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Comparative assessment of Al-Si alloy gassing degree with the application of the ‘first bubble’ and ‘solidification under decreased pressure’ methods

Porównawcza ocena stopnia zagazowania stopów Al-Si z zastosowaniem metody „pierwszego pęcherzyka” i metody „krzepnięcia pod obniżonym ciśnieniem”

Abstract

All aluminum alloys in a liquid state are characterised by easy oxidation and absorption of hydrogen from the surroundings (which are the main reasons for casting defects). The amount of hydrogen adsorbed by a liquid alloy depends mainly on temperature and melting time. The performed investigations were aimed at comparing two known methods of measuring a metal gassing degree; the first bubble method and sample solidification under decreased pressure. Liquid metal melting and holding processes were performed under different conditions that caused variability of its gassing degree, resulting in a variability of purity and quality of the liquid metal. The investigations were carried out with using the hypoeutectic aluminum-silica AK7 alloy.

Keywords: aluminum alloys, gassing degree, measuring the gas content

Streszczenie

Wszystkie stopy aluminiowe w stanie ciekłym charakteryzują się łatwym utlenianiem i pochłanianiem wodoru z otaczającej atmosfery, co jest główną przyczyną wad odlewniczych. Ilość wodoru zaabsorbowanego przez ciekły stop zależy głównie od temperatury i czasu topienia. Przeprowadzone badania miały na celu porównanie dwóch znanych metod pomiaru stopnia zagazowania metalu, metodę pierwszego pęcherzyka oraz metodę krzepnięcia próbki pod obniżonym ciśnieniem. Proces topienia i przetrzymywania ciekłego metalu odbywał się w różnych warunkach, co powodowało zmienność stopnia zagazowania, a tym samym czystości i jakości ciekłego metalu.

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Wykonane badania zostały przeprowadzone z wykorzystaniem podeutektycznego stopu aluminium-krzem AK7.

Słowa kluczowe: stopy aluminium, zagazowania, badania zawartości gazów

1. Introduction

A necessary condition for obtaining castings of required high technical parameters is applying charge materials of a high purity and quality. However, a charge material alone does not always guarantee casting 'without defects.' The final effect depends on several factors that can significantly lower the casting parameters. An important and essential factor constitutes the melting process and liquid metal preparation. Performed already at the melting stage, controlling such parameters as the alloy chemical composition, purity, and gassing degree allows us to prevent the formation of defects in the ready product. The most detrimental inclusions in liquid Al are gases – mainly H₂ and O₂ (in the form of oxide films and their inclusions). Oxide particles can act as the nuclei of hydrogen bubbles [1].

At hydrogen pressure of 0.1 MPa, in the solid state, in the liquid state at melting point, and at a temperature 100°C higher than the melting point hydrogen solubility in some non-ferrous metals equals, respectively:

- Al 0.034 – 0.71 and 1.3–1.4 cm³/100 g,
- Cu 1.9 – 5.2 and 5.6 cm³/100 g,
- Mg 15.0, 20–30, and 25–30 cm³/100 g,
- Ni – app. 14.0, app. 40.0, and app. 42 cm³/100 g [2].

The assessment of gassing degrees of metals and alloys is an important element in casting production processes. The gas adsorbed on the metal or alloy surface permeates into its depths by means of diffusion. The solubility effect can occur only when the quotient of the gas atom radius and the metal atom radius is smaller or equal to 0.59. Out of all gases, only hydrogen fulfills this condition; thus, it is the main reason for the gassing of metals and alloys. In respect of thermodynamics, hydrogen solubility is an endothermic process, which means that, at a constant pressure, a temperature increase causes its growth according to equation (1). Equation (2) provides the influence of pressure on solubility [3]:

$$S = C \frac{-E_s}{2kT} \quad (1)$$

$$S = C_t \sqrt{P_{H_2}} \quad (2)$$

where:

- S – solubility,
- E_s – heat of solution,
- k – Boltzman constant,
- C – material constant,
- C_t – constant dependent on temperature.

At points of phase transformations (mainly at the melting point), a sudden solubility increase occurs (in the case of aluminum, at a temperature of approximately 660°C, nearly a 20-time increase of hydrogen solubility occurs: from 0.034 cm³/100 g to 0.65 cm³/100 g at 1 atmosphere of pressure) [2]. The opposite occurs during cooling; a significant amount of dissolved hydrogen can be trapped in an alloy during its solidification.

Properly degassed metal contains 0.06–0.10 cm³/100 g of hydrogen, moderately degassed: 0.11–0.20 cm³/100 g, while the normally gassed metal bath contains more than 0.2 cm³/100 g [4]. An abrupt solubility change of hydrogen at the transition from liquid to solid is the reason of casting porosity. In order to avoid such porosity, various methods of metal bath refining are applied; among others are gaseous refining, gas-slag refining, refining by solid substances undergoing decomposition, vacuum refining, and pulsating refining. The efficient use of intensive refining procedures requires the application of the adequate method of measuring the metal bath gassing degree.

The correct determination of hydrogen content in the bath before casting is essential. Presently, there are several dozen methods of hydrogen determination in metals and alloys [5, 6]. Selection of the proper measuring technique is very important, since several problems related to obtaining casting production quality are attributed to unsatisfactory control of the hydrogen content in liquid metals and alloys. Individual measuring techniques (direct and indirect) are characterised by variable repeatability and reliability and are burdened by different error sources and limitations [7].

Applied estimation methods of the gassing degree for the liquid or solid states can be treated as technological tests or quantitative investigations. In addition, they can be divided into indirect and direct methods.

2. Methods of investigations of gas content

2.1. Method of solidification under decreased pressure

The effect described by the following principle is utilized in this method: decreasing pressure above the liquid metal surface simplifies the emission of gases dissolved in this metal and causes the growth of gas bubbles, which improves method accuracy. The gassing degree is determined qualitatively on the basis of the meniscus shape of the solidifying sample and quantitatively on the basis of the alloy density in the sample, or by comparisons of a sample's cross-section appearance.

An example of this investigation method constitutes the modified Straube–Pfeifer method (Fig. 1). The liquid metal sample is brought to solidification in a decreased-pressure chamber, utilizing the effect of emission and expansion and then keeping gases in solidifying metal. This measuring principle is applied, among others, in devices: Gas-meter LQ, Aluschmeltztester, FMA.

Performing the test is based on:

- 1) liquid metal sampling,
- 2) liquid metal pouring into a previously heated crucible placed in the chamber (2/3 of the crucible should be filled),
- 3) closing the chamber by means of a glass dome,
- 4) switching on the valve joining the chamber with the surge tank,
- 5) equalizing pressure to approximately 0.85–0.94 (app. 8 Pa), depending on the alloy type,
- 6) observation of the solidifying sample surface, switching off the device, and sample removal.

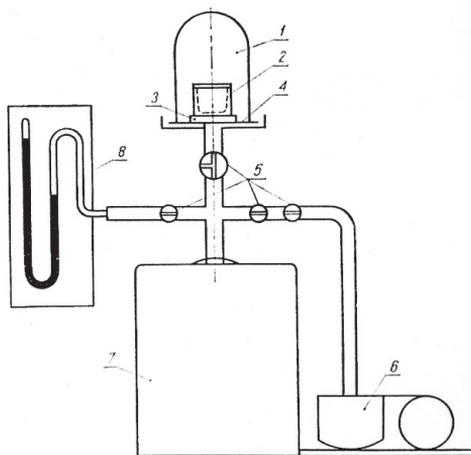


Fig. 1. Device of the gas-meter type and its schematic presentation for the modified Straube-Pfeiffer test: 1 – dome, 2 – crucible, 3 – graphite base, 4 – rubber seal, 5 – valves, 6 – vacuum pump, 7 – surge tank, 8 – manometer [2]

The gassing degree estimation can be roughly performed on the basis of an observation of the sample solidification process and on the sample meniscus shape. A large convex meniscus with eventual cracks indicates increased a large gassing. A concave meniscus indicates a small gassing.

The quantitative estimation of the liquid metal gassing degree is obtained by measuring alloy density in the sample solidifying under decreased pressure. Sample density measurements are carried out by means of the tensiometric balance by immersing in a liquid. The measuring stand is shown in Figure 2. Samples are twice subjected to mass measurements: one in the air, and the second in the liquid. Such a method is applied at testing densities of samples of 'indefinable' shapes. The measuring accuracy obtainable in the presented stand equals $\Delta\rho = 0.001 \text{ g/cm}^3$.



Fig. 2. Measuring stand for testing densities of metals and casting alloys by the immersing method

The gas number (LG) determination is reduced to a calculation of the quotient of alloy density in the sample solidifying under decreased pressure (ρ_p) to the alloy theoretical density (ρ_t) (not containing any gaseous or shrinkage porosity) [5].

$$LG = \frac{\rho_p}{\rho_t} \quad (3)$$

$$\rho_p = \frac{m_p \cdot \rho_c}{(m_p - m_c)} \quad (4)$$

where:

LG – gas number,

ρ_p – alloy density in the sample solidifying under decreased pressure,

ρ_t – alloy theoretical density, resulting from its composition,

m_p – sample mass measured in air,

m_c – sample 'mass' measured in the liquid,

ρ_c – density of the measuring liquid, applied in density measurements.

2.2. The first bubble method

The better results provides the Dardel method, called the first bubble method. This is based on measuring the negative pressure and metal temperature in the chamber during a gradual decrease of pressure from the moment when the first bubble appears on

the liquid metal surface. Recorded parameters p and T allow us to determine the hydrogen content in the liquid metal. The Dardel method is utilized in devices: Aluschmelz-tester, Hycon Tester, FMA, and ALU COMPACT.

Such devices contain a vacuum chamber, a set of pressure and temperature sensors, a vacuum controller, a precise membrane vacuummeter (1%), and a step-less furnace heating control. The crucible of resistance heating and thermocouple immersed in the liquid metal are placed in the vacuum chamber. A peephole for sample surface observation is built into the chamber cover. This chamber is connected to a vacuum pump via control valve (Fig. 3). After pouring liquid metal to the crucible and closing the cover of the vacuum chamber, the pressure is gradually decreased. Such a system allows us to determine the hydrogen content at an arbitrary temperature. At the moment when the first bubble is seen, two parameters (pressure and temperature) are recorded. Based on the pressure and temperature readings (on the basis of standards or nomograms), the hydrogen content is determined. The result after recalculation is seen on the computer screen and printed.

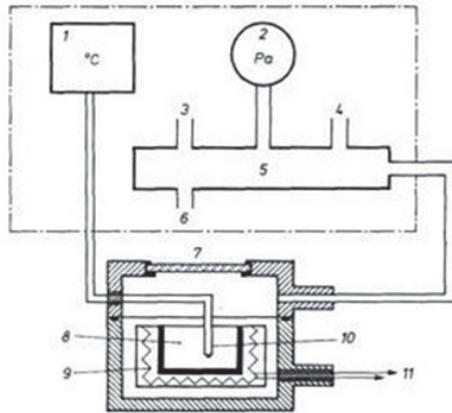


Fig. 3. Schematic presentation of the first bubble test principle: 1 – thermometer; 2 – vacuummeter; 3 – needle valve; 4 – venting valve; 5 – suction conduit; 6 – vacuum pump; 7 – peephole; 8 – crucible; 9 – heating element; 10 – thermocouple; 11 – network connection [6]

$$\lg C = -\frac{A}{T} + B + \frac{1}{2} \log P_{H_2} \quad (5)$$

where:

- A, B – constants,
- T – temperature,
- C – amount of hydrogen dissolved in metal, $\text{cm}^3/100 \text{ g}$,
- P_{H_2} – pressure at the moment the first bubble emits.

3. Proceedings and investigation results

3.1. Purpose of the performed investigations

The investigations described below were aimed at comparing the results of the gassing degree estimations of Al-Si alloys performed by two methods: 'solidification under decreased pressure' and 'the first bubble.'

The 'solidification under decreased pressure' method allows us to qualitatively assess a liquid metal – in respect of its gassing – on the basis of the meniscus shape. This is a very fast assessment. It also allows us to quantitatively determine the gassing degree on the basis of the density measurement of the gasified alloy; however, this is not a fast assessment, and the result is obtained much later.

The 'first bubble' method belongs to a group of methods that allows us to obtain a quantitative assessment (of the amount of dissolved hydrogen) in a relatively short time. Thus, it can be rated into the group of fast methods of assessing the gassing degree of metals and Al-Si alloys. Performing the estimation by two methods should allow us to find connections between the results of the gassing degree measured by the gas number (LG) as well as the results obtained by measuring the amount of dissolved hydrogen (gas).

3.2. Results of investigations

The investigations were performed using the hypoeutectic aluminum-silica AK7 alloy and AK7Cu1 alloy with additions of other elements. The chemical composition of the investigated alloys is shown in Table 1.

Table 1. Chemical composition of the tested alloys and their theoretical densities calculated

| | Si | Fe | Cu | Mn | Mg | Cr | Ni | Zn | Ti |
|--------|--------|--------|--------|-------|-------|--------|----------|----------|-------|
| AK7 | 7.67 | 0.313 | 0.069 | 0.140 | 0.318 | 0.024 | 0.0063 | 0.094 | 0.144 |
| AK7Cu1 | 7.24 | 0.288 | 1.080 | 0.127 | 0.355 | 0.022 | 0.0077 | 0.434 | 0.205 |
| | B | Ca | Pb | Sr | V | Zr | Al | ρ_t | |
| AK7 | 0.0012 | 0.0012 | 0.0022 | 0.00 | 0.016 | 0.0011 | residual | 2.6981 | |
| AK7Cu1 | 0.0094 | 0.0012 | 0.0050 | 0.03 | 0.020 | 0.0011 | residual | 2.7530 | |

The theoretical density, which was used for the gas number (LG) determination, was calculated for these alloys. Cut alloy pigs were melted under various conditions: in a induction thiristor furnace of a medium frequency, in a silite furnace, and in a laboratory induction furnace R.S.

The melting and holding processes were performed under different conditions, which caused variability of the gassing degree and (as a consequence) the liquid metal purity and quality. Efforts were undertaken to maintain the liquid metal holding temperature at no higher than 760°C.

The refining operation was performed by means of an argon lance. AK7 alloy composition was corrected by foundry alloys: AlCu50, AlTi5B1, AlSr10. Assessments of the gassing degree were carried out by means of an ALU COMPACT II device, version 6 (Fig. 4a) – using ‘the first bubble’ method. For investigations of gassing by the method of ‘solidification under decreased pressure,’ the device of the GAS-METER type (Fig. 4b), as in the modified Straube–Pfeiffer test, was used. Both devices are shown in Figure 4. The analysis of the upper surface appearance of samples solidifying under decreased pressure was also performed.

a)



b)



Fig. 4. Devices for assessing the gassing degree: a) ALU COMPACT II; b) GAS-METER

Characteristics of the melts performed in individual furnaces are given in Tables 2–4. The results of the hydrogen concentrations obtained directly from the ALU COMPACT II device and the measured densities of samples solidifying under decreased pressure (shown in Tables) were used for the analyses of conditions and melting times, influences of alloying additions, and refining procedures on the gassing degree and alloy purity.

Table 2. Melt proceeding in the induction thiristor furnace of a medium frequency

| No. | Gas content [cm ³ /100 g] | Alloy density ρ_p [g/cm ³] | Gas number (LG) | Comments |
|-----|--------------------------------------|---|-----------------|------------------------------------|
| 1 | 0.16 | 2.620534 | 0.9713 | direct after melted |
| 2 | 0.12 | 2.643454 | 0.9797 | after 7 min |
| 3 | 0.15 | 2.643684 | 0.9798 | after 7 min |
| 4 | 0.11 | 2.643103 | 0.9796 | after 6 min |
| 5 | 0.08 | 2.643931 | 0.9799 | after 6 min |
| 6 | 0.12 | 2.642708 | 0.9795 | after 8 min |
| 7 | 0.10 | 2.644636 | 0.9802 | after 30 min, after refining argon |
| 8 | 0.11 | 2.652198 | 0.9830 | after 7 min |
| 9 | 0.17 | 2.647690 | 0.9813 | after 7 min |

Table 3. Melt proceeding in the silite furnace

| No. | Gas content [cm ³ /100 g] | Alloy density ρ_p [g/cm ³] | Gas number (LG) | Comments |
|-----|--------------------------------------|---|-----------------|--|
| 1 | 0.42 | 2.508769 | 0.9298 | AlSi7Mg0.3: $\rho_t = 2.6981$ [g/cm ³] |
| 2 | 0.35 | 2.489546 | 0.9043 | correction of the chemical composition |
| 3 | 0.24 | 2.556713 | 0.9287 | $\rho_t = 2.7530$ [g/cm ³] after refining argon, after 10 min |
| 4 | 0.22 | 2.570317 | 0.9336 | after 10 min |
| 5 | 0.22 | 2.567202 | 0.9325 | after add the Sr 0.01%, after 10 min |
| 6 | 0.23 | 2.618566 | 0.9512 | after refining argon |
| 7 | 0.17 | 2.609361 | 0.9478 | after 10 min |

Table 4. Melt proceeding in the laboratory induction furnace R.S.

| No. | Gas content [cm ³ /100 g] | Alloy density ρ_p [g/cm ³] | Gas number (LG) | Comments |
|-----|--------------------------------------|---|-----------------|--------------------------------------|
| 1 | 0.17 | 2.617582 | 0.9702 | direct after melted |
| 2 | 0.24 | 2.629391 | 0.9745 | after 14 min |
| 3 | 0.15 | 2.601579 | 0.9642 | after 23 min |
| 4 | 0.07 | 2.632546 | 0.9757 | direct after melted |
| 5 | 0.16 | 2.587596 | 0.9590 | after add the 0.02% Sr, after 10 min |
| 6 | 0.29 | 2.529094 | 0.9374 | after add the 0.10% Sr, after 6 min |

The melting process in the induction furnace is very fast – charge mass 2 kg of AK7 alloy. Immediately after a charge melting, a metal of satisfactorily good quality parameters is obtained (Fig. 5a); however, after approximately 20 minutes, a favorable stabilization of hydrogen concentration and gas number occurs. The refining process – blowing the liquid metal by argon (5 minutes) followed by waiting for approximately 7 minutes – help us to obtain the best values of the above-mentioned parameters (Fig. 5b).

Performing the melt, especially procedures aimed at improving the alloy quality in a silite furnace, is slightly hindered. The metal obtained after melting is gassed, and the surface of the sample solidifying at decreased pressure is porous (Fig. 5c). The performed refining brings certain improvements; but due to a temperature decrease, it is too short and must be repeated.



Fig. 5. Samples selected from individual melts solidifying under decreased pressure: induction thiristor furnace (samples a and b); silite furnace (samples c and d)

Melting in the laboratory induction furnace R.S. is slightly too long; 300 g of a charge is melted after approximately 40 minutes. However, in the case of melt 1, an alloy of good parameters is obtained between the 14th and 20th minute from melting. Melt 2 was aimed at showing that the introduction of strontium (in a form of an AlSr10 foundry alloy) causes an increase of liquid metal gassing.

Samples solidifying under decreased pressure were used for analyzing the melted metal quality, and photographs of the selected samples are shown in Figure 4. There is a relationship between the quality of cast samples and such parameters as the hydrogen concentration in an alloy and the gas number. The alloy with a low hydrogen content and a high gas number is characterized by a nice solidifying surface as well as a delicate concave meniscus of the sample.

3.3. Comparison of the results of the gassing degree investigations

In order to obtain a graphical image of the investigation results (shown in Tables 2–4), the diagrams presented in Figures 6 and 7 were prepared. The dependence between the Al-Si alloy density (determined by weighing in air and in the liquid of samples solidifying under decreased pressure) and the gas content (mainly hydrogen) determined during melting performed by means of ALU COMPACT II, is shown in Figure 6. This dependence, for the tested alloy (AK7) and the variability range of measuring data, can be described by a linear equation.

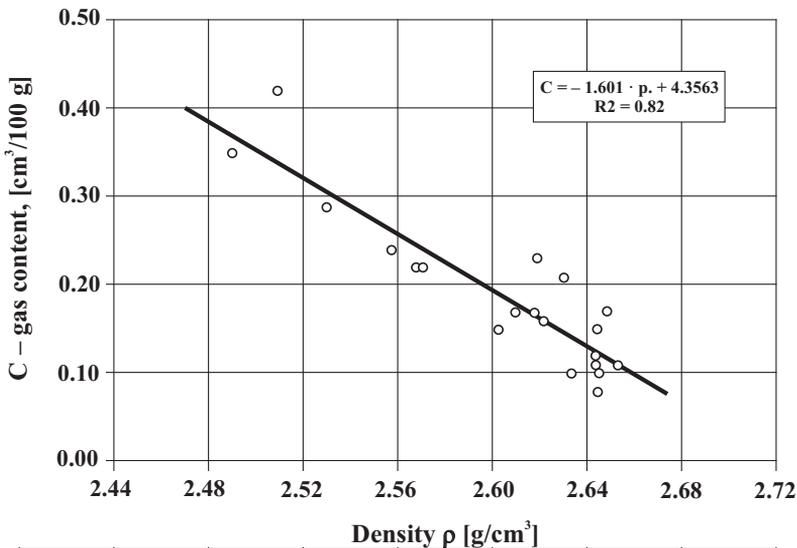


Fig. 6. Dependence between the Al-Si7 alloy density (ρ) and gas content (C) (mainly hydrogen)

The character of this relationship was as expected, which means that the increased gassing degree of the alloy was accompanied with a density decrease. The description of this dependence by the equation allows us – in further studies – ‘to forecast’ the alloy density on the basis of gas content measurements; that is, on the basis of the results obtained from the ALU COMPACT II device, which provides fast assessment.

The relationship worked out on the basis of parallel measurements of the Al-Si7 alloy gassing degree (with the application of two devices and two different investigation methods) is shown in Figure 7. The relationship between the gas number (LG) (measured by means of GAS-METER) and the gas content (measured by means of ALU COMPACT II) was obtained. Within the tested data variability range, the linear dependence was achieved of the correlation degree at level $R^2 = 0.814$. This moderate correlation coefficient indicates that both variables determined experimentally are burdened with measuring errors. The obtained relationship (in a similar fashion as the relationship shown in Figure 6) can be used for forecasting gas contents in the Al-Si7 alloy on the basis of the gas number (which is the dimensionless indicator of the alloy density). The dependence from Figure 7 can also be rearranged and the gas number calculated on the basis of the gas content measurements (which is relatively fast done by means of ALU COMPACT II).

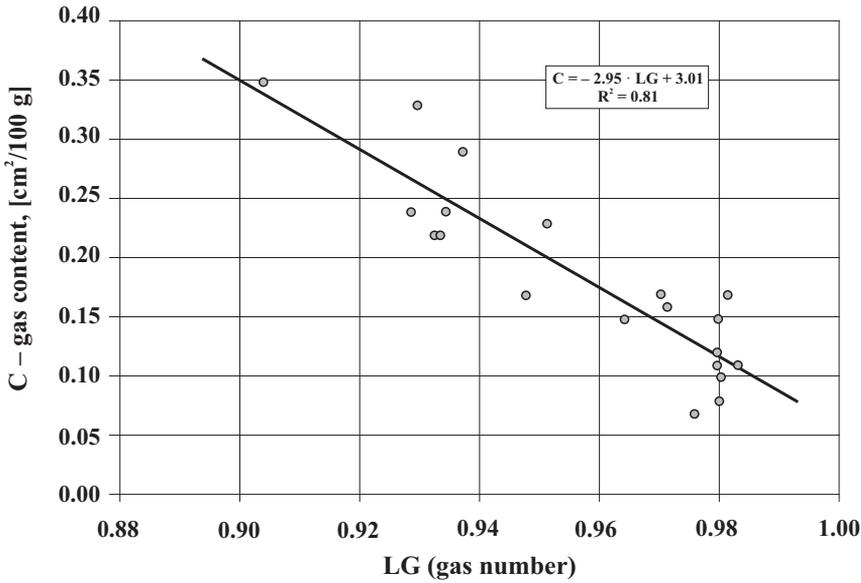


Fig. 7. Relationship between the gas number determined by the solidification under a decreased pressure (device – GAS-METER) and the gas (hydrogen) content determined by the first bubble method (device – ALU COMPACT II)

4. Conclusions

The presented results of the Al-Si7 alloy obtained under various melting conditions allowed us to compare two methods of metal gassing degree determination. The measuring of pressure and temperature at the moment of the first bubble appearance performed by means of the ALU COMPACT II device is a fast and reliable method that allows us to determine the gassing degree (hydrogen concentration in $\text{cm}^3/100 \text{ g}$). However, in a similar fashion as other methods, this one has its weaker point, which is the subjectivity of assessing the moment in which the first bubble appears. Thus, working with this device requires a lot of experience. On account of the short measuring time, there is a possibility of measurement repetition, which makes this device a very useful tool for the quality control of the melted casting alloys.

The Straube–Pfeifer method used in the devices of the GAS-METER type allows for the fast determination of the alloy quality on the basis of the appearance of the solidifying sample surface. The gassing of metals is determined only qualitatively; this means that it can be stated whether the metal is gassed or not and its quality can be assessed with regard to contaminations. Obtaining a rational result – in the form of the density or gas number – requires us to perform additional density measurements in the solidified sample (which means that the result is only of a documentary character).

The relationships between the Al-Si7 alloy density and the amount of gas (hydrogen) dissolved in this alloy (obtained as the result of the performed investigations) can be used for forecasting the alloy density in castings on the basis of the dissolved hydrogen amount determined by means of the ALU COMPACT II device.

The second determined relationship between the gas number (LG) and the gas content in the alloy allows us to connect the investigation results obtained with the application of two different methods of gassing degree assessment and two different measuring methods. Both relationships can be utilized in the casting practice.

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