameters and by fast ADC conversion of AE signals at 5-MHz frequency [4]. Each recorded AE signal was

discretely Fourier transformed (by the fast Fourier transform algorithm of Cooley--Tewkey), and the power spectrum smoothened by the running average technique (fig. 2).

Digital pattern recognition techniques were employed to arrange all signals into groups by the principle of similitude of spectral density profile. This was done under the assumption that while AE signals in different groups are of different origin, within each group their nature is the same. Mathematical treatment yielded spectral images of each group (see illustration in Fig. 3) described by three curves, more specifically, mathematical expectation of normalized spectral density and its peak-to-peak value for a given group.

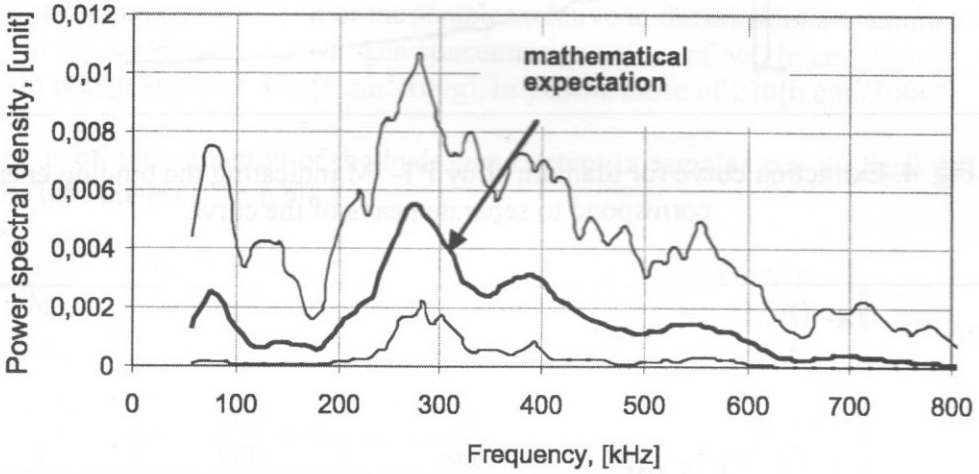

Fig. 3. Illustration of an averaged spectral profile for a group of signals

2. Assessment of the Hydrogen Binding Energy in Metal and of Diffusion Constants

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 [2].

Fig. 4 shows the experimental curve for titanium alloy PT-7M. Opposite the peaks, one can see the hydrogen binding energies that correspond to them.

Fig. 5 shows the experimental extraction curve for monocrystal silicon indicating the hydrogen binding energies that correspond to each peak.

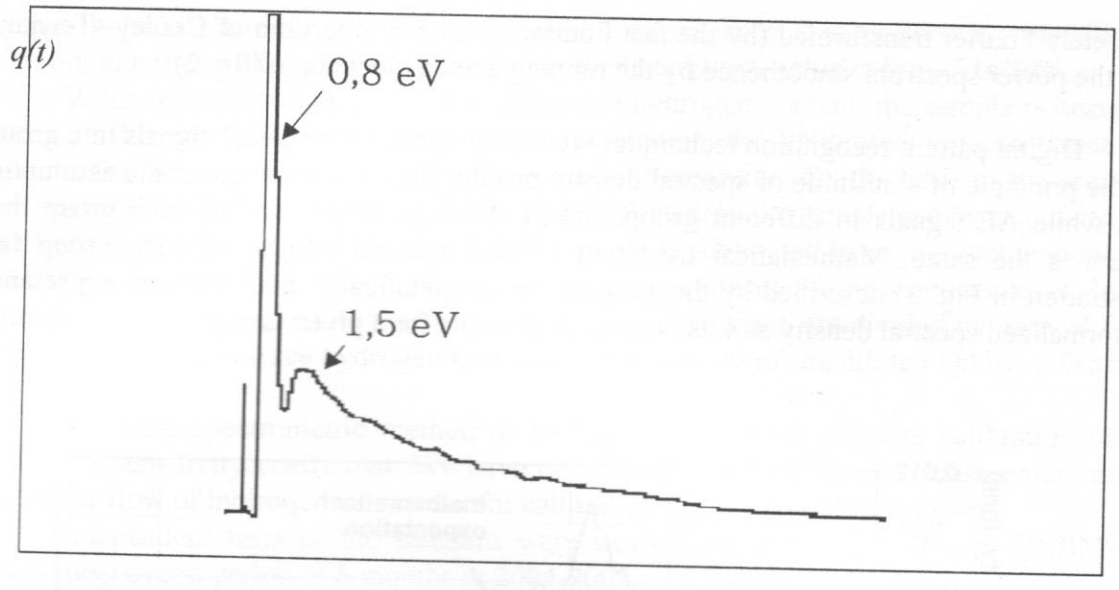

Fig. 4. Extraction curve for titanium alloy PT-7M indicating the binding energies that correspond to separate peaks of the curve.

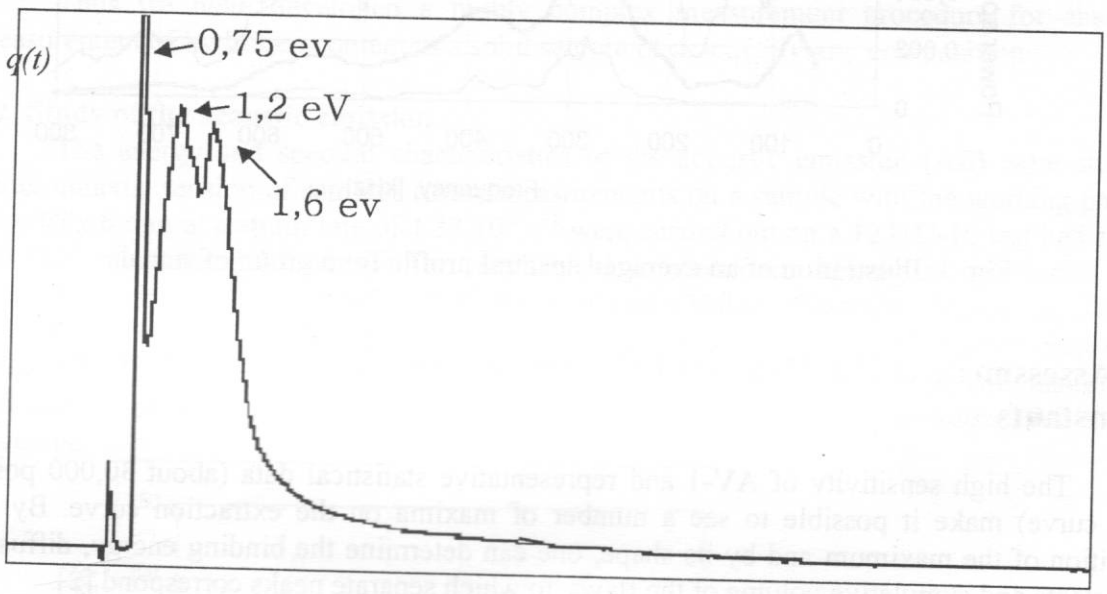

Fig. 5. Extraction curve for monocrystal silicon indicating the binding energies that correspond to separate peaks of the curve.

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.

Accumulation and Redistribution of Hydrogen in the Process of Operation of Structural Materials

Titanium tubes cut out from a steam generator (22 mm in dia., 2.6 mm thick) were subjected to prolonged cyclic non-uniform heating. The temperature of the cold part of the tube was 100 ^{0}C, that of the hot part 300 ^{0}C. The temperature drop over a 15 cm length of the tube was about 200 ^{0}C. The ends of the tube were fastened, which caused thermomechanical

strains. After approximately 15,000 loading cycles, fatigue cracks were formed in the point with the minimal temperature.

We cut the tubes to smaller samples in order to analyze the hydrogen content. The schematic arrangement of the samples relative to the crack is given in fig. 6.

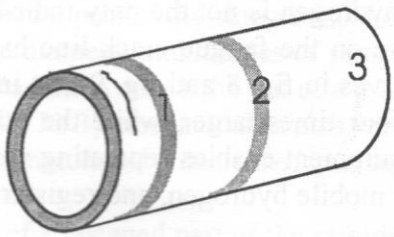

Fig. 6. Schematic positioning of the samples relative to the crack in a titanium tube.
In red are shown the hydrogen concentration values of 560 [n.cm^3/100g]
In orange those of 370 [n.cm^3/100g], in yellow those of 210[n.cm^3/100g]

The results of determination of the hydrogen content in samples cut out from different sections of the tube are given in table 1.

Table 1. Results of the analyses of hydrogen content

№ of sample	T extraction (^{0}C)	Mass of sample (mg)	Total content of hydrogen [n.cm^3/100g]
1	800	95	561.39
2	800	90	367.78
3	800	90	212.71

The hydrogen content in the tubes was controlled to 0.002% before operating the steam generator. Therefore in the process of operation, the hydrogen content in the tube went up more than 10 times, while that in the destruction zone increased 23 times.

In the destruction zone, the hydrogen concentration is 2.5 times higher than in the other parts of the tube. What occurred in this way was accumulation of hydrogen from the outside and its redistribution into the fatigue destruction zone.

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. 7.

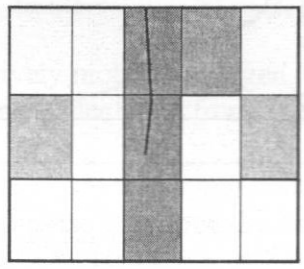

Fig. 7. Map of hydrogen distribution in the plate.
In red are shown the hydrogen concentration values of 1.9-2.0 [n.cm^3/100g],
In orange - 0.00017 [mass%], in yellow – 1.3-1.6 [n.cm^3/100g],
In violet – 1.2-1.3 [n.cm^3/100g]

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. 8 and fig. 9 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.

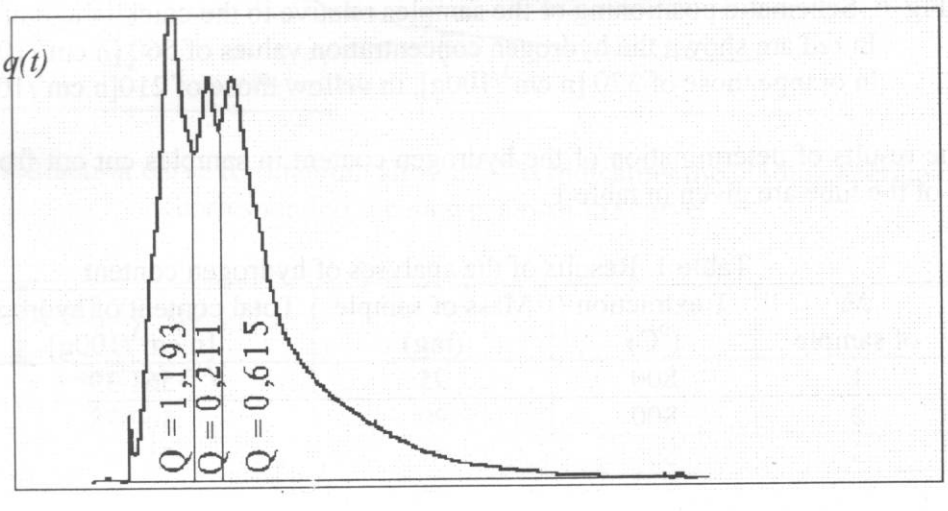

Fig. 8. Experimental extraction curve of the sample on the fatigue crack line

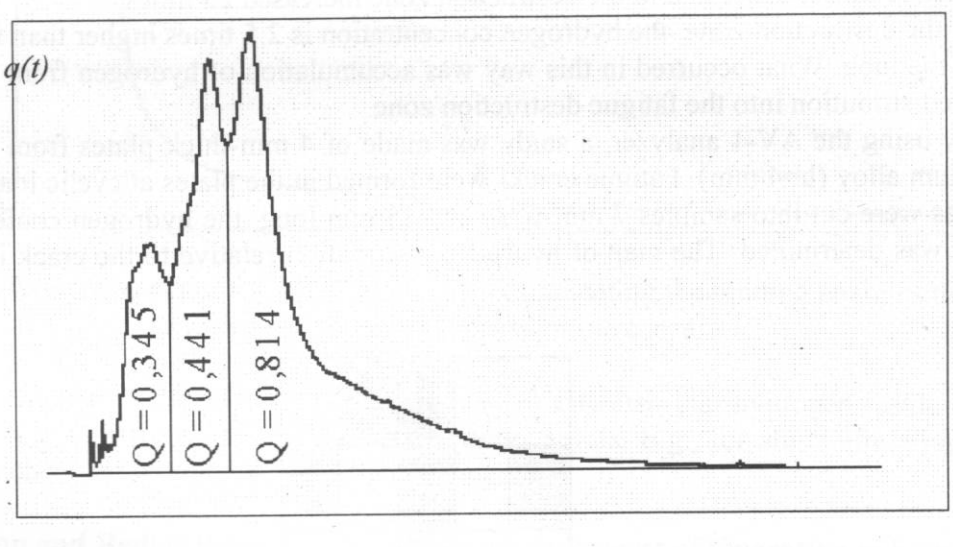

Fig. 9. Experimental extraction curve of the background sample

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. 10. The same photo shows the cutting scheme with the ordinal numbers of the samples for hydrogen content determination. It is clearly seen that the initially cylindrical part of the sample has been subjected to plastic flow at stretching. Therefore, the average diameter and masses of sample № 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 sample № 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.

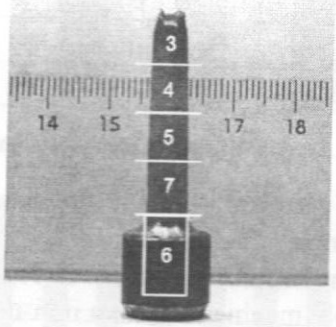

Fig 10. The St 3 sample destroyed at axial tension with a scheme for cutting testing samples. The upper part is the destruction zone; the lower part is the zone of fastening the sample in the tensile-testing machine.

The diagram of distribution of diffusively mobile hydrogen along the sample length is given in fig. 11.

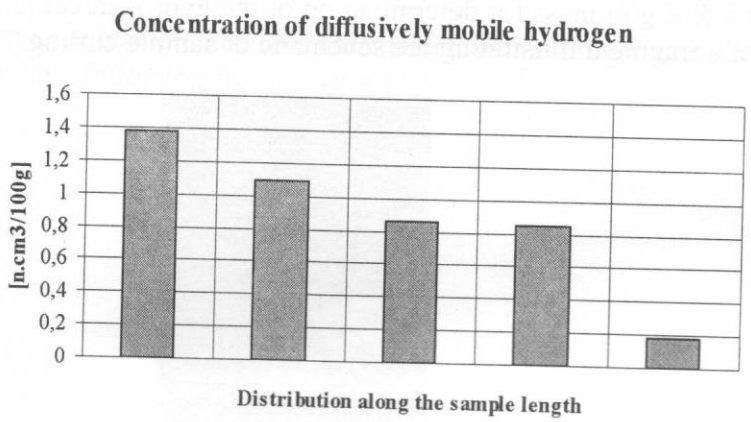

Fig. 11. Distribution of diffusively mobile hydrogen. On the left is the destruction points, on the right – the sample machined from a non-deformed section.

In the same way as in the previous case, strongly bound hydrogen has much larger concentrations in the non-deformed area. Fig. 12 shows a distribution diagram for concentrations of strongly bound and diffusively mobile hydrogen along the sample.

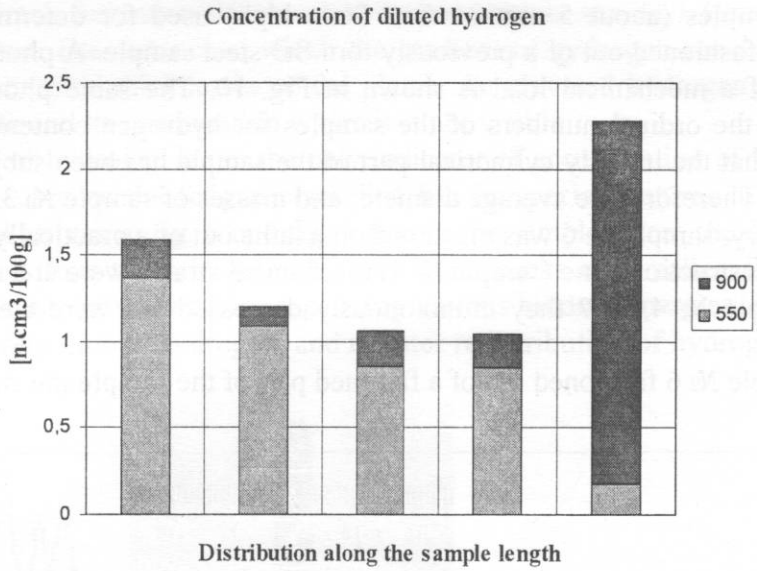

Fig. 12. Distribution of concentrations of diffusively mobile (550) and strongly bound (900) hydrogen along the sample. The upper level of the columns represents the cumulative concentration of hydrogen in the sample. On the left is the destruction point, on the right is the sample machined from a non-deformed 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.The samples of 35G2 pipe steel after high-temperature tempering were used for study of the energy and spectral characteristics of acoustic emission (AE) observed under uniaxial tension. Fragments of fractured 35G2 pipe steel specimens were cut into samples 0.5 to 2 g in mass for determination of the hydrogen content. Figure 13 displays a photograph of a fragment illustrating the schematic of sample cutting.

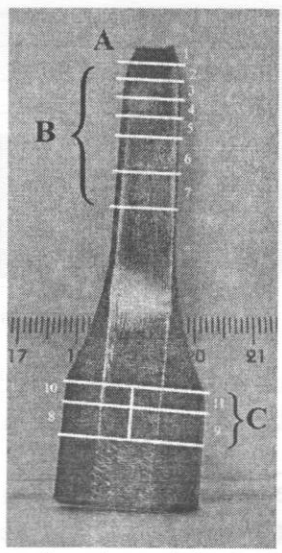

Fig. 13. A sample of 35G2 steel fractured under axial tension showing the schematic of test sample cutting. Upper part (zone A) - zone of fracture, lower part (zone C) - sample grip zone in the test bed.

The concentration of the diffusion-active hydrogen was established to increase strongly (up to a factor 4-5) in the fracture zone. A diagram of the distribution of the diffusion-active hydrogen in the corresponding sample is shown in Fig. 14. Strongly bound hydrogen is practically completely released after high-temperature tempering. Its concentration decreases several times with an increase of the tempering temperature and becomes substantially lower than that of the diffusion-active component of dissolved hydrogen.

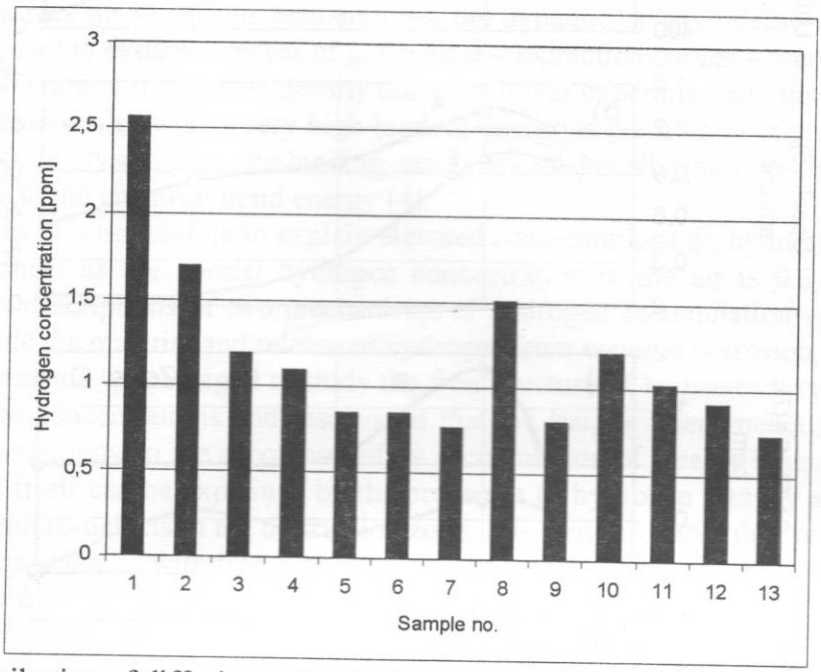

Fig. 14. Distribution of diffusion-active hydrogen. Sample numbers correspond to those shown in Fig.13

A correlation of the mechanical and acoustic parameters with hydrogen concentration variation has revealed the following features (Fig.15).

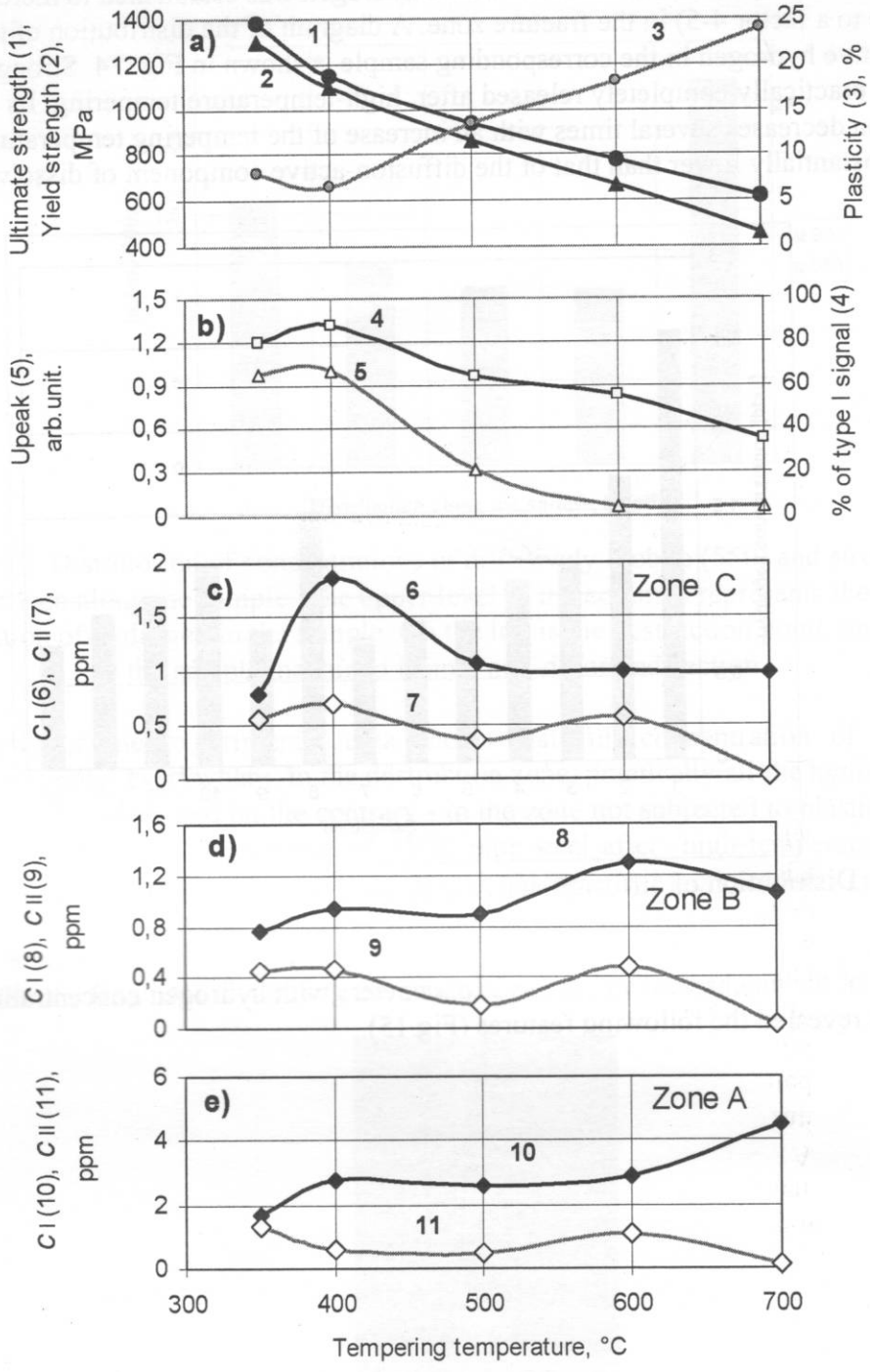

Fig. 15. Mechanical (a) and acoustic (b) characteristics and concentrations of weakly (c_I) and strongly (c_{II}) bound hydrogen (c-e) plotted vs. tempering temperature for 35G2 steel samples quenched from 850°C in water. 1– ultimate strength; 2 - yield strength; 3- relative residual elongation,; 4 - percentage of type I signals (group 1); 5 - AE envelope peak height; 6, 8, 10 - concentrations of diffusion-active hydrogen in the unstrained zone C and zones of strong (zone A) and weak (zone B) strain, respectively; 7, 9, 11 - concentrations of strongly bound hydrogen in zones C, B, and A, accordingly

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.

The variation of the diffusion-active hydrogen concentration in the unstrained part of a sample plotted vs. tempering temperature correlates with the metal plasticity, AE peak height, and percentage of AE signals belonging to the most representative group. Hydrogen concentration in plastically strained samples is considerably (several times) higher than that in the unstrained ones. The lowest plasticity state of the material can be identified with the highest concentrations of diffusion-active hydrogen, the highest AE peak amplitude, and the largest percentage of type Ia signals; as the magnitude of prestrain increases, this correlation exists only under low and medium temperature tempering.

We are of the 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 flaws and defects in metals reducing their surface energy. This results in reduced strength of the material.
- It was for 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 there is no chemically bound hydrogen in these alloys.
- This approach of 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 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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