DIAGNOSTICS OF MECHANICAL CONDITION OF STRUCTURAL MATERIAL BY METHOD OF HIGH-TEMPERATURE HYDROGEN VACUUM-EXTRACTION

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The correlation between hydrogen concentration in construction materials and the history of their thermal and mechanical stress is discussed. As an example we demonstrate experimental results shown that during thermal stress and mechanic stress the concentration of hydrogen in metal increases. The method of measurement of the hydrogen bending energies and diffusion constants in construction materials are proposed.

Keywords: *thermal stress, mechanical stress, hydrogen concentration, diagnostics of mechanical condition*

1 Introduction

Hydrogen is contained in all metallic construction materials. Accumulation of hydrogen occurs in a natural way, from vapours of water and other hydrogen-containing compounds. Control of hydrogen content is obligatory for all moulding (for aluminum alloys [1]).

At high concentration of hydrogen, the material becomes fragile and is easily destroyed. In some cases (e.g. for titanium alloys) the saturation by hydrogen, on the contrary, leads to increasing plasticity, though at decreased ultimate strength.

There is a well known method for studying the solid state structure using low-temperature saturation of metals with liquid inert gases (He, Ar etc.). In subsequent heating of probes to various temperatures dynamics of gas emission can be investigated. From dynamical gas-emission curves (extraction curves) dimensions of pores and dislocations and their velocity are determined [2, 3].

We propose to use the high-temperature hydrogen extraction method for analysis of the structure defects. When using this method the probe is not heated to the fusion temperature, so that the hydrogen should carry information on the state of the crystal lattice of the metal. Since this gas is always contained in aluminum, magnum and titanium alloys and steels, the preliminary saturation is not needed, and it is enough to investigate the natural content of hydrogen occurred inside the metal in the process of its production and exploitation.

2 Description of experiments

We have developed the hydrogen analyzer AV-1 for precise analysis of dynamics of hydrogen extraction from a solid probe (Fig.1.)

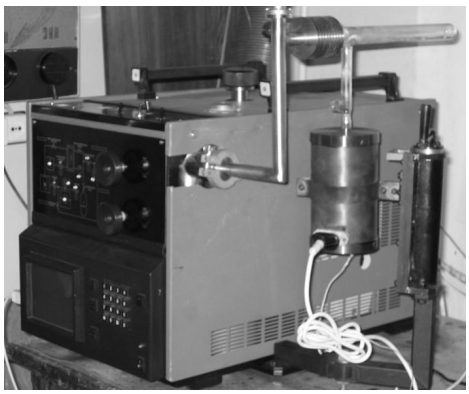

Figure 1: Hydrogen analyzer AV-1

The analyzer creation is based on mass-spectrometric principle. The probe preparation system consists of vacuum extractor and oven. In the process of analysis, a gradual heating of metal probe inside the extractor is made up to the extraction temperature 400-800^{0}C. This temperature is always lower then the fusion temperature of the probe. The gases emitted in the probe heating are analyzed by a mass-spectrometer. Time dependence *q(t)* of the hydrogen flux is fixed by digital registration system in the form of extraction

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curve. Such extraction curve for pure aluminum A8 is shown in Fig.2.

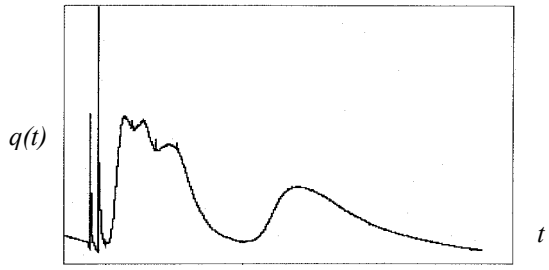

Figure 2: Extraction curve for pure aluminum A8

2.1 Investigation of preliminary stressed probe

2.1.1 Thermo-mechanical stress

Titanium tubes with diameter 22 mm and thickness 2.6 mm were subjected to cyclic non uniform heating for a long time. The temperature difference on the tube length of 15 cm is about 200^0C. The tube edges were fixed that led to creation of thermo-mechanical tensions. After about 15000 cycles of loading, fatigue cracks were formed at the point with minimum temperature.

The results of determination of hydrogen content in probes cut from various parts of the tube are presented in Table 1.

Table 1: Results of analysis of hydrogen content

Probe number	Extraction temperature	Probe mass (mg)	Hydrogen concentration [%] of mass
1	800^0C	95	0.056
2	800^0C	90	0.037
3	800^0C	90	0.021

The scheme of probe position with respect to crack shown in Fig.3.

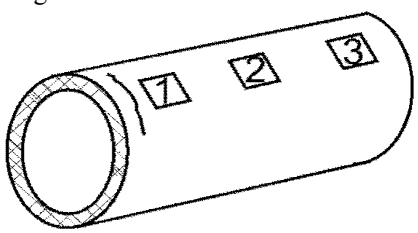

Figure 3: Scheme of probe position with respect to the crack in titanium tube.

The zone of destruction has hydrogen concentration 2.5 times higher than the rest part of the tube.

2.1.2 Mechanical stress

The analyzer AV-1 was used for studying of aluminum-magnum alloy with the thickness h=4mm. In cyclic stress, fatigue cracks were formed in the plates. After cutting of the plates in probes with the width 7mm and length 15mm the hydrogen content in the probes were determined. The map of hydrogen distribution with respect to the crack is given in Fig.4.

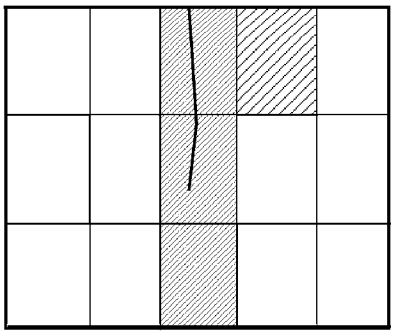

Figure 4: Map of hydrogen distribution in the plate. Thick shading – 2.0 ppm; sparsely shading – 1.7 ppm; in another parts – 1.2-1.3 ppm.

The zone of the line of the formation of the crack has the hydrogen concentration 1.5 times higher than the background concentration. The distance at which the concentration gradient is observed is about $3h$ (i.e. three plate thickness). The increased hydrogen content is observed on the crack line and its continuation where the line is not observed.

3 Estimation of defect density and volume from extraction curve

Suppose that the structure defects has a form of tubes created the joint of three grains, as shown in Fig.5.

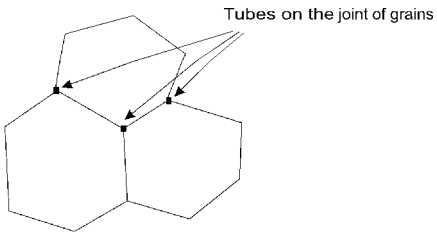

Figure 5: Scheme of the defect position on the joint grains

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:

$$b = \sqrt[3]{\frac{pd^3}{6}}$$

In this approximation the volume of one cavity equals $b^3\gamma^2 = 3.8\cdot10^{-9}$ cm^3. The amount of hydrogen at each maximum in Fig.2 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=4.2·10^5 cm^{-3}, Z_2=3.2·10^5 cm^{-3}, Z_3= 6.4·10^5 cm^{-3}, Z_4= 9.6·10^5 cm^{-3}.
In the above approximation the total number of traps in 1cm^3 of the probe, calculated from hydrogen amount, is Z=ΣZ_i=2.34·10^6 cm^{-3}, and the grain concentration is 2.58·10^6 cm^{-3}. The concentrations coincide within 10%. Thus the conclusion can be made that hydrogen at atmospheric pressure fills all cavities along the grain boundaries.

4. Estimation of hydrogen binding energy

The high sensitivity of the analyzer AV-1 and the representative statistics (about 30 thousand points on one curve) allows one to discern some maxima on the extraction curve. The maximum position and shape provides information about the binding energy and total volume of defects for individual peaks (e.g. see Fig.2.).

Let us consider the process of diffusion of hydrogen in titanium probe in heating in vacuum.

The probe cut form a tube has the from close to the parallelepiped with the sizes a=2.6 mm, l=4mm, b=4mm (Fig.6.)

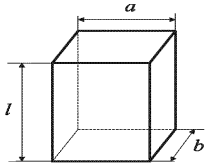

Figure 6: Probe for analysis

The extractor walls are made of quartz glass, their temperature being maintained at the constant level T_0. The quartz glass has practically zero heat conductivity, the contact between the probe and the extractor walls is pointed, so that the heat transfer occurs via radiation.

The quartz glass is not transparent for infrared radiation, so the probe is heating only by radiation from the extractor walls. The heat flux absorbed by the probe is

$$\frac{dQ}{dt} = s\,S e_t (T_0^4 - T^4), \tag{1}$$

where σ = 5.6687·10^{-8}W/m^{2}K^4 is the Stephan-Boltzmann constant, S is the probe surface area, T is the probe temperature, ε_t is the absorption coefficient for titanium in the temperature range of interest 200^{0}C – 900^{0}C, which can be taken as,

$$e_t = 0.2\,. \tag{2}$$

Under such conditions the heat capacity of titanium weakly depends on temperature and equals C=0.6kJ/kg·K. The heat dQ absorbed by the probe increases its temperature by dT:

$$dQ = C\,r\,V dT\,, \tag{3}$$

where ρ and V are the probe density and volume, respectively.

The use of (1) - (3) yields the following equation for the probe heating:

$$\frac{dT}{dt} = \frac{s\,S}{C\,r\,V}\cdot 0.2\cdot (T_0^4 - T^4). \tag{4}$$

The equation for time-dependent hydrogen diffusion on in the probe is

$$\Delta C = \frac{1}{D}\frac{\partial C}{\partial t} \qquad C\,|_S = 0 \quad C\,|_{t=0} = C_0 \tag{5}$$

where C is the hydrogen concentration in the probe, $D = D_0 \cdot \exp(-\frac{u}{kT})$ is the diffusion coefficient for hydrogen in metal, u is activation energy, D_0 is diffusion constant, k is the Boltzmann constant.

Taking into account the form of the probe, at given boundary conditions, the first term of the Fourier expansion of equation (5) can be written as

$$C(x,y,z,t) = \frac{C_0 p^3}{8}\sin\frac{px}{a}\cdot\sin\frac{py}{b}\cdot\sin\frac{pz}{l}\cdot f_1(t,u,D_0), \tag{6}$$

where l, a and b are the height, width and depth of the probe, respectively, and the function $f_1(t,u,D_0)$ is the solution of the equation:

$$\dot{f}_1 + D_0\cdot\exp(-\frac{u}{kT})(\frac{p^2}{a^2}+\frac{p^2}{b^2}+\frac{p^2}{l^2}) f_1 = 0 \qquad f_1(0,u,D_0) = 1 \tag{7}$$

In performing the analysis, the apparatus registers the total hydrogen flux $q(t)$ through the surface of probe. According to the Ficke low, this flux is

$$q(t) = -\int_S D\,\frac{dC}{dn} dS\,, \tag{8}$$

where S is the area of the probe surface.

After integration in (8) using the expression (6) for C, one obtains

$$q(t) = \frac{16 C_0}{p^2}\cdot\left[\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{l^2}\right]\cdot D_0\cdot\exp(-\frac{u}{kT})\cdot f_1(t,u,D_0). \tag{9}$$

When supposing that hydrogen in the probe is contained in traps with different binding energies u_i, and corresponding diffusion constant D_{0i} and hydrogen concentrations C_{0i}, one can use the superposition principle, due to linearity of diffusion equation (5). Then the total flux of hydrogen from the probe $q(t)$ can be expressed by the sum:

$$q(t) = \frac{16}{p^2}\cdot\left[\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{l^2}\right]\cdot\sum_i C_{0i}\cdot D_{0i}\cdot\exp(-\frac{u_i}{kT})\cdot f_1(t,u_i,D_{0i}), \tag{10}$$

where $f_1(t,u_i,D_{0i})$ are the solution of equation (7) at given values of the constants u_i, D_{0i}, C_{0i}.

Approximation of the experimental extraction curve by the calculated curve with a proper choice of the initial concentrations C_{0i} and constants u_i,D_{0i} allows one to obtain the activation energy and diffusion constants for hydrogen diluted in the metal. A plot of the approximating curve for the case of three maxima is shown in Fig.7.

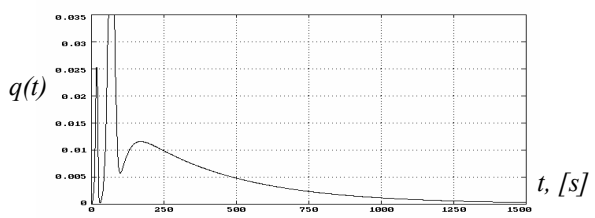

Figure 7: Calculated extraction curve with three maxima

The experimental curves for the titanium is shown on the Fig.8.

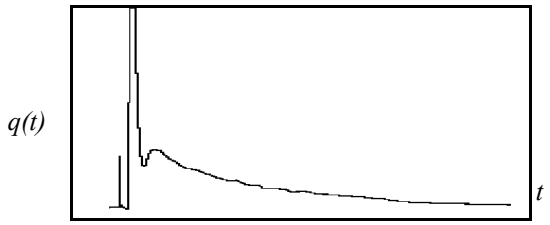

Figure 8: Experimental extraction curve for the titanium

5 Discussion of results

As a result of treatment of experimental extraction curves, the range of activation energies of the traps for aluminum and aluminum alloys and titanium was determined. For the titanium the maximum activation energy equals 1.5 eV. For aluminum and its alloys this range stretches from 0.2 eV to 0.8 eV. Consequently, one can suppose that there is no chemically bound hydrogen in the alloys.

Sharp maxima observed on some extraction curves (e.g. the peaks 1 and 2 in Fig.9) correspond to explosive character of hydrogen emission from the traps-defects.

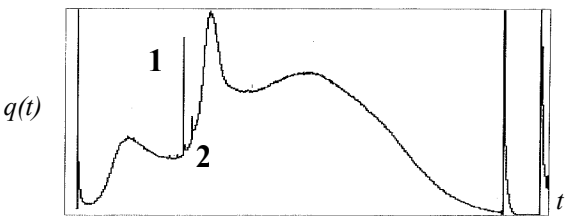

Figure 9: Experimental extraction curve for the aluminum alloy AD-31

Determination of parameters of the defects represents the aim of further studies, which should be combined with the studies of probe structure by other physical methods.

Correlation is found between the shape of extraction curve and the type of alloy. Experiments with probes of various shapes and masses show that the number of maxima on the extraction curve does not change.

Unique technical characteristics of method are achieved. The apparatus we developed allows precise determining the hydrogen concentration as low as 0.1ppm.

The number of hydrogen molecules corresponding to individual peaks on the extraction curve equals $5\cdot10^{11}$ that corresponds to the concentration 10^{-6} ppm.

7 Conclusions

Results of our work are as follows:

1. We have developed equipment, which allows obtaining information on the material structure from the hydrogen extraction curve in heating of a probe in vacuum. Accurate determination of the extraction curve provides information both on the hydrogen binding energy in metal and on concentration of spatial micro-traps.

2. It has been established experimentally that fatigue phenomena and destruction of construction materials are accompanied by increasing hydrogen concentration the destruction zone.

3. Comparison between the results of analysis of the hydrogen content and the data of other authors allows us to conclude that all defects in aluminum are filled with hydrogen at barometric pressure.

4. The proposed calculations procedure allows one to approximate the experimental extraction curve and to determine the diffusion constant and activation energy for each peak of the curve.

5. The values of activation energies obtained from treatment of the experimental data for aluminum and its alloys lie in the range from 0.2 eV to 0.8 eV that allows us to conclude that the chemically bound hydrogen is absent in this alloys.

6. The approach to the study of properties of materials considered above does not require preliminary saturation of the studied probes with hydrogen. Natural hydrogen available in a metal carries information on pre-history of the material that will allow obtaining more complete information from the extraction curves in the further development of the method.

References

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