DETERMINATION OF HYDROGEN BINDING ENERGY IN VARIOUS MATERIALS BY MEANS OF ABSOLUTE MEASUREMENTS OF ITS CONCENTRATION IN SOLID PROBE

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Abstract

A method for analysis of experimental dynamical curves of high-temperature vacuum-extraction is developed, which allows determining the binding energy and diffusion constants of hydrogen in the probe under study. The experimental data have been obtained using the measuring complex, which allows conducting the absolute measurements of the dynamical curves of high-temperature vacuum- extraction of hydrogen from a solid probe.

Keywords: Hydrogen binding energy, hydrogen analyzer, vacuum extraction, fatigue crack, standards

1. Introduction

The problem of hydrogen storage in metals is related with the problem of determination of hydrogen binding energy and diffusion constants in the metals.

On the other hand, the formation of structure defects (micro cracks, dislocations) in metals and alloys is accompanied by redistribution of concentration of hydrogen diluted in these species.

Hydrogen has very large diffusion mobility; it is accumulated not only in local defects and hydrides but also in zones of stretching mechanical stresses (the Gorski effect [1]).

The increased content of hydrogen in metal serves as an indicator of increased concentration of internal mechanical defects. For this reason, the hydrogen content is controlled in the production of moldings, for instance, the aluminum alloys [3].

Hydrogen influences mechanical properties of construction materials [2]. For example, accumulation of hydrogen inside the metal gives rise to the fact that the material becomes more fragile and easily destroyed. On the contrary, some materials (e.g. titanium alloys) saturated with hydrogen become more plastic, though their ultimate strength decreases.

The natural concentrations of hydrogen in metals are not very high (about 1-10 ppm). Inside the metal hydrogen is located in the traps of different nature (e.g. defects, hydride). The external saturation and mechanical stress leads to changing the picture of the hydrogen distribution between the traps.

Thus, the information about this distribution has the fundamental importance in investigation of the hydrogen – material interactions.

We have developed the high-precision analyzer AV-1 allowing accurate determination of the natural concentrations. The analyzer sensitivity is so high that one can measure the amount of hydrogen in the traps whose volumes are thousands times smaller than the total volume of hydrogen extracted from the probe. On other hand, the AV-1 can be used for the measurements of the high-level hydrogen concentrations (0.1-10 % of mass) in the pieces of material with mass 0.3-0.5 mg.

The high-temperature extraction method with analyzer AV-1 was applied for studying the defect structure of materials undergoing fatigue cracking. In 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.

The developed method for analysis of dynamical vacuum-extraction curves allows determination of the binding energy and total volume of the traps of different nature, as well as the diffusion constant of hydrogen in the probe under study.

2. Experimental technique

2.1. Hydrogen analyzer

The high-precision hydrogen analyzer AV-1 is developed for determination of the hydrogen content in metals and alloys in conditions of plant laboratory under exit control of moldings from different alloys. The analyzer works during five years at the metallurgic plants in Kamensk-Uralsk and Samara. The analyzer is included into State list of Measurement Means. The design of apparatus provides very high sensitivity and stability of metrological characteristics. The picture of analyzer is given in Fig.1.

Figure 1. Hydrogen analyzer AV-1

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

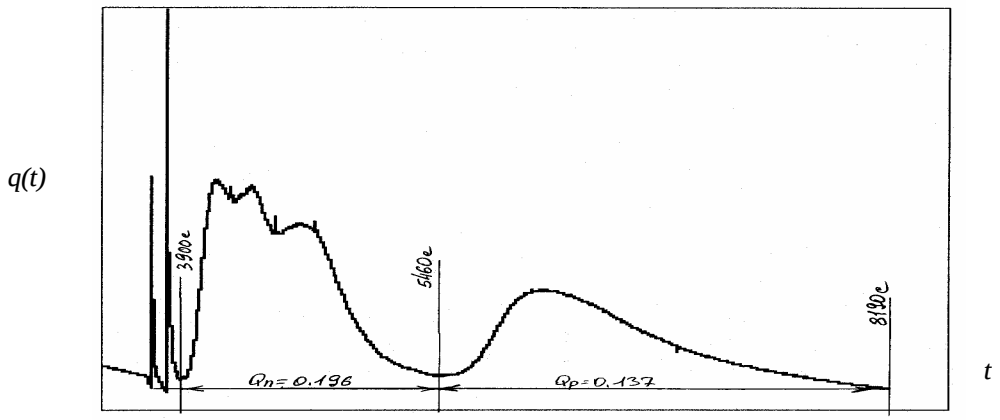

Figure 2: Extraction curve for pure aluminum A8

2. 2. Standards

In determining the hydrogen content in solid probes of titanium, copper and magnesium alloys and in steels, two express-methods are widely used, namely, the spectral method and method of melting in the flux of inert gas carrier. These fast methods require regular (by one shift of even one hour) calibration on the hydrogen content standards – State Standard Probes (SSP). In the SSP passport, the certified concentration of hydrogen in the probe and the allowed deviation with 95% confidence is indicated. For aluminum alloys, the relative value of the allowed deviation varies from 5 to 30%.

When using the absolute methods for determination of the hydrogen content, the probe is heated in vacuum. The gas emitted from the probe is accumulated in a calibration volume. After extraction is finished, the pressure in this volume is measured. From this pressure, the total amount of extracted hydrogen and its content in the probe can be calculated. In such calculations, the hydrogen adsorbed on the probe surface is subtracted from the total amount as a correction known in advance. Such approach can lead to considerable systematic error. The peaks in Fig.2. corresponding to the surface and diluted hydrogen are separated by vertical lines. The amount of the surface hydrogen Q_n is in 2.4 times lager than that of the diluted hydrogen Q_p.

Fig.3. shows results of determination of the hydrogen content in the SSP of the AMg6 alloy.

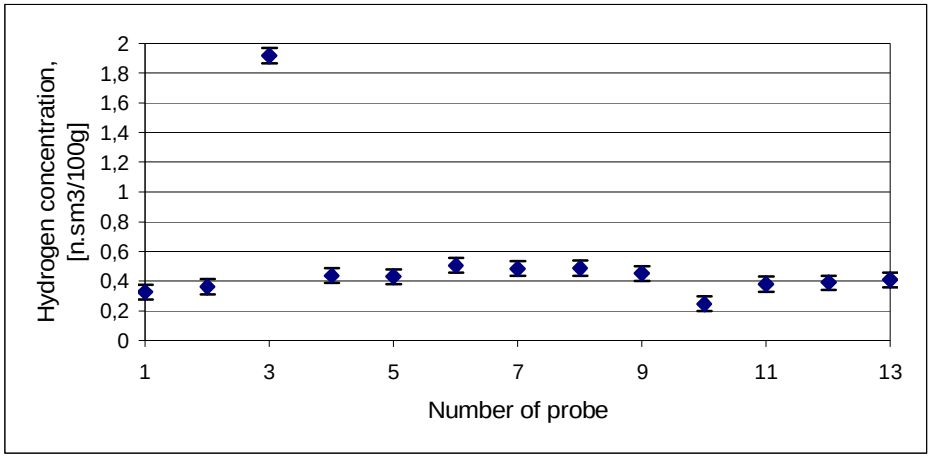

Figure 3: Results of analysis of hydrogen content in SSP of the alloy AMg-6

The certified value of hydrogen concentration is 0.42 [n.sm^3/100g], the certified allowed deviation at 95% confidence is ±0.02 [n.sm^3/100g] (error bars at the plot). In presented sample of 13 probes only 46% of results instead of 95% falls into the certified interval, while one probe (8%) has concentration 3.5 times larger, than the certificated one.

It is necessary to note that the calibration is usually made on two probes, so that the probability that one of them will not fall into the certified interval exceeds 0.75, as follows from above experimental data.

In the mass-spectrometric method for hydrogen registration requires calibration of sensitivity of analyzer. The experimental data obtained show that it is necessary to have the standard more stable than the investigated SSP.

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

Independent testing of the standard was made during 8 months in 2004-2005 at Mendeleyev State Metrology Institute.

The mean value of the hydrogen flux is $7.7 \cdot 10^{-7}$ m^{3}Pa/s, and the relative value of standard deviation of the accidental component of error of measurements is ±1%. The relative value of allowed deviation at the confidence 90% is 1.7%.

Thus we have the high–precision complex for absolute measurements of hydrogen content in the solid probe of any composition.

3. The study of preliminary stressed probe

3.1. 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^{0}C. 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.4.

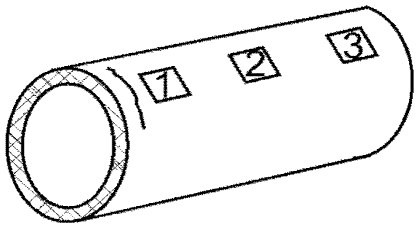

Figure 4: Scheme of probe position with respect to the crack in titanium tube.

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

3.1. Mechanical stress

The analyzer AV-1 was used for studying aluminum-magnesium 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.5.

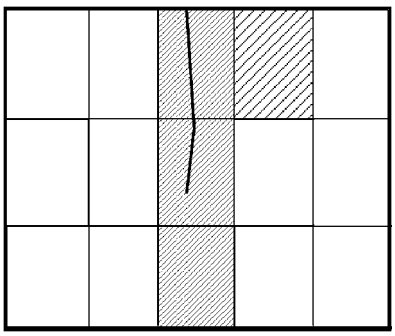

Figure 5: Map of hydrogen distribution in the plate. Thick shading – 2.0 ppm; sparsely shading – 1.7 ppm; in another parts – 1.2-1.3 ppm.

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 3*h* (i.e. three plate thicknesses). The increased hydrogen content is observed on the crack line and its continuation where the line is not observed.

4. Estimation of defect density and volume from extraction curve

Suppose that the structure defect has a form of tubes created the joint of three grains, as shown in Fig.6.

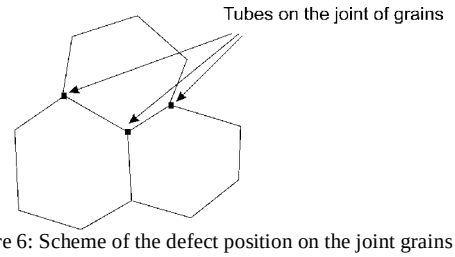

Figure 6: Scheme of the defect position on the joint grains

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:

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

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 Q1=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 $Z=\Sigma Z_i$=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.

5. 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 aluminum probe in heating in vacuum.

The sample has the form of cylinder (see Fig.7.).

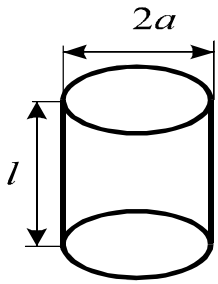

Figure 7: Sample for analysis.

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

$$\frac{dQ}{dt} = sSe_t(T_0^4 - T^4), \qquad (1)$$

were $s = 5{,}6687 \cdot 10^{-8}$ W/m^{2}K^4 is the Stephan-Boltzmann constant, S is the surface area, T is the sample temperature, e_t is the absorption coefficient for aluminum, which can be written as,

$$e_t = 7 \cdot 10^{-5} \cdot (T + 64{,}3). \qquad (2)$$

The Debye temperature for aluminum is 160^{0}C, so that in the temperature range of interest, 200^0-600^{0}C, the heat capacity weakly depends on temperature and equals $C = 1{,}15$ kJ/kg K. The absorbed heat dQ increases the sample temperature by dT,

$$dQ = CrVdT, \qquad (3)$$

Were r is sample density, V is sample volume.

The use of (1)-(3) leads to the following equation for sample heating:

$$\frac{dT}{dt} = \frac{sS}{CrV} \cdot 7 \cdot 10^{-5} \cdot (T + 64{,}3)(T_0^4 - T^4). \qquad (4)$$

The equation for time-dependent hydrogen diffusion in the sample is

$$\Delta C = \frac{1}{D}\frac{\partial C}{\partial t} \qquad (5)$$

$$C|_S = 0$$

$$C|_{t=0} = C_0$$

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

Taking in to account cylindrical form of the sample, at given boundary conditions, the first term of Fourier expansion of equation (5) can be written as

$$C(r,z,t) = \frac{C_0 p}{0{,}836} \sin\frac{pz}{l} \cdot J_0(g_1 \tfrac{r}{a}) \cdot f_1(t,u,D_0), \qquad (6)$$

were l, a are the cylinder height and radius, respectively, g_1 is the first root of equation $J_0(g_1) = 0$, $f_1(t,u,D_0)$ is the solution of equation:

$$\begin{aligned} &f_1' + D_0 \cdot \exp(-\frac{u}{kT})(\frac{p^2}{l^2} + \frac{g_1^2}{a^2}) f_1 = 0 \\ &f_1(0,u,D_0) = 1 \end{aligned} \qquad (7)$$

In performing the analysis, the apparatus registers the total hydrogen flux $q(t)$ through the surface of sample. According to the Fick law, this flux is:

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

where S is the area of the sample.

Integration of (6) using (8) yields the following expression for the first term of expansion:

$$q(t) = 14{,}56 \cdot g_1 J_1(g_1) \cdot C_0 \cdot l \cdot \left[\frac{p^2 a^2}{2 g_1^2 l^2} + 1\right] \cdot D \cdot f_1(t,u,D_0) \qquad (9)$$

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:

$$q(t) = 14{,}56 \cdot g_1 J_1(g_1) \cdot l \cdot \left[\frac{p^2 a^2}{2 g_1^2 l^2} + 1\right] \cdot \sum_i C_{0i} \cdot D_{oi} \cdot f_1(t,u_i,D_{0i}) \qquad (10)$$

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 two maxima is shown in Fig.8.

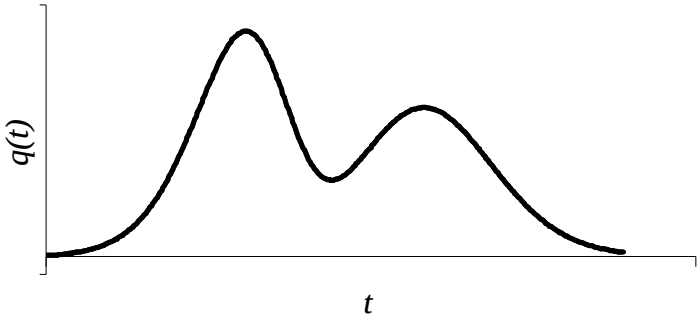

Figure 8: Results of the mathematical modeling for probes of aluminum A8

A plot of the approximating curve for the case of three maxima is shown in Fig.9.

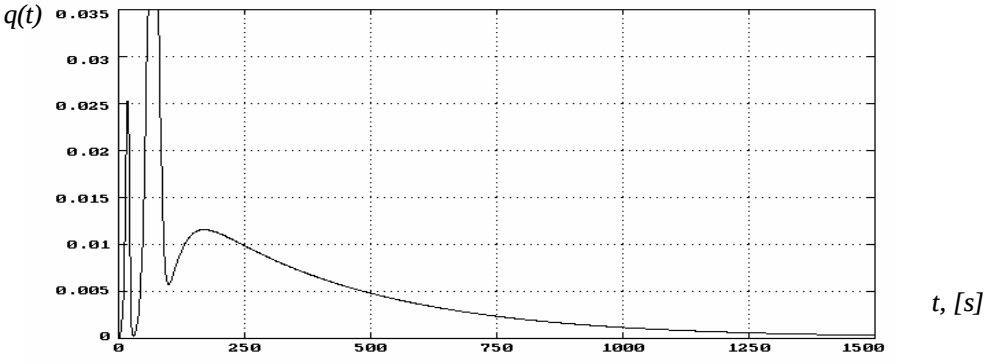

Figure 9: Calculated extraction curve with three maxima

The experimental curves for the titanium alloy PT-7M is shown on the Fig.10.

Figure 10: Experimental extraction curve for the titanium alloy PT-7M

6. 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 was determined. 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. For the titanium alloys, the maximum activation energy equals 1.5 eV.

The conclusion that hydrogen in technically pure aluminum is concentrated in defects on the edges of grains agrees well with the data of radio graphical investigations. Fig. 11. shows the radio graphical picture of aluminum, saturated with tritium [6].

Figure 11: Distribution of tritium on the edges of grains in aluminum. Micro photographical picture [6]

The sharp maxima observed on some extraction curves (e.g. the peaks 1 and 2 in Fig.12.) correspond to explosive character of hydrogen emission from the traps-defects.

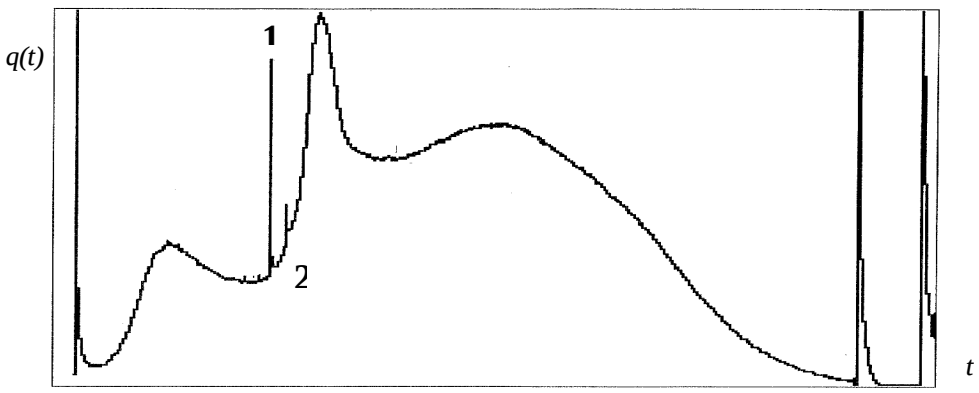

Figure 12: Experimental extraction curve for the aluminum alloy AD-31

When supposing that hydrogen inside the defects is contained at barometric pressure the volume of defects can be determined from the peak areas. The number of hydrogen molecules corresponding to separate small peaks on the extraction curve is about 10^{11}, that corresponds to the defect volume of about 10^{-6} mm^3. For aluminum this volume corresponds to the volume of age dislocation.

By comparison, the minimum volume of the defect registered by the methods of ultrasonic inspection is about 0.1 mm^3 that is about four orders of magnitude larger; in the optical microscope, the surface defect with the volume of about 10^{-6} mm^3 can be seen.

The results obtained on the fatigue stress show capability of the suggested method to study surface and bulk structure of metal and, in particular, to estimate the volume of inner fatigue micro-cracks.

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 allow metrological reliable determining the hydrogen concentrations as low as 10^{-5} [%] of mass.

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 in 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

7. The metrological complex including the hydrogen analyzer and the calibration standards allows realization of the principle of unity of measurement means in conducting analysis of various metals and alloys and obtaining additional information on the volume and structure of bulk and surface mechanical defects

8. References

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