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Application of multichannel diffusion model to analysis of hydrogen measurements in solid

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ABSTRACT

Measurements have been performed of the hydrogen contents in reference samples of aluminum alloy using the methods of vacuum hot extraction, vacuum melting and melting into the graphite crucible in the flux of gas carrier or argon carrier fusion method. The effect of additional “squeezing out” of hydrogen from the metal under its crystallization was not observed. It has been shown that during the sample heating time typical for the analysis by argon carrier fusion method the bound hydrogen with high activation energy is not extracted completely. This leads to errors in performed measurements. It has been proved that the mean velocity of hydrogen transport and mean coefficients of diffusion depend on the initial population of the energy levels, and they can vary for the same material.

Introduction

An adequate description of the hydrogen diffusion in solid is necessary for prediction of the working resource of constructions, development of the storage systems and safe technologies and also for reliable measurement of hydrogen concentration.

The systems for storage and transport of gas are designed to withstand high pressure. Hydrogen diffuses into metal of the walls and other parts of such systems cf. [1]. The gradual accumulation of hydrogen in metal leads to the hydrogen embrittlement and destruction.

There are some hydrogen storage systems in which the hydrogen is accumulated in metals, composites and

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nanostructures. The hydrogen diffusion is the main working process in charging and discharging, cf. [2].

In the thermonuclear reactors the diffusion of hydrogen and its isotopes leads to saturation of inner parts of reactor, cf. [3]. Increasing the temperature of the inner walls leads to backward diffusion of hydrogen from the walls to plasma, cf. [4]. This process destroys the plasma's stability during energy pumping. Hydrogen accumulation leads to cracking on the inner parts of reactor due to the hydrogen embrittlement and the temperature shocks. The tritium diffusion through the reactor walls leads to reducing the level of radiation safety of technology of thermonuclear synthesis.

In all these cases, the hydrogen concentrations are close to the limits for structural materials.

However, hydrogen is always present in metals and semiconductors. For majority of metals, the “normal” values of hydrogen concentration fall in the range from 0.2 ppm (for aluminum alloys and high strength steels) up to 80 ppm (for titanium alloys). Even the double excess of the “normal” hydrogen concentration leads to that the material loses the property of plasticity.

This is why for some metals (titanium, aluminum alloys and steels) the measurement of hydrogen concentration is an obligatory procedure for technologically control of castings before its treatment (rolling, pressing, forging, etc.). Due to the wide industrial testing, the measurement of low concentration of hydrogen is the most frequently used procedure in the hydrogen investigations.

The whole measurement process can be distributed into two steps: (1) – The hydrogen extraction from the solid or liquid probe; (2) – Registration of the extracted hydrogen.

The systematic errors of the step of “registration” may be revealed using fixed amounts of hydrogen (gas calibration) and they are taken into account in computer processing of the measurement results. The errors of the first step of measurement are more difficult to account for.

To accelerate the extraction of hydrogen from the tested probe it is necessary to speed up the process of its diffusion from the sample's material to the surface. Heating the sample is often used to this end. The hydrogen diffusion and desorption from the sample surface depend on many factors: chemical composition, conditions of crystallization, method of the mechanical treatment of metal. These factors hamper the production of reference samples for testing the measuring instruments. Besides it is practically impossible to produce a sample with zeroth concentration of hydrogen, so that any measurement of the residual amount of hydrogen yields a non-zeroth result. The unambiguous separation between background and diffusion fluxes is not always possible, thus some additional assumptions are needed, cf. [5].

As a result, it is not always to achieve the accuracy and reliability of measuring the hydrogen concentration without adequate description of diffusion of small amounts of hydrogen into the tested sample.

Initially, the hydrogen diffusion was considered as a process that is described by Fick's equation with the diffusion coefficient depending upon the temperature governed by Arrhenius low. The available experimental data show a very large dispersion in the diffusion coefficients and activation energies for the same materials.

Darnken and Smith [6] have shown that there exists a limit of the concentration which depends on the method and temperature regime of the sample treatment. The authors introduced the concept of trapped hydrogen and trap sites intrinsically presented in the material in the description of interaction between the hydrogen and solid. These trap sites include grain boundaries, precipitates, or defects, such as dislocations, vacancies etc. Refs. [7–9]. Even more complicated mathematical models were used for description of hydrogen diffusion, namely from model by McNabb and Foster [10] to model by Oriani [11].

Practically, all the authors support the idea that hydrogen diffusion in solids is caused by motion of hydrogen atoms, and in some cases by motion of their nuclei (protons). In the model of hydrogen transport the traps of different origin are considered to be distributed over the material volume, and only one “diffusion channel” is responsible for it. Hydrogen proceeds through this channel. In Refs. [12,13]the experimental data are generalized and their comparison with results of mathematical modeling is given. In addition to the values of activation energy and diffusion coefficients Ref. [13] introduced the trapping and detrapping activation energies which proves the adequacy of Oriani model, cf. [11]. The physical estimations of sorption parameters of the hydrogen at different defects of the metal were made in Ref. [14] which allows one to determine the binding energy level in the different traps.

The concept of the single-cannel character of diffusion is supported by experimental method for determination of the binding energies of hydrogen which is called “method TDS”. Justification of this method is given by Kissinger in Ref. [15]. According to work [15] the change of the energy state and hydrogen diffusion in solids are treated as chemical reactions of first order. Detrapping of hydrogen is considered as a process which is slower than diffusion. As far as we know diffusion is taken to account only in work [16], however this account is based on the single-channel model by Oriani [11].

The convection fluxes and hypothesis of squeezing of hydrogen by means of the crystallization's border are additionally taken into account when the hydrogen transportation is described inside the metal melting and during its crystallization, cf. [17].

Application of these models of hydrogen transport to the description of experimental data (e.g. Refs. [18–21]) shows that particular values of binding energies (or activation energies) and diffusion constants can differ by 2–3 times for the same types of the traps in the alloys with the similar structure and chemical composition.

This is related to the fact that the main physical mechanisms of hydrogen transport in solids are of the complex character. They are as follows: capturing of hydrogen by moving dislocations, diffusion by the vacancies, diffusion on grain boundaries, diffusion by the different types of interstices of crystalline lattice. A model description of even some of these mechanisms, e.g. using density functional theory, cf. [22] requires cumbersome calculations and does not allow modeling of the materials with macro defects, with non-regular structure and with relatively small hydrogen concentration.

The values of coefficients of hydrogen diffusion in solids are small under normal conditions, Refs. [23,24]. Thus, to reduce the measurement time the sample is heated up to melting temperature or close to it. The strong variation of temperature in the course of measurement leads to additional difficulties in modeling since the model should be adequate in a wide range of temperatures, up to melting temperature for the studied sample. Under such conditions the model of Kissinger [15] becomes very approximate. This model is not appropriate for adequate description of physical processes occurring at measuring the hydrogen content in a probe.

The TDS method has a low sensitivity, therefore the samples are charged with hydrogen in a electrolyte or in gaseous hydrogen at high pressure, cf. [25]. This operation introduces additional errors in the process of determination of diffusion coefficients. It is necessary to note that practically all results on determination of the binding energies of hydrogen were obtained either by using special hydrogen charging of samples or by determining the membranes permeability to hydrogen. In this case the finite capacity of traps has a most important role in the diffusion processes, cf. [12]. The results obtained in the hydrogen charging of material could be used directly in mechanical engineering about 30 years ago. From that time the technology of alloys production has made a great progress. The values of normal hydrogen concentrations are of the order of tenths ppm in the modern high-strength alloys. In this case, due to non-linearity of the processes, the hydrogen charging of samples up to 10 ppm does not permit one to obtain the results applicable to practical problems.

In our articles [26,27]a model of the multichannel diffusion was suggested. We reported the use of this model for determination of activation energies and diffusion constants in solids.

For practical purposes, it is necessary to have a simple model of hydrogen diffusion in solids, which can give an adequate description of the transport of small natural concentration of hydrogen in a wide temperature range, for different sizes and shapes of studied samples (wire, films and components of machines).

In the presented work, we use the model of multichannel diffusion for mathematical description of the first stage of the process of measuring of the hydrogen concentration in aluminum alloys, namely, the hydrogen extraction from the sample.

Measuring equipment and preparation of the samples

The two industrial hydrogen analyzers were used for the measurements:

1. AV-1, which is based on the Vacuum Hot Extraction (VHE) method, see Refs. [5,28–30] and Vacuum Hot Melting (VHM) method. The analysis method and the analyzer have been described in Ref. [26] in detail.
2. LECO RH 402 hydrogen analyzer, which is based on argon carrier fusion (ACF) method, cf. Ref. [31].

The reference samples manufactured by Alcoa SMZ were used in the experimental study. These reference samples or the reference material are rods of the alloy D-16 (analog of 2024, $AlCuMg_2$). The rod diameter was 12 mm that was typical for industrial measurement sample (aluminum alloys). The rod was specially fabricated. According to our measurement experience the concentration of hydrogen is uniform along the rod. The rod did not undergo mechanical loading.

The cylindrical samples were carved on a lathe from the rods. The measurements by the VHE and VHM extraction (Analyzer AV-1) were performed with the samples of diameter 6 mm (VHM) and from 7 mm to 8 mm (VHE). The sample length was 15 mm. The measurements by method ACF (Analyzer RH 402) were carried out with samples of diameter 9 mm and length 35 mm. Initially the workpieces of diameter 8.5 mm and 9.5 mm were turned. After that the surface of samples were turned using automatic feeding of a support. Spindle rotation speed was from 1200 to 1500 rpm, feed rate of a support was from 0.04 to 0.10 mm per revolution of the spindle, the cutting depth was from 0.1 to 0.2 mm. The cutting edge of the cutting tool was previously polished with diamond paste. Processing was performed without emulsions according to Ref. [32]. Complying with these conditions allows us to reduce the amount of “superficial hydrogen” (adsorbed on the sample surface) that gives rise to systematic errors in the measurements of hydrogen concentration in aluminum alloys, cf. Refs. [31,33,34].

Let us now consider a scheme of measurement of hydrogen concentration by the vacuum hot extraction method by analyzer AV-1. The scheme of extraction system is shown in Fig. 1.

The extraction system consists of the quartz glass extractor and furnace. This extractor is connected to a vacuum system AV-1 and is continuously pumped out by the vacuum pump of the analyzer. This design corresponds to standard [32]. The heating of samples was performed by means of furnace with resistive heater attired on the vertical analytic branch of the extractor. The temperature of the furnace is set and maintained by controller within accuracy of ±2 °C. The cylindrical samples are situated in the cold horizontal branch of the extractor.

Under steady-state conditions the furnace temperature coincides with the temperature of analytic branch of the extractor and is understood as the “extraction temperature”. The extraction temperature is in the range 400–800 °C for the majority of metals.

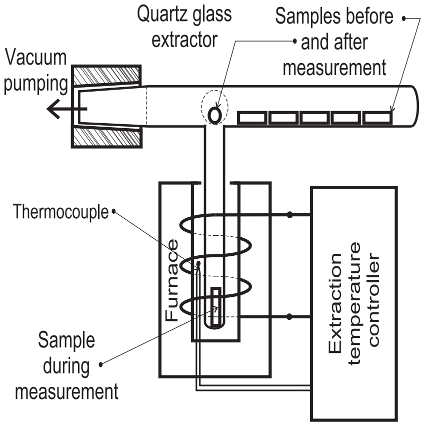

Fig. 1 – Extraction system of analyzer AV-1.

Removal of remaining hydrogen that was adsorbed at inner surfaces of the measurement devices is carried out using a vacuum degassing procedures described in standard [32]. A 2-h preparation results in the equilibrium hydrogen concentration on the inner walls which depends only on the temperature of the system walls and practically independent of the hydrogen flow because of the high vacuum.

The 100 μPa operating pressure is maintained in the extraction system during measurements by the analyzer pump. Sample is discharged into the analytical branch from the cold branch by a magnetic tappet without destroying the vacuum. Thereafter, the sample temperature is increased slowly to the extraction temperature. The flux of the extracted hydrogen is measured by the mass-spectrometer and is calibrated initially on reference samples. The time dependence of hydrogen flux from the sample is called the extraction curve. The typical extraction curve is shown in Fig. 2.

The area under the curve is proportional to the amount of extracted hydrogen. The first peak of the curve is related to the “superficial hydrogen”, other peaks are related to the “dissolved hydrogen” (according standard [32]). The square of colored area on Fig. 2 is proportional to the amount of dissolved hydrogen.

The state standard [32] defines superficial hydrogen as the hydrogen adsorbed on the sample surface. Ref. [32] indicates two ways of measuring the superficial hydrogen:

1. The VHE method suggests that the area under the first peak extraction curve is proportional to the amount of superficial hydrogen.
2. The rods are degassed under high vacuum at a temperature above 500 °C for 10–15 h. Then they are cooled and removed from the vacuum volume. The samples for measuring the hydrogen concentration are machined from these rods and the hydrogen amount extracted from these samples is measured. This hydrogen is considered to be the superficial one.

The investigators face a number of problems while measuring the amount of superficial hydrogen and the separation of superficial and dissolved hydrogen however this broad topic is beyond the scope of this particular article.

In the VHM method realized in the AV-1, the sample is discharged into the analytical branch where a graphite crucible is situated and heated up to the extraction temperature 700 °C. The VHM curve for the sample of D-16 alloy is shown in Fig. 3.

The sample mass is 0.8 g whereas the mass of the graphite crucible is 2.5 g. So, the sample temperature becomes equal to 500 °C (the temperature of the start of dissolved hydrogen extraction) in 10–15 s due to thermal conductivity and heat capacity of the crucible. The value of coefficient for absorption of IR radiation of graphite is close to 1. Hence the time necessary for heating and melting of the sample is about 300 s. As seen from the extraction curve given in Fig. 3, the extraction time is about 2000 s, that is within 30% coincides with the extraction time of VHE in which the extraction temperature below the melting point.

It is worth noting that in the VHM extraction the working temperature (700 °C) is considerably higher than the melting point of D-16 alloy (638 °C). The melting point is the working temperature for the ACF method. Thus the rate of hydrogen transport by diffusion of VHM should be higher and the extraction time should be considerably lower than that for ACF method, however this is not observed.

The measurement of hydrogen concentration using the analyzer RH 402 consists of three main operations:

1. Degassing of empty graphite crucible at the temperature 1100–1200 °C.
2. Extraction of superficial hydrogen. The sample is discharged into the crucible becoming cool after degassing. Then induction heating of the crucible-sample system is made during 20 s. The power of HF heater at this stage is about 5 kW. The sample is heated to a temperature of 240–260 °C. It is supposed that this temperature is sufficient for complete desorption of superficial hydrogen, but it is not sufficient for diffusion of dissolved hydrogen.
3. Extraction of dissolved hydrogen. The sample slightly cooled after previous operation is reheated during 40 s by

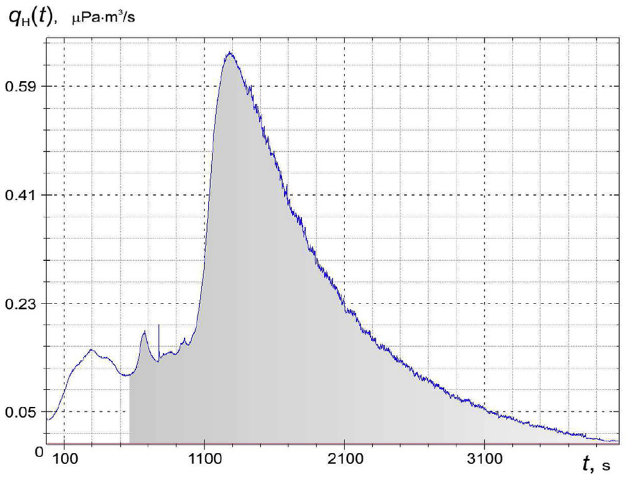

Fig. 2 – VHE extraction curve for the sample of D-16 alloy. Mass of the sample is 2 g. The extraction temperature is 530 °C.

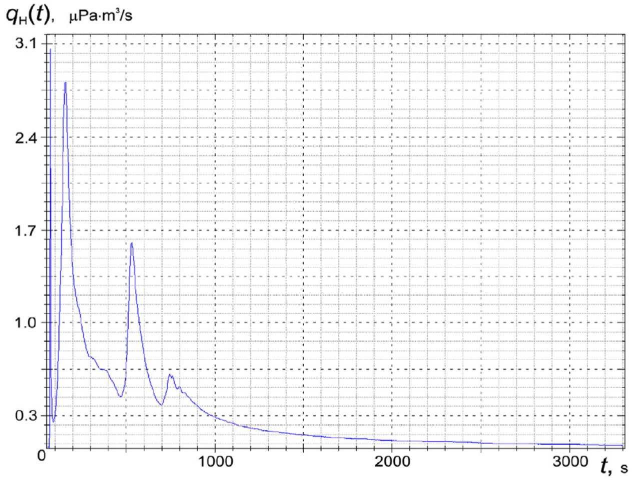

Fig. 3 – The VHM extraction curve for the sample of D-16 alloy. Mass of the sample is 0.8 g. The extraction temperature is 700 °C.

the HF heater. The duration of heating is selected such that the sample is warmed to its melting point (560–660 °C) and is fully melted.

The duration of impulse of HF heating is empirically chosen for each group of alloys. For aluminum alloys it is important to prevent the evaporation of the ligatures polluting the analyzer. Therefore, the total sample melting should occur during the measurements at the lowest possible temperature. In some analyzers the feedback is arranged on the crucible luminosity. At the moment of the sample solidus the surface of the crucible is darkened, that is the signal for switching off the heating.

Measurements on RH 402 occur in a graphite crucible which is individual for each sample. As indicated in Ref. [35] these crucibles can be a source of additional hydrogen which reduces reliability of the measurements.

After closure of the measurement and cooling a sample one can heat this sample together with the crucible in a HF heater, thus one can measure the residual hydrogen without removing it from the analyzer.

The remelted sample can be extracted from the crucible as a cylindrical ingot of 9 mm diameter and about 35 mm height. This ingot can also be used for repeated measurements of the hydrogen concentration.

Completeness of extracting hydrogen analyzer is checked during configuration by re-measurement of the concentration. According to standard [36], the hydrogen concentration should be less than 0.03 ppm at re-measurement. It is from 10% to 30% of the initial content of dissolved hydrogen for most aluminum alloys.

Time dependences of the HF power and the hydrogen flux from the sample of alloy D-16 obtained using analyzer RH 402 are shown in Fig. 4.

It is clearly seen that the extraction cycle for dissolved hydrogen (second maximum) lasts only 120 s, after that the hydrogen flux is ceased. The sample heating up to full melting lasts for about 40 s.

Results of experiment with sample of alloy D-16

In the experiments we used reference samples from a single ingot of the alloy D-16, which already passed the preliminary study. During this study two small samples were cut and tested by the method of VHE from each rod. Average value of concentration of dissolved hydrogen is 0.31 ppm on batch of rods. The confidence interval at P = 0.95 is equal to [0.28–0.34] ppm (or ±0.03 ppm). 55 cylindrical samples were made from these rods to perform the measurement by RH 402. The treatment of the measurement results was made automatically by the analyzer. Three results were negative value (hydrogen concentrations were less than zero). The results of other 52 measurements were as follows:

- The average value of concentration of dissolved hydrogen is 0.271 ppm;
- Standard deviation is 0.095 ppm;
- The average value of concentration of superficial hydrogen is 0.08 ppm.

Bar chart of distribution of measurement results is shown in Fig. 5.

The maximum of distribution of experimental results on RH 402 is systematically shifted to the left with respect to the average value on batch of rods 0.31 ppm.

After measurements with RH 402 we re-tested 52 samples once more using VHE by the analyzer AV-1. We turned a sample of diameter 9 mm and height 35 mm for RH 402 and another one of diameter of 7 mm and height of 15 mm for AV-1.

The results of re-measurements for the ensemble of 52 samples are as follows:

- The average value of concentration of dissolved hydrogen is 0.148 ppm.
- Standard deviation is 0.042 ppm;
- The average value of concentration of superficial hydrogen is 0.271 ppm.

The bar chart of distribution of the measurement results is shown in Fig. 6.

Comparison of the experimental results presented in Figs. 5 and 6 show that the dispersion increased considerably.

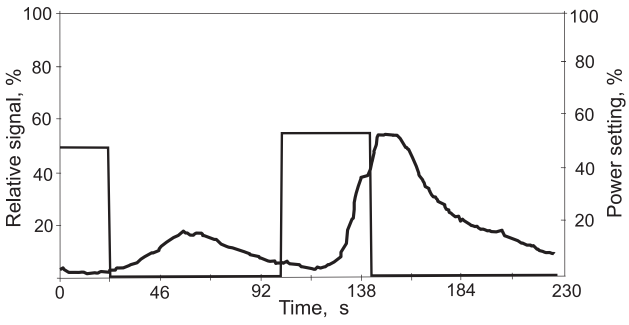

Fig. 4 – Time dependences of the HF power and the hydrogen flux from the sample of alloy D-16 obtained using analyzer RH 402.

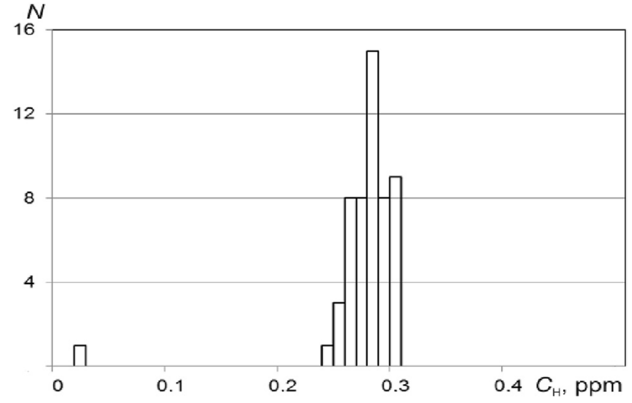

Fig. 5 – Bar chart of distribution of concentration of dissolved hydrogen in small samples cutted from reference sample D-16 and measured by RH 402. (N is the number of samples in the range.)

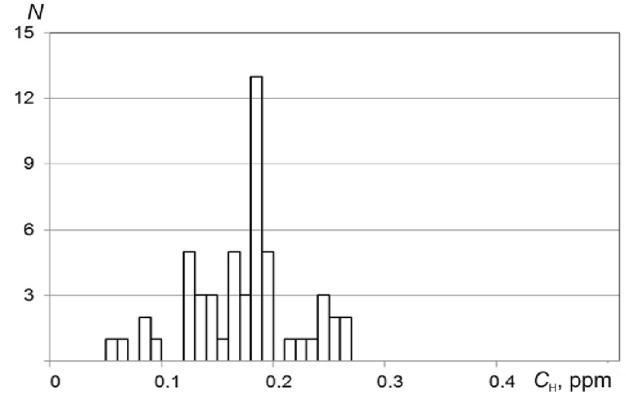

Fig. 6 – Bar chart of distribution of concentration of dissolved hydrogen in D-16 was re-measured by AV-1. (*N* is the number of samples in the range.)

There are four peaks corresponding to the hydrogen content of 0.08 ppm, 0.13 ppm, 0.18 ppm (main) and 0.25 ppm (Fig. 6). The distribution of the results in initial samples (Fig. 5) looks like a normal distribution.

About a half of the amount of dissolved hydrogen remains inside the sample after the measurement by ACF method. The dispersion of value of concentration of the dissolved hydrogen in the repeated measurements is considerably higher than that for initial samples (Fig. 5).

Thus the fast ACF method leads to degassing of sample which is both incomplete and unreliable on the value of concentration of residual hydrogen.

Control of concentration of residual hydrogen in measurements using the RH 402 is made by means of repeated analysis of samples. The value of content of residual hydrogen must not exceed 0.030 ppm. This value is 5 times smaller than the value of amount of dissolved hydrogen (0.148 ppm) in the samples analyzed by using RH 402, as follows from our measurements.

In aluminum alloys for aero cosmic branch, the content of dissolved hydrogen is strictly limited by requirements of standards. For this reason, the reliability of result on measurement of concentration of dissolved hydrogen is of great importance. It was shown in Refs. [37–39] that excess of hydrogen content by two times leads to essential decrease of the yield limits and durability. This can cause instability and the destruction of carrying structures.

The main results of 52 repeated experiments, in which content of dissolved hydrogen has been measured using the VHE method, are as follows:

1. High content of dissolved hydrogen up to the half of the initial value is detected.
2. There is a large sweep of values of concentration of dissolved hydrogen, namely from 0.05 ppm up to 0.25 ppm.

The reasons for these large discrepancies of measurement results from different methods can be explained with the help of the model of a multi-channel diffusion, cf. [26].

Modeling the degassing process during measurements of hydrogen concentration using VHE

Consider the process of the sample heating in vacuum. The sample has the form of cylinder with diameter $2a$ and height l.

The extractor walls are made of quartz glass. The temperature of analytic branch (or appendix) is maintained by the regulator of a furnace on the constant level T_0 equal to the extraction temperature. Quartz has practically zeroth thermal conductivity, contact between the sample and walls is practically absent. Thus the heat transfer from the wall of extractor to the analyzed sample occurs due to radiation. The power of heat radiation absorbed by the sample is:

$$\frac{dQ}{dt} = \sigma S \varepsilon_T \left(T_0^4 - T^4\right), \tag{1}$$

where σ=5.6687·10^{-8} W/m^2 K^4 is the Stephan-Boltzman constant, S is the sample area, absorbing radiations, T is the current temperature of sample at the moment t, ε_T is the absorption coefficient, whose dependence on temperature has the form:

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

The Debye temperature for aluminum is 160 °C, thus, the heat capacity in the range of temperature of interest weakly depends on temperature and equals C_s=1.15 [kJ/kg K]. The heat dQ, absorbed by the sample increases its temperature by dT,

$$dQ = C_s \rho V dT, \tag{3}$$

where ρ is the density, V is the sample volume.

The equation for the sample heating is derived from the relations (1)–(3)

$$\frac{dT}{dt} = \frac{\sigma S}{C_s \rho V} \cdot 7 \cdot 10^{-5} \cdot (T + 64.3)\left(T_0^4 - T^4\right). \tag{4}$$

Consider the hydrogen diffusion in a sample whose temperature obeys relation (4). The equations for time-dependent hydrogen diffusion in the sample have the form:

$$\Delta C = \frac{1}{D}\frac{\partial C}{\partial t} \tag{5}$$

$$C\big|_S = 0$$

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

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

Taking into account the cylindrical form of the sample and given initial and boundary conditions one obtains the following first member of Fourier expansion for solution of Eq. (5):

$$C(r,z,t) = \frac{C_0 \pi}{0,836} \sin\frac{\pi z}{l} \cdot J_0\left(\gamma_1 \frac{r}{a}\right) \cdot f_1(t,u,D_0) \tag{6}$$

where l and a are the height and radius of cylinder, respectively, r and z are the standard denotation for the coordinates in the cylindrical frame system, γ_1 is the first root of the equation $J_0(\gamma_1) = 0$, and the function $f_1(t, u, D_0)$ is a solution of the equations:

$$\dot{f}_1 + D_0\cdot\exp\left(-\frac{u}{kT}\right)\left(\frac{\pi^2}{l^2}+\frac{\gamma_1^2}{a^2}\right)f_1 = 0 \tag{7}$$

$$f_1(0,u,D_0) = 1$$

In performing measurements the apparatus registers the flux of hydrogen $q(t)$ through the surface of sample. According to the diffusion equation this flux is:

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

Let us substitute expression (6) for the first member of Fourier expansion into formula (8). After integration over the sample surface we obtain the hydrogen flux with the activations energy u and diffusion constant D_0 as a function of time:

$$q(t) = 14,56\cdot\gamma_1 J_1(\gamma_1)\cdot C_0\cdot l\cdot\left[\frac{\pi^2a^2}{2\gamma_1^2l^2}+1\right]\cdot D_0\cdot\exp\left(-\frac{u}{kT}\right)\cdot f_1(t,u,D_0) \tag{9}$$

If one supposes that hydrogen in the sample is contained in traps with different activation energy u_i, corresponding diffusion constant D_{0i} and initial hydrogen concentration C_{0i}, then the superposition principal can be used due to linearity of the diffusion Eq. (5). In that case the full flux of hydrogen from the sample $q(t)$ can be represented by the following sum:

$$q(t) = 14,56\cdot\gamma_1 J_1(\gamma_1)\cdot l\cdot\left[\frac{\pi^2a^2}{2\gamma_1^2l^2}+1\right]\cdot\sum_i C_{0i}\cdot D_{0i}\cdot\exp\left(-\frac{u_i}{kT}\right)\cdot f_1(t,u_i,D_{0i}), \tag{10}$$

where $f_1(t, u_i, D_{0i})$ is a solution of Eq. (7) at fixed values of the constant u_i, D_{0i}, C0i.

The plot of the components of approximating curve together with experimental curve is shown in Fig. 7.

As a result of performed approximation we have obtained the values of diffusion parameters, such as the activation energy u_i and the diffusion constant D_{0i} for the hydrogen which is dissolved in metal.

The analysis of experimental curve for different alloys shows that the values of activation energy of hydrogen diffusion in aluminum alloys lies in the range from 0.3 to 1.3 eV. The relative mass fraction of hydrogen with low activation energy amounts about 50% and depends considerably on the alloy compositions. Under the uniform and long heating of the sample it is expected that the entire hydrogen will be extracted from the sample. Increasing the temperature of analysis leads to acceleration of diffusion process. When comparing Figs. 2 and 3 it should be noted that the sample diameter in Fig. 3 is 30% smaller than that of the sample in Fig. 2, therefore at the same temperature the extraction time even should be 30% smaller.

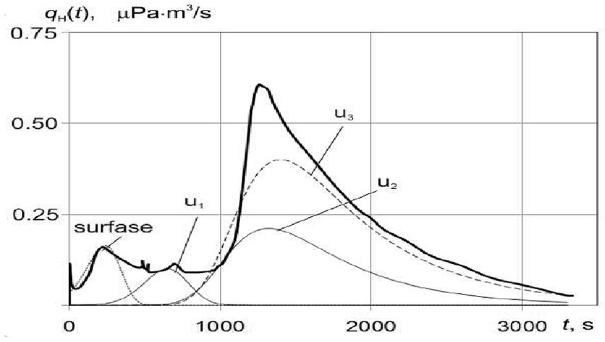

Fig. 7 – Extraction curve for sample of alloy D-16 (solid line) and result of its approximation as a superposition of peaks.

However relative increase of temperature in Kelvin in transitions from the VHE to VHM of the sample amounts from 10 to 25%. Therefore the extractions time in VHM method differs not so much (about 30–40%) from the extraction time in the VHE method.

Modeling of degassing process in analysis of hydrogen content using the ACF method

A very large difference between hydrogen extraction time in ACF method and vacuum methods (2–3 min and 30–60 min, respectively) has been observed. The apparatus developed for

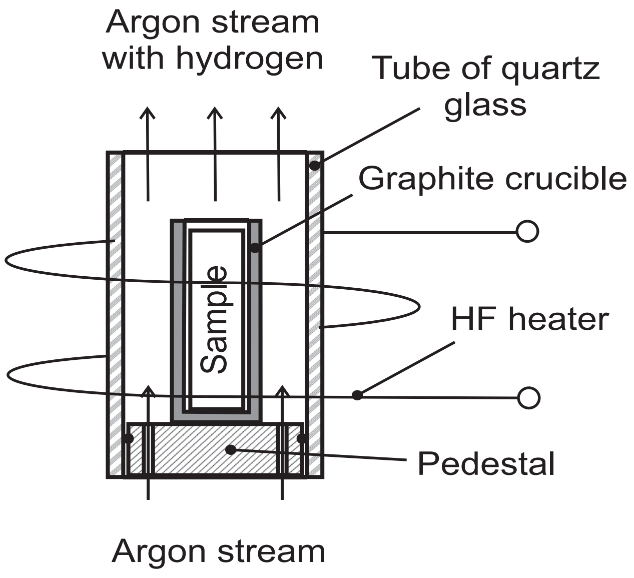

Fig. 8 – Scheme of probe preparation in the analyzer RH 402.

mathematical modeling of hydrogen diffusion in solids makes it possible to calculate the hydrogen diffusion process during the HF heating of sample in the argon flux. The scheme of probe preparation of the analyzer RH 402 is shown in Fig. 8.

The stable flux of gas carrier (pure argon) flows through holes in pedestal forming cylindrical jet of gas around the graphite crucible with the tested sample. The crucible and sample are heated by HF heater up to the material melting temperature. Extracted from sample hydrogen penetrates into the flux of gas carrier. After that the gas is cleaned by a sorbent and analyzed for determination of hydrogen concentration in gas using the thermal conductivity detector. The heating of crucible with sample up to its melting temperature takes 40 s. The HF power of heater is 5 kW.

The cooling of sample occurs due to heat transfer to gas carrier and to heat radiation of the samples and graphite crucible. The equation of heat balance for sample and crucible can be written as:

$$(C_s \cdot m_s + C_c \cdot m_c)dT = \left(- q_{cnv} - q_{rad} + q_{hf} \right) dt, \tag{11}$$

where $C_c = 917$ J/(kg K) is the heat capacity of graphite, m_c is the mass of crucible, $m_s = \rho V$ is the mass of the sample, q_{cnv} is the power of heat flow carried out by crucible blowing of carrier gas stream, q_{rad} is the power returned at the expense of radiation, q_{hf} is the HF power absorbed by the crucible with sample. When the sample begins to melt its temperature does not change until complete melting. Then

$$dT = 0 \tag{12}$$

The whole energy received from HF heater is used to melt formation. The mass of melted metal is determined from the equation:

$$\lambda_{sl} dm_{sl} = \left(- q_{cnv} - q_{rad} + q_{hf} \right) dt, \tag{13}$$

where m_{sl} is the mass of melted metal, $\lambda_{sl} = 400.3$ kJ/kg is the specific melting heat of aluminum alloy. When switching of the HF heater the sample temperature does not change. This means that the condition (12) is justified until the heat stored in melt metal is spent. After the mass of melt m_s becomes equal to zero, Eq. (11) will be justified again and the sample begins to get cool.

The variables in Eqs. (11)–(13) are related by the following relations:

$$q_{cnv} = \alpha \cdot (T - T_{Ar}) \cdot A, \tag{14}$$

where α is the coefficient of heat transfer from the crucible walls to the flux of gas carrier, T_{Ar} is the temperature of gas carrier, T is the temperature of sample and crucible (due to high heat conduction of aluminum and graphite the temperature distribution is considered uniform). A is the area of free surface of the sample and crucible which is blown by gas.

$$q_{rad} = \sigma A \varepsilon_c \left(T_{Ar}^4 - T^4 \right), \tag{15}$$

where ε_c is the absorption coefficient (about 1 for graphite).

Taking into account that the gas flux along the walls of crucible is laminar we can write:

$$\alpha = K_m \cdot (T - T_{Ar})^{0.25}, \tag{16}$$

where

$$K_m = \frac{\lambda_{Ar}}{2D} \cdot \left(\frac{\rho_{Ar}^2 g D^3 C_{Ar}}{a_{Ar} T_{Ar} \lambda_{Ar}} \right)^{0.25}, \tag{17}$$

is the coefficient depending on properties of gas carrier and geometric sizes of the surface of heat transfer, D is parameter defining the channel, λ_{Ar} is the coefficient of heat conductivity of gas carrier, a_{Ar} is viscosity of the carrier gas, C_{Ar} is the specific heat capacity of the carrier gas, ρ_{Ar} is the density of the carrier gas.

Finally, the equation describing dependence of the sample temperature on time takes the form:

$$\frac{dT}{dt} = -A \cdot \frac{K_m}{C_{sis}} \cdot (T - T_{Ar})^{1.25} - \frac{\sigma A \varepsilon_c}{C_{sis}} \left(T^4 - T_{Ar}^4 \right) + q_{hf}(t)/C_{sis}, \tag{18}$$

where $C_{sis} = C_s \cdot m_s + C_c \cdot m_c$ is the heat capacity of the system “sample and crucible”.

The initial conditions are set by the value of the temperature after degassing of the sample surface, $T(0) = 100$ °C.

The results of integration of Eqs. (12), (13) and (18) are shown in Fig. 9.

As seen from this Figure, when HF heater is switched off the temperature of the analyzed sample falls down to 200 °C within 200 s, i.e. to the temperature of degassing of surface, when diffusion of ”solved” hydrogen from aluminum alloy does not occur from the sample.

This is the reason that leads to decrease of hydrogen flux observed in Fig. 4. The calculation does not take into account the heat exchange with the pedestal on which the crucible is installed. This process can accelerate the cooling process.

When using the law 7 for dependence of temperature of the analyzed sample on time and the values of initial concentration C_{0i} and diffusion constants u_i, D_{0i}, chosen from the VHE data it is possible to construct the time dependence of hydrogen concentrations with different activation energy

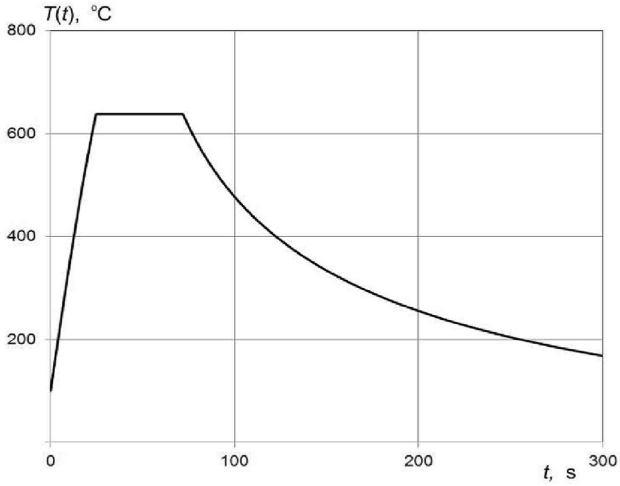

Fig. 9 – Time dependence of temperature of the system “crucible and sample” in the process of heating of the system by HF heater and followed cooling in flux of gas carrier.

(time evolution of populations of energy states). For alloy D-16 this dependence is shown in Fig. 10.

As follows from the calculation results, only parts of hydrogen with high diffusion mobility (or minimum activation energy u_1) are completely extracted in using “fast” ACF method of measuring of the hydrogen concentration. Hydrogen with low diffusion mobility (activation energy u_2, u_3) is extracted only partly.

The example of above calculation shows that 0.167 ppm of hydrogen is left in the sample. This value agrees well with the mean value 0.148 ppm measured by us in the repeated analysis of 52 sample of alloy D-16.

The use of the constructed model makes it possible to calculate the results of repeated analysis by the ACF method realized in RH 402. The hydrogen diffusion in the repeated analyses will begin at lower hydrogen content. The diffusion rate is proportional to the concentration gradient, therefore, if 36% of hydrogen with low diffusion mobility is extracted in the first analysis (that is 30% of initial concentration), then only 14% will extract in the repeated analyses (that is 0.04 ppm, that differs by only 30% from the value of residual hydrogen content allowed by standard for the repeated analyses by RH 402 (0.03 ppm)). The difference between these values (0.04 ppm and 0.03 ppm) is 0.01 ppm. This difference is 3 times smaller than deviation of measurement results in the repeated analysis allowed by standard (0.03 ppm). Hence, the results of modeling of measuring equipment and experimental data for repeated analysis obtained by RH 402 coincide if we take into account the inevitable experimental uncertainty. It is necessary to understand that in real analysis the sample cooling is accompanied by recrystallization process. The diffusion channels shrink due to decreasing the pores which leads to additional decreasing the fraction of hydrogen extracted in repeated analysis.

Discussions of results

It has been suggested that the hydrogen diffusion has activation character and does not depend on aggregate state of sample. A large body of publications has been devoted to the hydrogen diffusion in solid aluminum (see e.g. Refs. [17,40–42]). There is no established glance on the hydrogen diffusion in liquids, since the developed methods for calculation of diffusion coefficients assume existence of crystal lattice which is absent in liquid phase.

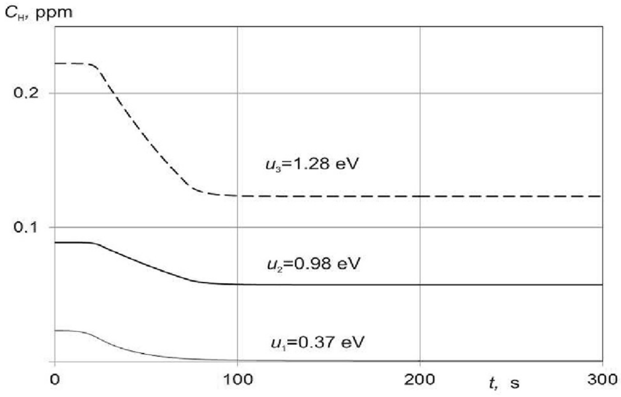

Fig. 10 – Time dependence of hydrogen concentrations with different activation energy for the sample of D-16 alloy. The values of activation energy of the D-16 alloy are: u_1 = 0.37 eV, u_2 = 0.98 eV, u_3 = 1.28 eV.

We studied the hydrogen diffusion in the probe being both in solid and in liquid state at the melting temperature. In this case the convective fluxes and boiling of metal components are absent. Destruction of crystal structure occurring in melting of the sample does not lead to essential increasing of the rate of hydrogen diffusion. This rate is practically equal to the mean value of time of analysis of hydrogen content by method of VHM and VHE that amounts about from 40 to 60 min for aluminum alloys.

Heating an aluminum sample up to the melting temperature does not lead to essential decrease of time for the hydrogen extraction. The characteristic times for measurement of hydrogen concentration into aluminum alloy by methods of VHE and VHM are practically coincident with account for the inevitable experimental uncertainty.

“Fast” melting of sample in the ACF method leads to partial degassing of analyzed sample. It has been proved by repeated measurements of hydrogen concentration by method of VHE using RH 402 that 0.148 ppm of dissolved hydrogen is contained in the series of 52 samples after the measurements. The initial concentration of dissolved hydrogen in the alloy D-16 is 0.31 ppm. Thus, only 0.16 ppm (one half of initial concentration of dissolved hydrogen) is extracted in the ACF method.

Hence, we have experimentally proved that there does not exist any significant effect of “squeezing out” of hydrogen during the process of solidification of the aluminum alloy. The modeling that we carried out allows us to exclude the existence of this effect, at least in the samples with a typical size of 1 cm and a weight of about 1–3 g. However this effect can only justify the technique ”of fast measurements” which is the central idea for the industrial hydrogen analyzers Juwe H-mat 221, Leco TCH 600, Leco DH 603, Leco RH 402. These analyzers are widely used in industry. The problems of these analyzers measuring the hydrogen concentrations less than 1 ppm were pointed out in the report [35]. This issue is extremely important for the industry since these technological measurements deliver inaccurate data.

The results of calculation using the model of multichannel hydrogen diffusion show that 0.125 ppm of hydrogen should remain inside the sample. The results of 52 tests yield the mean value of content of dissolved hydrogen equal to 0.148 ppm. Disagreement between the experimental results (0.148 ppm) and the prediction of model (0.125 ppm) is 0.023 ppm, that is less than the difference between results of measurement allowed by the standard (0.03 ppm). The model of multichannel diffusion is confirmed by particular diffusion mechanisms working in parallel. For example, Ref. [43] suggests the existence of several channels of hydrogen diffusion in the martensitic steels. The results of applications of the model of multichannel diffusion to steels are shown in Ref. [44].

The modeling of results of repeated measurements on RH 402 yields the value of hydrogen concentration equal to

0.040 ppm that agrees with the standard for repeated analysis (0.030 ppm). The difference between results predicted by the mathematical model and standard is 0.01 ppm. This is twice smaller than the allowed difference between the measurement results which at the hydrogen concentrations is less than 0.08 ppm is 0.030 ppm (see Ref. [32]).

Taking into account the usual measurement uncertainty and the allowed difference between the measurement results we can make the following statements:

1. The time of hydrogen diffusion from the sample to its surface in the method of VHE (the temperature of extraction is 530 °C) and VHM (the temperature of extraction is 750 °C) is almost the same;
2. The amount of hydrogen remaining in the probe after analysis by the ACF method measured experimentally in repeated test of sample by the method of VHE coincides with the result of mathematical modeling by multichannel diffusion;
3. The residual concentration of hydrogen in repeated analysis of probe by the ACF method coincides with the result of modeling of the process of multichannel diffusion.

It is evident that the diffusion mobility is determined by the type of traps in which the hydrogen is contained. The limitations on the value of total hydrogen concentration in metal guarantee that its content in any type of traps is less than the given value. The fact that only extraction of hydrogen with high diffusion mobility occurs at fast melting deprives us the confidence that the results of this analysis can be considered as qualitative rather than quantitative ones.

It is known that “fast” ACF method of measurement of the hydrogen concentration yields much larger spread of results than the VHE method. This is explained by strong dependence of heating rate and cooling rate (and hence the hydrogen concentration) on the following hardly controlled conditions: quality of the heat contact between the crucible and pedestal, the speed of flux of the gas carrier inside the quartz tube containing the crucible with sample, the quality of contact between crucible and lateral surface of sample, etc. All these factors determine the rate of heat exchange in the process of test of the sample.

The crystallization process also influences the value of determined hydrogen content. After fast heating of sample the modification of its crystal structure occurs. This can decelerate the hydrogen diffusion remaining in the sample.

Conclusions

The model of multichannel diffusion of hydrogen in solid has been used for comparative study of the process of hydrogen extraction in the ACF method and vacuum methods VHE and VHM.

The main results of studying the ACF method are as follows:

- Only hydrogen on traps with high diffusion mobility is extracted completely during sample testing.
- The experimental data obtained on aluminum alloys shows that about 50% of the initial concentration of dissolved hydrogen remains inside the sample after the measurement.
- The repeated measurement of sample allows one to extract 0.03 ppm of hydrogen, that is 1/5 of the remaining 50% of dissolved hydrogen. This creates an illusion of complete extractions of hydrogen from the probe.
- Heating up to the melting point does not lead to essential acceleration of hydrogen extraction from sample.
- We have experimentally proved that there does not exist any significant effect of “squeezing out” of hydrogen during the process of solidification of the aluminum alloy.

The use of VHE method allows one to control the completeness of hydrogen extraction in a natural way by excess of the value of the hydrogen flux at a constant temperature of analysis over background and to obtain reliable information the hydrogen content inside the material.

Using the VHE method the diffusion parameters such as the value the energy states and their populations, the diffusions constant have been determined. The use of the diffusion parameters allowed constructing an adequate model of multichannel diffusion whose results agree with the experimental data. It has been proved that the mean velocity of hydrogen transport and mean coefficients of diffusion depend on the initial population of the energy levels and they can differ for the same material.

Information about the diffusion parameters makes it possible to perform an adequate prediction.

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