Chapter 13
Hydrogen Diagnostics of Industrial Parts of Aluminum Alloys

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Abstract Aluminum alloys are very popular in a variety of technical applications. The strong influence of hydrogen on the properties of aluminum alloys is known, however, as in the case of steels; it is continuously increasing as new alloys with extreme properties are developed and introduced. Scientific research in the field of the hydrogen effect on the properties of aluminum alloys is mainly focused on the fundamental aspects such as the diffusion coefficients of hydrogen in aluminum, possible types of hydrogen traps, and their effect on the microstructure of alloys. At the same time, the industry has a problem of cracking ingots and semi-finished products (sheets, pipes, and plates), including their further processing and welding. In contrast to the high-strength steels, scientific research does not actually provide specific values for critical hydrogen concentration. The problem of separating the hydrogen adsorbed on the surface and dissolved during measurements has not been solved. There are only a few types of aluminum alloy reference specimens. The article is intended to partially fill this gap. It provides specific examples of the study of technological problems and proposes the measurement methods that allow the separation of hydrogen dissolved and adsorbed on the surface.

Keywords Hydrogen analyzer · Aluminum alloys · Surface hydrogen · Measurement of hydrogen concentration

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13.1 Introduction

Aluminum alloys are widely used in all areas of technology, from street lighting to space systems.

Hydrogen appears in aluminum alloys during their manufacture due to the reaction of aluminum with water and therefore is a critical element of these alloys. The presence of dissolved hydrogen completely determines the porosity of aluminum alloys [1–8]. Hydrogen leads to hydrogen embrittlement, crystallization cracking of ingots, environment-assisted cracking [9, 10], and a decrease in fatigue strength [10, 11].

Much attention in the published articles is paid precisely to the study of various aspects of the interaction of hydrogen with aluminum and its influence on the microstructure of aluminum-based alloys.

In Refs. [12–14], on the basis of experimental data, various mechanisms of the formation of vacancies and pores in aluminum during its crystallization from the melt are discussed. The paper [15] discusses the mechanisms of hydrogen diffusion on the surface and inside an aluminum single crystal. An increase in the concentration of vacancies and pores and the effect of dissolved hydrogen are modeled on the basis of the first principles in [1]. Reference [16] is concerned with the nature and density of hydrogen traps in Al–Zn–Mg alloys, while [17] experimentally investigated the mechanism of pore formation in AlSi7Mg0.3 ingots.

Microdefects arising in a single crystal of aluminum and polycrystalline aluminum are investigated when the surface of samples is bombarded with proton beams and interacts with hydrogen plasma; see [18, 19]. An increase in the concentration of vacancies and the main energy relationships of this process are discussed too.

Micromechanisms of hydrogen traps in aluminum alloy 6061-T6 are investigated in [20].

The effects of cathodic hydrogen charging of aluminum alloy samples were studied in [21, 22].

The temperature dependence of the hydrogen diffusion coefficient was obtained in [23–26].

The limiting solubility of hydrogen in aluminum alloys and the activation energies of hydrogen traps were studied in [27–35].

At the same time, experimental data on the parameters of the interaction of hydrogen with aluminum and its possible states in aluminum alloys published over the past 30 years have a wide spread. For example, the published values of diffusion constant have range $4\cdot10^{-6}$–$1\cdot10^{-9}$ m^2s^{-1} and diffusion activation energies vary between 0.3 and 1.3 eV, cf. [25, 36–40].

The reasons for this spread may be strong surface effects typical for aluminum alloys [15]. In [41], the influence of the oxide layer and vacuum cleaning of the surface on the permeability of aluminum membranes was studied, and it was concluded that the state of the surface has a large effect on the permeability and the actually measured diffusion coefficient of hydrogen.

Modern aluminum alloys, like high-strength stills, are characterized by the values of the mass fraction of hydrogen at the level of 0.04–0.05 ppm. For aluminum, a hydrogen concentration of 0.1 ppm means that for every molecule of H_2 absorbed by the metal, there are about a million aluminum atoms.

Most of the various studies have been carried out without quantitative measurements of the hydrogen concentrations in aluminum and aluminum alloys and without the discussion of specific values of these concentrations. This fact significantly reduces their practical value. Only in a small number of works, for example in [3, 5, 8, 21, 22, 42–44], the hydrogen concentrations were measured and the dependence of the studied effects on these concentrations was studied. Moreover, in some of these works, concentration ranges were investigated up to 7 ppm [22] or even 400 ppm [21] which is not feasible in practice.

Such a spread in the experimental data on concentrations is explained by the fact that when measuring the hydrogen concentration in aluminum alloys, the hydrogen adsorbed on the surface of samples or "surface" hydrogen [44] is a big hindrance, which introduces significant distortions in the measurement results. The standard [45] establishes rules for the exclusion of surface hydrogen, but only for cylindrical samples of two standardized diameters of 8 and 10 mm. In other cases, there are no approaches to the separation of surface hydrogen from the total flux of hydrogen desorbed from the sample. This makes quantitative measurements much more difficult.

Unlike steels, the effect on the properties of low natural concentrations of hydrogen has been little studied, and it is these concentrations that are most often encountered in practical problems. The proposed article is intended to partially fill this gap.

13.2 Experimental Equipment

For the control and determination of hydrogen concentration, we use the hydrogen analyzer AV-1. It can be used to reliably measure both natural, ultra-low hydrogen concentrations, and after special saturation, when concentrations can reach several thousand ppm. The precision hydrogen analyzer AV-1 has been designed for hydrogen detection in metals and alloys under the plant laboratory conditions during the outgoing moldings control with various alloys [44, 46–48]. The operating principle of the analyzer is mass-spectrometric.

The sample processing is shown in Fig. 13.1, which includes a vacuum extractor and a heater (4). The vacuum extractor is made of quartz glass and has three setoffs. The first setoff (1) contains the samples before the test. The hydrogen content analysis takes place in the second setoff (2). The samples which have been tested are kept in the third setoff (3).

Before testing, the heater (4) with a previously set temperature is placed upon the second setoff (2) of the extractor. With the help of a magnetic push rod, the test sample from the first setoff is thrown into the second analytic setoff of the extractor. During the test, the metal sample within the second setoff is subjected to gradual

Fig. 13.1 The sample processing of hydrogen analyzer AV-1

heating up to the extraction temperature. The extraction temperature for the sample is lower than its flowing temperature, as a rule, it is within the interval of 200–900 °C.

The fumes that have been emitted during heating are evacuated from the extractor before the pressure reaches 50 micro Pascal and are analyzed with a mass spectrometer which is located in the vacuum pumping pass customized for the hydrogen line. The end of the testing is identified with the help of a background signal. The background signal remains constant before the beginning and at the end of the testing. As soon as the level of the signal from the sample becomes equal to the background signal, the test stops and the sample from the analytical setoff (2) is placed into the setoff for the samples which have been analyzed (3). For this purpose, the heater (4) is lowered down with the help of a hoisting gear, and the extractor keeps turning about itself until the sample being tested falls down from setoff (2) into setoff (3) under gravity. After that, the extractor is returned to the original position, and the heater is placed on setoff (2) with the help of a hoisting gear. After setting the background hydrogen value, the test continues for the next sample from setoff (1). In such a manner, the next sample is analyzed without vacuum failure. It should be emphasized that the extraction temperature doesn't change during the test. This makes it possible to reach the high stability of the background signal.

The time dependence of hydrogen flow $q_H(t)$ is recorded by the system of digital registration as an extraction curve. Figure 13.2 shows an extraction curve for aluminum alloy AMg6, which is a simple example to describe.

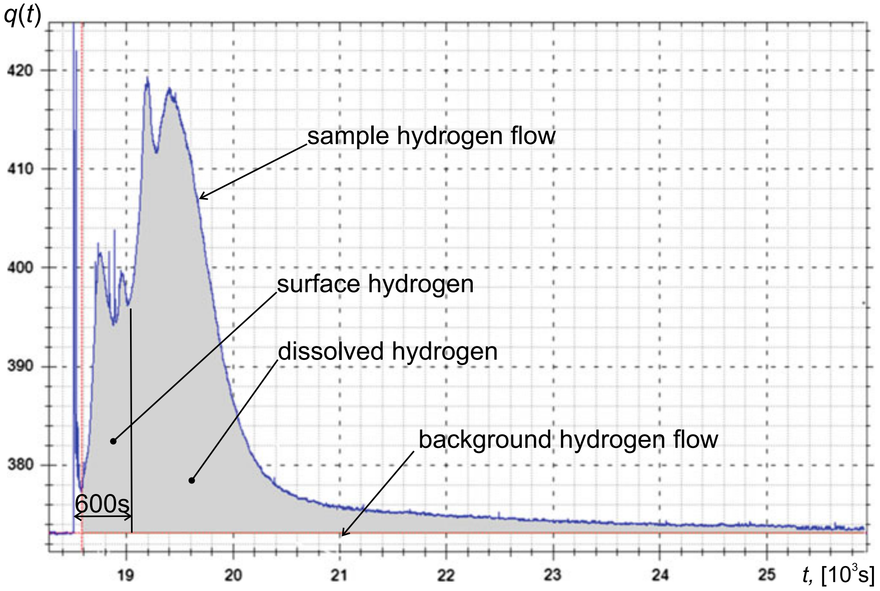


Fig. 13.2 Extraction curve for aluminum alloy AMg6

The time integral from the extraction curve (painted gray in Fig. 13.2) in reference to the background hydrogen flow is proportional to the hydrogen evolved from the sample. The proportionality factor is set during analyzer calibration.

The background hydrogen flux is determined prior to heating the sample. When cylindrical samples with a diameter of 8 mm are used, the first 600 s after the start of heating, hydrogen flux adsorbed on the sample surface or "surface" hydrogen is observed [44, 45]. All subsequent hydrogen flux refers to the extraction of dissolved or internal hydrogen [45].

Each peak of the extraction curve can be correlated with its hydrogen binding energy [44].

13.3 Investigation of the Causes of Rupture of Aluminum Tubes

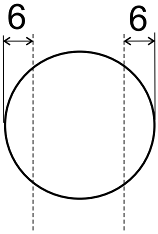
Aluminum tubes are made by impact extrusion. A striker made of high-strength steel at high speed hits a round plate which is a rondole (tablet) of high-purity aluminum alloy. It causes high-speed plastic deformation of the tablet in the mold and the formation of all parts of the tube from one workpiece. High plastic deformations of thousands of percent are observed. The tablets and produced tubes are shown in Fig. 13.3.

Fig. 13.3 Aluminum tablets and produced tubes

Table 13.1 Composition of alloy A7 (%)

Fe	Si	Ti	Al	Cu	Zn
<0.16	<0.16	<0.02	99.7	<0.01	<0.04

Fig. 13.4 Scheme of cutting samples from tablets



With this method of tube production, a significant number of ruptures were observed on the tube surface, shown in Fig. 13.3. The wall thickness of the tube is less than 1 mm. In this case, strong surface effects are observed associated with the hydrogen sorption on the surface and the non-uniform formation of the oxide film; see [41]. In this regard, it was decided to conduct a study of a batch of the material of tablets with a diameter of 23 mm and a thickness of 3 mm made of alloy A7 with aluminum 99.7%. The alloy composition is shown in Table 13.1.

Two specimens were cut from the tablets as shown in Fig. 13.4.

Standard measurements of hydrogen concentration by hot vacuum extraction were carried out. A representative extraction curve is shown in Fig. 13.5.

Surface hydrogen was separated by the extraction curve according to [44, 45]. In this case, only two peaks of the extraction curve are observed, moreover, the samples

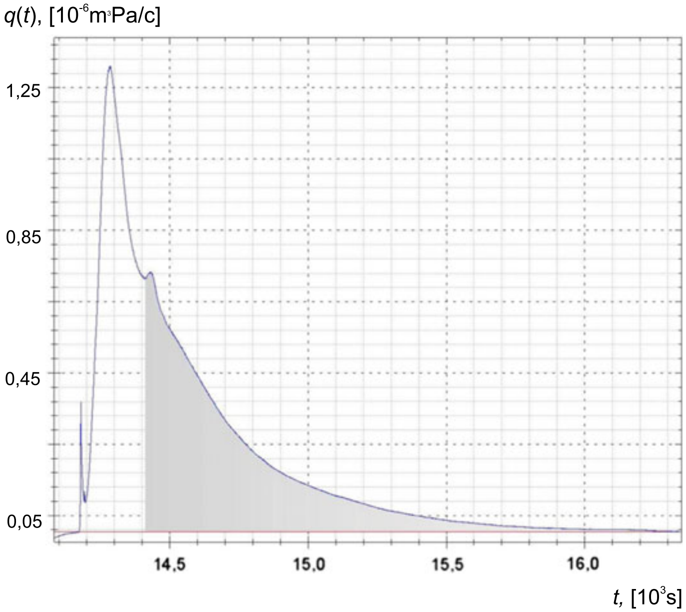


Fig. 13.5 Extraction curve for tablets

Table 13.2 Results of measuring the concentration of hydrogen in tablets. Q_s and Q_d denote surface and dissolved hydrogen, respectively

#	Q_s, [ppm]	Q_d, $[ppm]$
1	1.407	0.883
2	0.376	0.581
3	1.219	0.934
4	0.435	0.613
5	0.923	0.960
6	0.575	0.821
7	0.616	0.887
8	0.552	0.814
9	0.436	0.640
10	0.546	0.683

have a characteristic size close to the standard and the duration of the first peak of ca. 500s is slightly less than the standard time of extraction of the surface hydrogen. In this case, the standard method, when only the first peak is associated with surface hydrogen, gives an adequate result.

The data averaged over two samples for each tablet are presented in Table 13.2.

Table 13.3 Composition of alloy AMg6 (%)

Fe	Si	Mn	Ti	Al	Cu	Be	Mg	Zn
<0.4	<0.4	0.5–0.8	0.02–0.1	91.1–93.68	<0.1	0.0002–0.005	5.6–6.8	<0.2

One can single out the main factor that speaks of the low quality of the table metal: all the tablets belong to the same batch, that is, they are made from one ingot, but there is a strong spread in the measured hydrogen concentrations. The minimum values of Q_d = 0.581 ppm are approximately four times higher than the hydrogen concentration typical for this alloy (in the range of 0.1–0.2 ppm).

An important point is that the normal concentration of hydrogen in aluminum, as a rule, lies in the range of 0.06–0.2 ppm. The values we measured are several times higher, but still make up one atom per hundreds of thousands of aluminum atoms. As the data from [5] show, an increase in hydrogen concentration by 0.1 ppm corresponds to a decrease in the specific density of an aluminum alloy by 10–20% due to the growth of pores. Thus, it can be concluded that, in this case, the excess hydrogen porosity led to a loss of tube wall continuity during extrusion.

The given example shows that the technique of surface hydrogen evolution is the most important element of the metrological system. Without this technique, it is not possible to obtain a reliable quantitative result when measuring the hydrogen concentration in aluminum alloys, since the hydrogen adsorbed on the surface can significantly exceed the internal one.

13.4 Investigation of the Causes of Pipe Cracking During Plastic Deformation

We analyzed samples of aluminum pipes of the AMg6 alloy with a diameter of 120 and 160 mm and a wall thickness of 7 mm, from which the high-pressure gas cylinders are made by pressing. Samples of two types of pipes were taken. Samples of the first type belonged to a batch of pipes from which high-quality cylinders were obtained. Samples of the second type were cut from a batch of pipes, from which the cylinders are obtained with cracks in the walls. The alloy composition is shown in Table 13.3.

To determine the hydrogen content, short annular sections with a length of 15 mm were cut off from the pipes. They were cut along the generatrix of the pipe, according to the diagram in Fig. 13.6.

In all pipes, which are prone to cracking when the cylinders are pressed from them, there is an increased average concentration of dissolved hydrogen of 0.65 ppm and a large spread of the results of individual measurements in each ring (Fig. 13.6) from 0.4 ppm to 0.95 ppm. Please note that these were samples cut with an interval of 10–20 mm between samples.

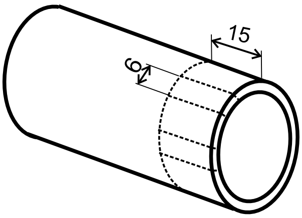


Fig. 13.6 Scheme of cutting samples from a pipe

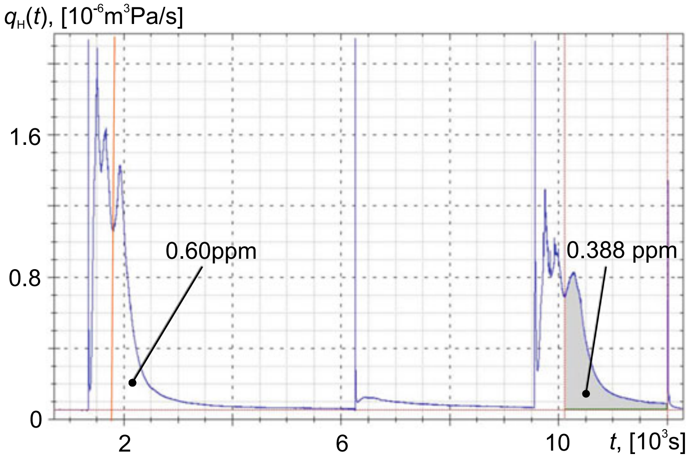


Fig. 13.7 Extraction curves of samples of alloy AMg6

The average hydrogen content of samples of the first batch of proper quality was 0.38–0.39 ppm. The evolution of surface hydrogen remains an important problem. Figure 13.7 shows the extraction curves obtained by analyzing the hydrogen content for these samples. Three peaks are clearly visible on the curves, according to the requirements [45]; only the first peak is related to surface hydrogen. But if we focus on the characteristic time of desorption of the surface hydrogen from samples with a characteristic size of 6–8 mm (about 10 min), then the first two peaks must be attributed to the surface hydrogen.

Figure 13.7 on the left shows the extraction curve for a sample from a low-quality tube, and on the right the curve for a normal sample is shown. With the general similarity of the curves (the number of maxima and their location), it is clearly seen that the area under the first curve is noticeably larger than the area under the second curve.

The area under the extraction curve is proportional to the hydrogen concentration. Taking into account the mass of the sample, the concentration of dissolved hydrogen differs by 2.5 times (the third peak in each of the curves in Fig. 13.7).

Table 13.4 Alloy composition of AD0

Fe	Si	Mn	Ti	Al	Cu	Mg	Zn
<0.3	<0.3	<0.025	<0.1	99.5	<0.15	<0.03	<0.07

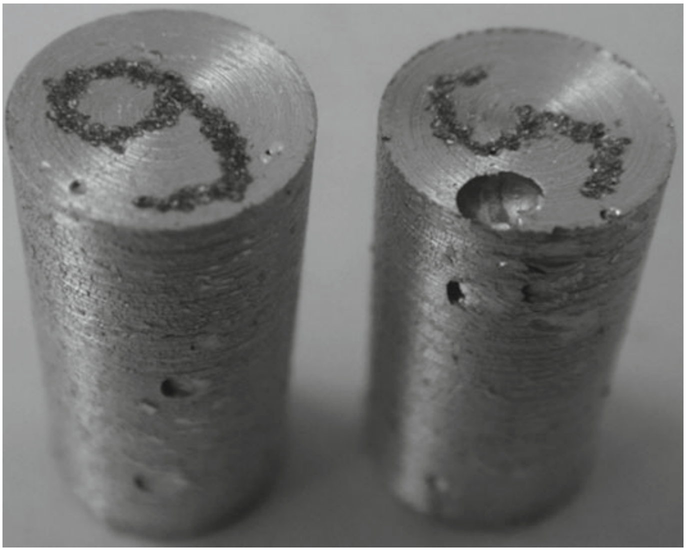


Fig. 13.8 Samples for analysis from alloy AD0

Such a spread in hydrogen concentration can be explained by the increased porosity or the presence of the non-uniform distribution of magnesium over the volume of the alloy. Recently, an increased hydrogen concentration associated with a significant proportion of non-metallic inclusions has been increasingly encountered.

13.5 Investigation of the Causes of Poor Weldability of AD0 Alloy Sheets

Foaming and subsequent cold cracking of the weld were observed when welding AD0 alloy sheets. Samples for analysis shown in Fig. 13.8 8 × 15 mm in size were cut from a sheet of 10 mm thickness. The photograph shows that the entire surface of the samples comes out with relatively large pores. The alloy composition is shown in Table 13.4.

When analyzing these samples, one observes numerous peaks on the extraction curve; see Fig. 13.9. When pores are emptied, a sharp release of hydrogen occurs into the vacuum system of the AV-1 hydrogen analyzer, which is recorded by the mass spectrometer as narrow peaks of large amplitude.

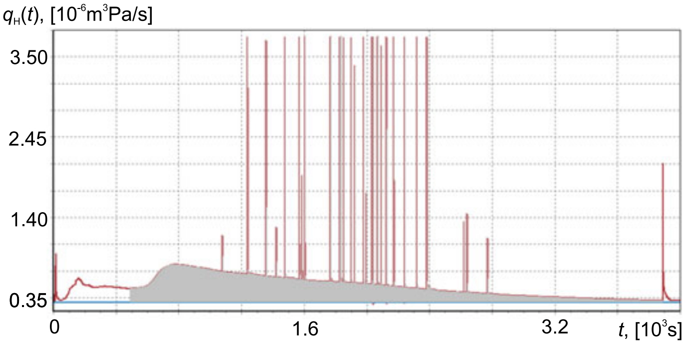


Fig. 13.9 Extraction curve of the sample of aluminum alloy AD0

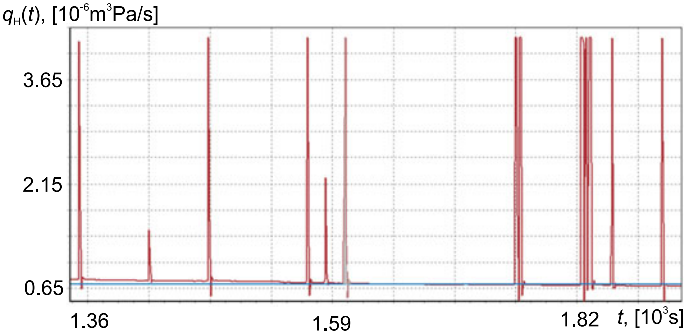


Fig. 13.10 An enlarged fragment of the extraction curve alloy AD0

An enlarged fragment of the extraction curve in Fig. 13.10 demonstrates that the release of hydrogen from the pores occurs smoothly over a finite time interval of 5–10 s. This makes it possible to reliably determine the hydrogen content at such maxima.

The entire curve is calibrated against standard samples for measuring on AV-1; thus, it is possible to calculate the hydrogen amount corresponding to the concentration of hydrogen in each peak. Under normal conditions, it corresponds to a volume of hydrogen of 0.125 norms mm^3. If we assume that the hydrogen in the pore is at approximately atmospheric pressure and that the pore is spherical, then its diameter will be 0.6 mm. The pores of exactly this size, coming out to the surface, are clearly visible in Fig. 13.6. Thus, 20–30 such pores contain the amount of hydrogen, which increases the total hydrogen concentration in the metal by 0.1–0.2 ppm. This effect was observed in the samples studied, where the average hydrogen concentration was 0.4 ppm, that is, it was only twice the normal concentration of dissolved hydrogen for AD0.

Consequently, even a twofold excess of the hydrogen concentration significantly increases the porosity of aluminum alloys, which can lead to cracking and hydrogen embrittlement during the subsequent processing and operation of the metal.

The hydrogen content is controlled for the most critical industries, but only in an ingot. In various technical processes, the concentration of hydrogen can both increase and decrease. Therefore, it is necessary to control the hydrogen content in semi-finished products. At the moment, there is no methodological basis for such control.

13.6 Examination of Samples from AlMn Sheet

Plastic deformation leads to significant measurements in the distribution of dissolved hydrogen concentrations [49, 50]. At the same time, the methodological issue of the separation of surface hydrogen becomes especially important, since during rolling there is a significant deformation of the metal surface in a heated state, which should change not only the distribution of dissolved hydrogen, but also the distribution of surface hydrogen.

For the experiments, 10 samples were taken, which were cut from a rolled sheet with a thickness of 15 mm of the AlMn alloy. The alloy composition is shown in Table 13.5.

The cutting diagram is shown in Fig. 13.11.

Two prismatic specimens were cut from the resulting prismatic specimens, as shown in Fig. 13.12. The dimensions are based on material loss per cut width. A layer

Table 13.5 Composition of the AlMn alloy

Fe	Si	Mn	Ti	Al	Cu	Mg	Zn
<0.7	<0.6	1–1.6	<0.2	96.35–99	< 0.15	< 0.2	<0.1

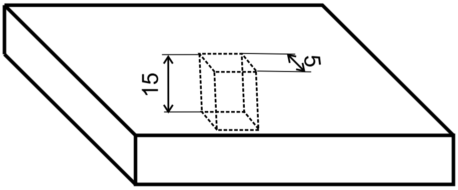


Fig. 13.11 Scheme of cutting samples from a sheet

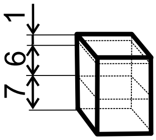


Fig. 13.12 Sample cutting scheme for measurements

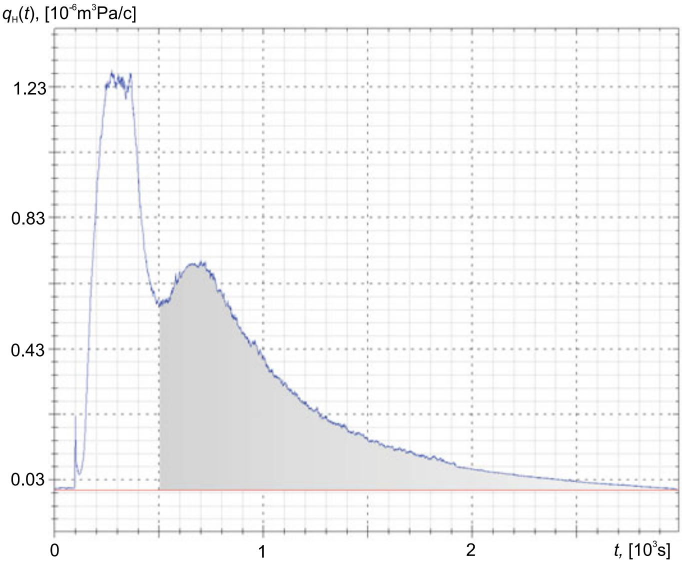


Fig. 13.13 Extraction curve of a sample with a rolling layer. The area corresponding to dissolved hydrogen is highlighted in gray

of the rolling surface of 1 mm thickness was removed from one of the samples by grinding; see Fig. 13.12.

Measurements of hydrogen concentration were carried out on AV-1 by the vacuum heating method in a standard way. Two typical extraction curves are shown in Figs. 13.13 and 13.14.

Surface hydrogen was released in accordance with the procedure [44, 45]. The concentration of dissolved hydrogen in the samples with the removed rolling layer was from 0.185 to 0.215 ppm. The concentration of dissolved hydrogen in the samples with the rolled bed was from 0.46 to 0.64 ppm. As is clearly seen in Figs. 13.13 and 13.14, the amount of surface hydrogen differs by about tens of times, but the desorption time is the same (400 s) which is due to the smaller size of the samples as compared to the standard 8 mm size.

One of the results of this study is a multiple increase in the concentration of dissolved hydrogen in the surface layer of the metal as a result of deformation during rolling. By comparison, the concentration value can be estimated at 2.45 ppm, which is 12 times higher than the values in the middle part of the sample. This is one of their manifestations of the surface effect during plastic deformation, which we have already described in [49, 50]. The data obtained also indicate that the desorption time of surface hydrogen depends on the sample size, which must be taken into account when measuring the hydrogen concentration in thin samples with a characteristic thickness of less than 7–8 mm.

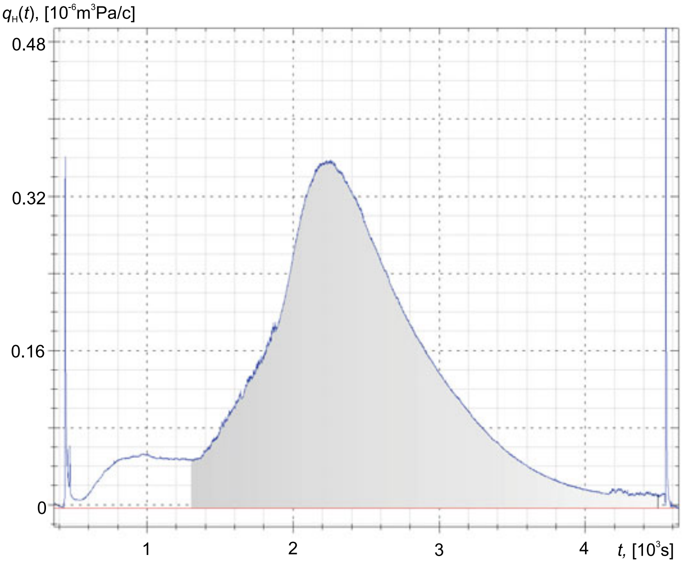


Fig. 13.14 Extraction curve of a sample with a removed rolling layer. The area corresponding to dissolved hydrogen is highlighted in gray

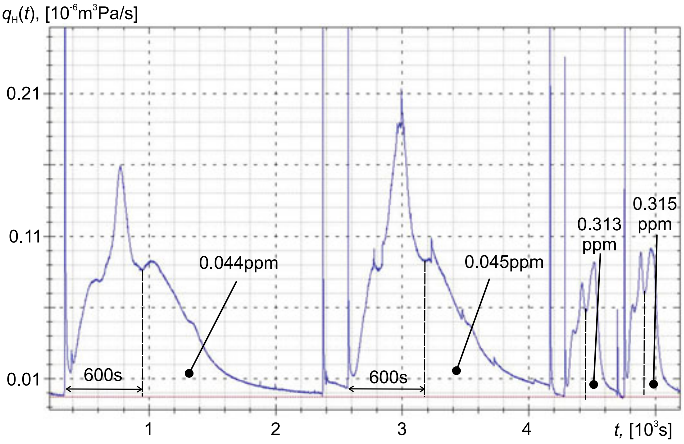


Fig. 13.15 Extraction curves of the AMg6 alloy samples: 2 curves on the left are for a bar and 2 curves on the right are for a wire

13.7 Release of Surface Hydrogen in Thin Samples

Measurements of the hydrogen concentration were carried out in samples of AMg6 alloy, machined from a 9 mm diameter rod and a 1.2 mm diameter wire. The wire was obtained by extrusion from rods of the same batch as those studied. This wire is used in automatic welding. We used samples D7 × 15 mm^2 turned from a bar on a lathe and samples 15 mm long without surface treatment, cut from the wires. Figure 13.15 shows the extraction curves for two bar samples and two wire samples. In a time interval of 10 min, the first two peaks of the extraction curve appear in the samples from the bar; see Fig. 13.15.

The extraction curves of thin wire samples are also characterized by three peaks, and the first two peaks should probably be attributed to surface hydrogen (focusing on more bulk samples). Taking these assumptions into account, the hydrogen concentration we measured in the 9 mm diameter AMg6 alloy was from 0.04 to 0.07 ppm, and in the wire extruded from this rod it was from 0.31 to 0.33 ppm.

It should be noted that during extrusion, the hydrogen concentration increased fourfold, remaining in the usual range of natural hydrogen concentrations for an alloy of this type. This result should be taken into account, since it is generally accepted that the hydrogen concentration during production from an ingot to finished product cannot change significantly due to the low diffusion mobility of hydrogen in aluminum. Therefore, the control over the concentration of hydrogen is carried out only at the stage of manufacturing ingots. Note that the first two peaks of the extraction curve responsible for surface hydrogen become noticeably smaller after extrusion, which is probably related to the properties of the wire surface and requires additional structural studies.

13.8 Conclusions

Nowadays, the industry is increasingly faced with problems caused by the effect of hydrogen on the structure and strength of metals and alloys. The effect of dissolved hydrogen in aluminum alloys and high-strength steels is especially strong. The concentrations critical of the properties of these metals are much less than 1 ppm.

A significant contribution to the results of measurements by standard methods of hydrogen adsorbed on the surface is characteristic for aluminum alloys.

The studies described in the present article show that the critical hydrogen concentrations for most alloys are of the order of 0.2–0.4 ppm; their excess by two times leads to rupture and cracking during processing, welding, and excessive porosity.

We have proposed a technique for separating surface hydrogen which has been tested on specific examples and gives adequate results. Further verification and metrological testing of the method are required as well as the determination of the possibility of its application for a wide range of aluminum alloys.

It is generally accepted that the hydrogen concentration does not change during technological processes, that is, the hydrogen concentration in the casting is equal to its concentration in the finished product. Our experiments have shown that this is not the case. During extrusion and in rolled products, the concentration of dissolved hydrogen can increase significantly, but this fact is in no way taken into account by the modern system of standards regulating the maximum permissible hydrogen concentrations, including the thin rolled materials. At the moment, this concentration is assumed to be equal to the concentration of hydrogen in the metal of the original ingot.

One of the reasons for the modern hydrogen problems in aluminum alloys is the markedly increased proportion of secondary metal in finished products. At the same time, standard measurements of hydrogen concentration from two or three hydrogen samples do not guarantee the quality of the material. Our experiments show that the spread in the values of hydrogen concentrations reaches 3–4 times in samples cut from one section of the product with an interval of 15–20 mm.

The quantitative data on hydrogen concentrations available in the modern literature are extremely scanty, do not contain a description of how the surface hydrogen was removed, and this raises many questions, especially if the indicated concentrations significantly exceed 1 ppm. Probably, it is necessary to expand the research, which is usually carried out for steels, to the aluminum alloys and to determine the ranges of safe and dangerous concentrations in terms of structure and strength of the metal more precisely.

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