

## INVESTIGATION OF THE COMPLETENESS OF SPECIMEN DEGASSING IN AN ANALYSIS OF THE HYDROGEN CONTENT OF ALUMINUM ALLOYS

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*Experiments and mathematical modeling of the dynamics of the heating of metallic specimens and the diffusion of hydrogen inside them show that not all the hydrogen which has a high bond energy is extracted from the specimens by the method of melting them in a stream of a carrier gas. This finding might present serious obstacles to reliably determining hydrogen content by this method in aluminum-magnesium and aluminum-lithium alloys.*

**Key words:** *analysis of hydrogen content, diffusion, industrial analyzer, melting in a stream of a carrier gas, vacuum-melting.*

Analyzing the hydrogen content of aluminum alloys is a mandatory part of the quality control of ingots of such alloys. Analytical methods based on vacuum-heating and vacuum-melting and involving recording of the absolute amount of hydrogen released by a specimen were developed as far back as the 1930s. The time required to perform an analysis by these methods ranges from 45 min to 2 h.

Modern technology makes it possible to use the more productive method *of melting in a flow of a carrier gas*. The leading instrument manufacturers (LECO, CIHA JUWE, Germany) make hydrogen analyzers that operate on the basis of this method and employ induction heating. The main distinction of this approach is the short analysis time – 2–5 min for aluminum alloys. Given the global competition that exists, the time factor has become decisive in choosing a method to analyze hydrogen content at the factory. The prevailing opinion of specialists in the given field is that the classical methods are obsolete and should not be used in factory laboratories.

It is generally believed that the time required to fully extract hydrogen from a metal specimen by melting it in a flow of a carrier gas can be reduced significantly by using induction heating to rapidly heat the crucible holding the specimen to the melting point of the metal and then having hydrogen rapidly displaced from the specimen by the crystallization front formed after the induction heating is discontinued. To prevent sublimation from taking place, the induction heating is ended the moment the specimen has completely melted. Thus, the crystallization of the alloy begins immediately after melting has ended.

At the same time, there are empirical data that are in conflict with the above opinions.

One study of the diffusion of hydrogen during the crystallization of aluminum [1] did not reveal any changes in the flow of hydrogen extracted from the specimen at different crystallization rates. The explanation for this is that the crystallization front is not continuous but instead consists of single crystals that are growing in different directions and are separated from one another by a liquid phase.

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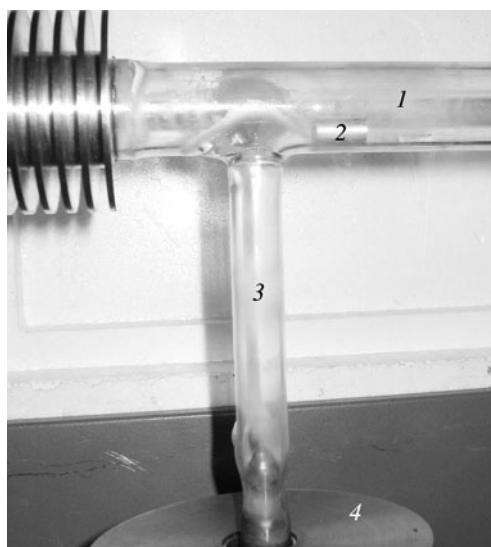


Fig. 1. Extraction system of the analyzer.

In the classical vacuum-heating method, where hydrogen is extracted from the specimen near the melting point of the metal (500–600°C), the extraction process takes from 45 min to 1.5 h – depending on the type of alloy. Thus, the rate of diffusion of hydrogen has been increased by a factor of 10–20 in the rapid analytical methods that have been developed. Then the analysis should take even less time in vacuum-melting, where the time needed to melt the specimen in a crucible holding pre-melted metal is 20–30 sec and the extraction temperature is 700–750°C (the melting point of most aluminum alloys is below 650°C). At the same time, the complete extraction of hydrogen in vacuum-melting is known to take roughly 40 min.

A number of experimental studies [2–4] have shown that the hydrogen dissolved in aluminum alloys has different values for the bond energy. The diffusion of hydrogen-bearing components with different bond energies may accelerate at different rates as the temperature of the metal rises. Thus, it cannot be said that all of the hydrogen dissolved in an alloy is rapidly and completely extracted from the alloy. *Hydrogen with a low bond energy will be extracted quickly and completely, while hydrogen that is strongly bound in the metal will not be extracted within 5 min and will remain in the metal after that length of time.*

The wide use of the “rapid” method of melting in a flow of a carrier gas to determine the hydrogen content of aluminum alloys shows that the measurement scatter which is seen in practice is appreciably greater than the scatter that occurs in the method of vacuum-heating.

Thus, the available data indicate that hydrogen is not fully extracted in a rapid analysis and that some of the dissolved hydrogen should still be inside the specimen after the analysis. The goal of our investigation was to theoretically and experimentally determine the amount of hydrogen that remains in the specimen.

In studying the process of extracting hydrogen from aluminum alloys, we used experimental data obtained both with the classical methods of vacuum-melting and vacuum-heating and with the “rapid” method of melting in a stream of a carrier gas. The technology used for vacuum-heating has been standardized (GOST 21132.1-98) and realized in the form of hydrogen analyzer AV-1 (made by the Russian company EPT). This instrument can also be used to analyze the hydrogen content of aluminum alloys by the vacuum-melting method.

The technology used to perform analyses by melting in a carrier-gas flow is nearly the same on instruments made by different manufacturers. Thus, we chose to perform our analysis with hydrogen analyzer RH402 (made by LECO), which is widely used in the metallurgical industry.

In performing *analyses of hydrogen content by the method of vacuum-heating with the use of an AV-1 analyzer* (Fig. 1), the cylindrical specimens 2 are placed in the cold holder 1 of the extractor, which is made of thin quartz glass.

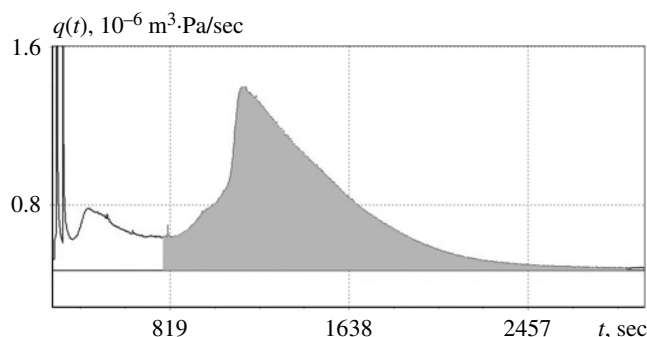


Fig. 2. Extraction curve for a specimen of alloy AMg-5; extraction temperature 530°C.

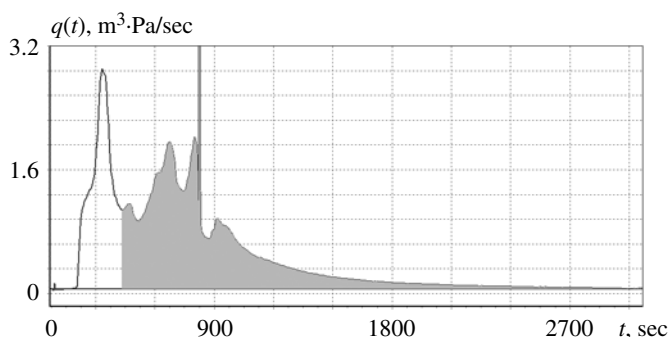


Fig. 3. Extraction curve obtained in the vacuum-melting method for a specimen of alloy D16; extraction temperature 750°C.

The extraction unit satisfies the requirements of the GOST 21132.1-98 standard. A furnace with resistive heaters is used for heating, and the temperature is set and kept within 2°C of the set point by a regulator.

A constant extraction temperature is automatically maintained in holder 3 by stove 4. For most metals, the extraction temperature is within the range 400–800°C. The volume of the extractor is tightly connected to the vacuum pump of the analyzer. A working pressure of 100 μPa is maintained in the extraction system during the analysis. A pusher pushes the specimen into heated analytical holder 3, where its temperature is slowly increased to the extraction temperature. The amount of hydrogen that leaves the specimen is measured by a mass-spectrometric analyzer that has already been calibrated using specimens with a standard hydrogen content. The extraction curve (Fig. 2) shows the time dependence of the flow of hydrogen leaving the specimen. The area under the curve is proportional to the amount of hydrogen that was extracted. In accordance with the GOST 21132.1-98 standard, the first peak of the extraction curve is for surface hydrogen and the other peaks are for dissolved hydrogen. Figure 2 shows the area under the curve that is proportional to the amount of dissolved hydrogen.

When the AV-1 analyzer is used with the method of vacuum-melting, the only difference in the technology employed for the analysis is that the specimen is ejected into an empty graphite crucible heated to 750°C. Figure 3 shows the extraction curve obtained for a specimen of alloy D16 by the vacuum-melting method. We tested a specimen weighing about 1 g in a crucible weighing 2.5 g. Thus, due to the thermal conductivity and heat capacity of the crucible, the specimen had a temperature of roughly 500°C after just 10–15 sec. The coefficient that expresses the absorption of infrared radiation is close to unity for graphite, so that it took approximately 300–400 sec to heat and melt the specimen. It can be seen from the extraction curve (see Fig. 3) that the entire analysis took about 47 min.

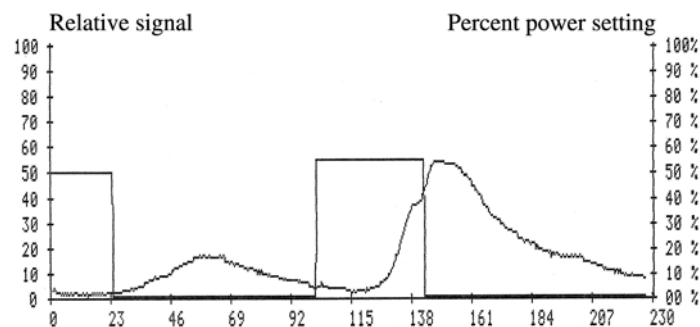


Fig. 4. Recording of oscillogram showing the hydrogen flow and the HF furnace feed in an RH402 analyzer.

It must be pointed out that the hydrogen extraction temperature is appreciably higher than the melting point of aluminum (638°C), i.e., the rate of diffusion of hydrogen should be appreciably greater and hydrogen extraction time should be appreciably shorter than in the “rapid” method. However, this is not seen in practice.

*Analysis of hydrogen content by the method of melting in a carrier-gas flow with the use of an RH402 analyzer* entails the completion of three main operations:

- 1) degassing of the graphite crucible at 1100–1200°C;
- 2) extraction of the surface hydrogen. The specimen is ejected into the crucible, which is cooler after the degassing operation. Induction heating is carried out for 20 sec, which raises the temperature of the specimen to 240–260°C. It is being suggested that this temperature is sufficient for complete extraction of the hydrogen adsorbed on the specimen surface but is inadequate for diffusion of the dissolved hydrogen; and
- 3) when the specimen has cooled after extraction of the surface hydrogen, it is again subjected to induction heating for 40 sec. In order to extract the dissolved hydrogen, the specimen is heated to the melting point of the metal (560–660°C) and completely melted.

The length of time that the specimen undergoes high-frequency (HF) heating is chosen experimentally for each specific group of alloys. Some analyzers provide feedback based on the brightness of the crucible. Such analyzers indicate that the crucible becomes darker when the specimen reaches the solidus temperature, and this is taken as a signal to turn off the HF heating. In accordance with the GOST R 5096.5-96 standard, a repeat analysis of a specimen that has already been analyzed should show a hydrogen content of less than 0.03 n.cm<sup>3</sup>/100 g. For most aluminum alloys, this amount is 10–30% of the initial hydrogen content of the specimen.

It is apparent from oscillograms of the supply current of the induction furnace (rectangles) and the results obtained by using the RH402 analyzer to record the flow of hydrogen out of a specimen of alloy D16 (Fig. 4) that the cycle for the extraction of dissolved hydrogen only lasts roughly 120 sec. The flow then stops. It takes about 40 sec to heat the specimen until it is completely melted.

*Experimental results.* An extruded 12-mm-diam. bar of alloy D16 was used to study the hydrogen that remains inside a specimen after an analysis is performed by the method of melting in a flow of a carrier gas. The bar was used to make 54 cylindrical specimens 9 mm in diameter and 35 mm in height. The specimens were then automatically analyzed on the RH402 analyzer. Three of the analyses that were performed showed a zero hydrogen content and one analysis showed a negative hydrogen content. If these four results are discarded, then the below results are obtained from the analyses of the remaining 50 specimens (the confidence intervals shown are for a confidence level of 0.95):

- average content of dissolved hydrogen  $0.307 \pm 0.0004$  n.cm<sup>3</sup>/100 g;
- average content of surface hydrogen  $0.105 \pm 0.028$  n.cm<sup>3</sup>/100 g.

For the sake of comparison, the same bar was used to make 20 specimens 8 mm in diameter and 15 mm in height to be analyzed on the AV-1 analyzer. The average hydrogen content of the bar was  $0.35 \pm 0.001 \text{ n.cm}^3/100 \text{ g}$  (the indicated confidence interval is for a confidence level of 0.95).

The difference between the average hydrogen contents obtained by the two methods is substantial:  $0.350 - 0.307 = 0.043 \text{ n.cm}^3/100 \text{ g}$ . This difference is larger than the differences that the GOST 21132.1-98 and GOST R 5096.5-96 standards allow between analytical results for a given hydrogen content.

In accordance with the requirements of the standards, cylindrical specimens 7 mm in diameter and 15 mm in height were bored out of the specimens analyzed on the RH402 analyzer in order to compare the results obtained from the determination of hydrogen content.

Numerous experiments performed on standard government-certified specimens of alloys GSO 1201, D16, and AMg-6 with specified hydrogen contents showed that decreasing the dimensions of the specimen compared to the dimensions stipulated by GOST 21132.1-98 (diameter 8 mm, height 25 mm) does not affect the determination of the content of dissolved hydrogen by the vacuum-heating method on analyzer AV-1. The results obtained from analyses of the sample of 50 specimens are as follows (the confidence intervals are for a confidence level of 0.95):

- average content of dissolved hydrogen  $0.166 \pm 0.013 \text{ n.cm}^3/100 \text{ g}$ ;
- average content of surface hydrogen  $0.303 \pm 0.030 \text{ n.cm}^3/100 \text{ g}$ .

Thus, about half of the hydrogen initially in specimen remains in it after an analysis performed by the method of melting in a carrier gas. The scatter of the values for the content of dissolved hydrogen is appreciably greater than in the initial specimens. Consequently, the degassing of the specimens in the rapid method is not only incomplete, but also unstable – with a large scatter of residual hydrogen content. This is understandable if one considers that with an analysis time of roughly 120 sec, such small components of the measurement system as the initial gap between the specimen and the walls of the crucible, the spot where the crucible is in contact with the pedestal, and contaminants on the crucible can play a large role in the degassing process because they significantly affect the rate of heat transfer and specimen temperature.

Residual hydrogen content is checked regularly on analyzer RH402 by performing a repeat analysis, and according to these checks the residual content of hydrogen is less than  $0.030 \text{ n.cm}^3/100 \text{ g}$ . That value is appreciably lower than the values which we measured.

To explain the differences between the experimental results obtained by the two methods, we resorted to modeling the extraction of hydrogen during the analysis of its content in a specimen.

*Modeling the degassing process in the determination of hydrogen content.* We will examine the process of heating a specimen in a vacuum (the methods of vacuum-heating and vacuum-melting in a crucible). The specimen has the form of a cylinder. The extraction curves can be approximated by using equations that describe the diffusion of hydrogen from the specimen and equations that describe heating in a vacuum [6]. By performing this approximation, we obtain the activation energy  $u_i$  in different hydrogen “traps,” the distribution of hydrogen concentration in relation to activation energy, and the diffusion constants.

Analysis of the extraction curves for different alloys shows that the activation energy of hydrogen in aluminum alloys is within the range 0.3–1.0 eV. The content of hydrogen with a low activation energy is roughly 50%, the exact content depending on the composition of the alloy. If the specimen is uniformly heated over a long period of time, all of the hydrogen should diffuse out of it and be recovered.

An increase in the temperature at which the analysis is performed speeds up diffusion. At the same time, there is a relative increase in temperature (on the Kelvin scale) of 5–15% going from vacuum-heating to vacuum-melting of the specimen. This explains the fact that the time required for hydrogen extraction in vacuum-melting differs slightly from the time required in vacuum-heating. However, there is a clear discrepancy between hydrogen extraction time in the carrier-gas flow and the time required to perform the analysis in a vacuum. The unit that was developed to model diffusion [6] makes it possible to calculate the diffusion of hydrogen in the case of rapid induction heating in a flow of a carrier gas. Let us take a closer look at the method used to prepare specimens for the RH402 analyzer (Fig. 5).

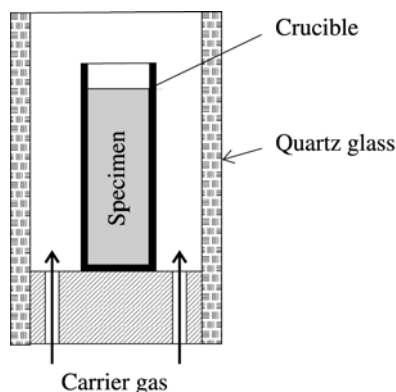


Fig. 5. Diagram of specimen preparation in an RH402 analyzer.

The carrier gas (nitrogen or argon) flows through an opening in the pedestal and around the graphite crucible. The crucible and the specimen are heated to the melting point of the specimen in 40 sec inside an induction furnace. Cooling takes place as a result of the transfer of heat to the carrier-gas flow and thermal radiation by the graphite crucible.

We obtain a differential equation for temperature from the heat-balance equation for the specimen and the crucible with allowance for the aerodynamics of the carrier gas and the heat capacity and heat of fusion of the specimen. As the initial conditions, we take the temperature of the specimen after degassing of its surface  $T(0) = 100^\circ\text{C}$ . An analysis of the results obtained by integrating this equation shows that 200 sec after the end of operation of the HF heater the temperature decreases to  $200^\circ\text{C}$ , i.e., to the temperature at which the surface is degassed. As is known, almost no dissolved hydrogen diffuses out of aluminum alloys at this temperature.

The foregoing explains the drop in the flow of hydrogen from the specimen which is seen in Fig. 4. Heat exchange between the crucible and the pedestal in the analyzer only accelerates the cooling process.

Proceeding on the basis of the pattern of temperature change that was observed, using the diffusion equations in [6], and using values for initial concentration, activation energy, and diffusion constant that were chosen on the basis of vacuum-extraction data, we calculate the time dependence of these concentrations. It follows from the calculations that only the hydrogen components with high diffusional mobility are extracted when rapid analytical methods are used to determine hydrogen content. The hydrogen that has low diffusional mobility is partially extracted.

The calculations show that in the example being examined the residual hydrogen content of the specimen is  $0.14 \text{ n.cm}^3$  per 100 g. This figure is consistent with the average value of  $0.166 \text{ n.cm}^3/100 \text{ g}$ , minimum value of  $0.06 \text{ n.cm}^3/100 \text{ g}$ , and maximum value of  $0.22 \text{ n.cm}^3/100 \text{ g}$  that we measured experimentally for different specimens.

The model that was constructed can be used to obtain results in a repeat analysis performed by the above-indicated rapid method. The analysis is begun at a lower hydrogen content. The rate of diffusion is proportional to the concentration gradient. Thus, if 36% of the hydrogen with low diffusional mobility is extracted in the first analysis and this amount is 30% of the initial concentration of hydrogen in the specimen, the repeat analysis will be able to extract just 14% of the initial concentration, or  $0.045 \text{ n.cm}^3/100 \text{ g}$ . This amount is only slightly greater than the residual hydrogen content allowed by the GOST standard.

It must be taken into account that in an actual analysis the cooling of the specimen is accompanied by recrystallization. The diffusion channels become narrower due to a decrease in the number of pores in the specimen, which in turn further reduces the amount of hydrogen extracted in the repeat analysis.

**Discussion of the Results.** The model was constructed with the assumption that the diffusion of hydrogen is activation in character and is independent of the state of aggregation of the specimen. This validity of this assumption is open to debate. Many studies have been devoted to the diffusion of hydrogen in solid aluminum (see [1–4], for example). No consistent agreement has yet been reached on the diffusion of hydrogen in liquids, since the methods that have been developed

for calculating diffusion coefficients presume the presence of a crystalline lattice. The crystalline lattice is destroyed in the liquid state.

We adopted the hypothesis that the mechanisms of diffusion of hydrogen are identical in solid metal and in the same metal at the solidus point, since there is no convective flow or boiling of the components of the metal in latter state. Moreover, the collapse of the crystalline lattice at the melting point does not lead to a substantial increase in the diffusion coefficients of hydrogen. This is shown by the average amount of time it takes to analyze the hydrogen content of aluminum alloys by the method of vacuum-melting (40 min).

The results obtained here make it possible to explain the difference between the lengths of time required for analyses performed by the “rapid” method and the “classical” methods, since not all of the hydrogen is extracted from the specimen in rapid methods.

The completeness of the extraction process is checked by performing a repeat analysis by a rapid method. This analysis gives a result lower than  $0.03 \text{ n.cm}^3/100 \text{ g}$  because rapid methods completely extract only the hydrogen characterized by high diffusional mobility. They partially extract the hydrogen with low diffusional mobility in both the initial analysis and the repeat analysis. Even then, the result of the repeat analysis depends more on the diffusional mobility of the hydrogen than on its concentration.

The diffusional mobility of hydrogen in materials obviously depends on the type of “traps” in which the hydrogen is located. The physical nature of these traps determines the effect that the hydrogen will have on the mechanical and corrosion properties of the materials. Limiting the total content of hydrogen guarantees that its concentration in any type of trap will be less than the specified value. However, the fact that only hydrogen with high diffusional mobility is completely extracted by rapid melting in a carrier-gas flow deprives us of that confidence and makes the analytical results qualitative in character.

The greater measurement scatter of rapid methods compared to the vacuum-heating method can be explained by the fact that the rates of heating and cooling of the specimen and, thus, the measured hydrogen content, are heavily dependent on such hard-to-control conditions as the quality of the contact between the crucible and the pedestal, the flow velocity of the carrier gas inside the quartz tube, the quality of contact of the lateral surface of the specimen with the crucible, and other factors that determine the rates of heat transfer and heat exchange during the analysis.

The process of crystallization of a material is related to its hydrogen content. The crystalline structure of the specimen is modified after rapid analysis, and this change can slow the diffusion of the hydrogen that is still in the specimen.

In actuality, rapid methods only allow monitoring of the homogeneity of a specimen. This is at least true for aluminum alloys. If the state of the hydrogen inside an alloy undergoes changes – if it forms chemical compounds, for example – then the same given hydrogen content may be measured completely differently by the instrument that is being used.

If the process of making alloys and alloy products is completely automated, then it might be sufficient to just monitor their homogeneity. Otherwise, the use of rapid methods to determine hydrogen can lead to sizable errors. This consideration is especially important for the acceptance control of alloys at metallurgical plants, since the metal may be coming not only from different factories but also from different countries.

The standards used in Russia for the hydrogen content of aluminum alloys were developed on the basis of the vacuum-heating method. Those standards should be re-examined if rapid methods are going to be used for analytical control purposes, since the results of the analysis may underestimate the actual hydrogen content of an alloy.

The data that have been obtained in this investigation show that the vacuum-heating method makes it possible to obtain additional information on the hydrogen bond energies. That information could be used to find correlations between the types of hydrogen traps in materials and the properties of those materials. Taking such an approach would open up a new area of research. The existence of a linkage between hydrogen traps and material properties has already been established, and a method has already been developed for determining the bond energies and diffusion constants of hydrogen.

Eliminating use of the method of vacuum-heating from factory operations without first establishing special regulations for maximum allowable hydrogen content in analyses performed by rapid methods could lead to poor quality control in factory laboratories.

**Conclusions.** The studies completed here have made it possible to determine the reasons for the apparent decrease in the amount of time required to analyze the hydrogen content of alloys when the analysis is performed by melting specimens of the metal in a stream of a carrier gas:

- 1) only hydrogen with high diffusional mobility is extracted from “traps” in the alloy;
- 2) the experimental data indicate that as much as 50% of the hydrogen initially in the alloy remains in it after the specimen has been melted in the stream of carrier gas;
- 3) repeat analysis of the extracted specimen does not make it possible to extract the hydrogen that remains in it, which creates a false impression that all of the hydrogen has been removed from the given alloy;
- 4) heating the specimen to the melting point does not significantly accelerate the extraction of hydrogen from it;
- 5) it is necessary to correct existing standards for hydrogen content if this parameter is to be determined by using rapid methods of analysis; and
- 6) use of the method of vacuum-heating makes it possible to check for the completeness of the extraction of hydrogen in a natural manner, based on the presence of a flow of hydrogen from the specimen at a constant analysis temperature; the vacuum-heating method also makes it possible to obtain new information on the character of the hydrogen bonds inside the material.

## REFERENCES

1. C. Dupuis, Z. Wang, J.-P. Martin, and A. Allard, “An analysis of factors affecting the response of hydrogen determination techniques for aluminum alloys,” in: *Light Metals*, The MMM Society (1992), pp. 1055–1067.
2. P. N. Anyalebechi, “Hydrogen diffusion in Al–Li alloys,” *Metall. Mater. Trans. B*, **21**, No. 4, 649–655 (1990).
3. E. Hashimoto and T. Kino, “Hydrogen diffusion in aluminum at high temperatures,” *J. Phys. F: Met. Phys.*, No. 13, 1157–1165 (1983).
4. C. Wolverton, V. Ozolins, and M. Asta, “Hydrogen in aluminum: First-principles calculations of structure and thermodynamics,” *Phys. Rev. B*, No. 69, 144109 (2004).
5. A. P. Babichev, N. A. Babushkina, A. M. Bratkovskii, et al., *Physical Quantities: Handbook* [in Russian], Energoatomizdat, Moscow (1991).
6. A. M. Polyanskii, V. A. Polyanskii, and Yu. A. Yakovlev, “Studies of the fatigue and fracture of metallic materials with the use of a method for determining hydrogen bond energy in a solid,” *Deform. Razrush. Mater.*, No. 3, 39–43 (2009).