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COMPARATIVE EVALUATION OF METHODS FOR DETERMINATION OF HYDROGEN AND NON-METALLIC INCLUSIONS CONTENT IN ALUMINUM ALLOYS

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ABSTRACT

Aluminum and its alloys are widely used in various branches of modern industry with special requirements for the construction materials used. Hydrogen and oxygen are gases, the impurities of which are in solid and liquid metals in solution or in the form of inclusions of excess phases. Gaseous compounds of hydrogen and oxygen are sorbed on metal surface as a result of physical absorption processes, dissociate into atoms, and accumulate on structural defects. When the impurity concentration exceeds the solubility at a given temperature, a secondary solid solution is formed. Hydrogen is one of the most significant gas impurities, which has a negative effect on the technological properties of products made of aluminum and its alloys. Hydrogen dissolved in solidified metal contributes to formation of gas and gas-shrinkage porosity, which increases with increasing hydrogen concentration. Therefore, the essence of this study is to compare different methods for determining hydrogen, which is especially important in the production of aluminum cast parts. The experimental part was carried out on samples of AK12 alloy (DIN AlSi11, ISO AlSi12).

Keywords: casting, density index, vacuum heating, hydrogen, aluminum melt, silumin, oxide film, refining.

INTRODUCTION

In the modern world, more and more fundamentally new high-end technology devices are appearing; existing ones are being improved and complicated, with constantly increasing requirements for them. This leads to aids in improve operational characteristics of ferrous and non-ferrous alloys [1-5].

Melting and casting of aluminum alloys is accompanied by interaction of melt with furnace lining, moisture, atmospheric gases. The main danger in castings is hydrogen and oxygen soluble in liquid aluminum [6, 7]. Hydrogen, which is present in the quantity of 70-90% from total gas content, is in the form of an interstitial solid solution. In molecular state, it can fill voids and pores, form chemical compounds - hydrides (most often with alkali or alkaline earth metals), and adsorb on highly dispersed inclusions of aluminum oxides inside the metal with formation of chemical complexes [8, 9]. The high content of hydrogen in melt leads to formation of porosity in castings, decrease in fatigue and operational characteristics [10-14].

Oxygen is the main cause of cast product destruction under dynamic loads, since it participates in formation of aluminum oxide (γ-Al2O3) in the form of oxide films, on which nucleation and development of fatigue cracks occurs. The tendency to development of such cracks is revealed during tests to determine fatigue resistance of cast products in bending rotary test (Figure-1). Fractographic analysis of the fracture structure revealed a multi-site character of crack initiation, cause of which is oxide films. The presence of oxide films in focus zone was confirmed by microstructure studies (Figure-2) [8].

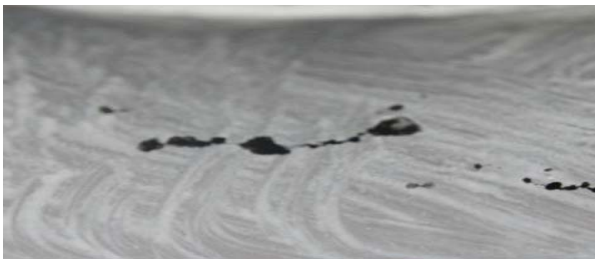

Figure-1. Crack nucleation zone [8].

A possible consequence of such destruction is creation of an emergency situation during the operation of finished cast products. Therefore, in production of castings, it is necessary to control the hydrogen content in alloys, which can be produced by various methods. It is extremely important to accurately determine the actual hydrogen content in metal (dissolved hydrogen), which is associated with specific difficulties:

- Difficulties in determining hydrogen at its low content in aluminum alloys;
- Presence of alloying components in alloys with high vapor pressure and absorbed moisture on the oxide film covering the metal surface.

Figure-2. Microstructure of casting near the destruction zone.

Currently, there are many domestic and foreign methods for determining the hydrogen content in aluminum alloys [15-19]. Based on this, the aim of this work is to compare the results of determining hydrogen by different methods.

RESEARCH METHODOLOGY

The alloy AK12 (DIN AlSi11, ISO AlSi12) was prepared in an induction furnace IAT-2.5 using the following charge materials: primary aluminum of grade A7 (DIN 3.0275, ISO Al99.7), crystalline silicon Kr00 (according to GOST 2169-69), recycled waste (sprues, rejected castings).

The hydrogen content was determined by direct (using an ALSPEK h Mini device, vacuum heating) and indirect (determination of the density index) methods.

The ALSPEK h Mini device allows simultaneous measurement of dissolved hydrogen content and temperature. An electrochemical sensor mounted in tip of probe measures the hydrogen content (ml/100 g).

To control hydrogen in alloy by the vacuum heating method (GOST 21132.1-98), samples were taken into a Rensley chill mold. The disadvantage of this method is duration of the analysis; therefore, it cannot be used as an express method for prompt adjustment of technology for preparing alloys and casting products.

The indirect method for determining the hydrogen content includes density index method, which was calculated by measuring density of samples taken from one bull ladle using a 3vt device.

RESULT AND DISCUSSIONS

To determination comparability of measuring results of the hydrogen content in alloy by vacuum heating methods and the density index, metal samples were taken (Figure-3, 4).

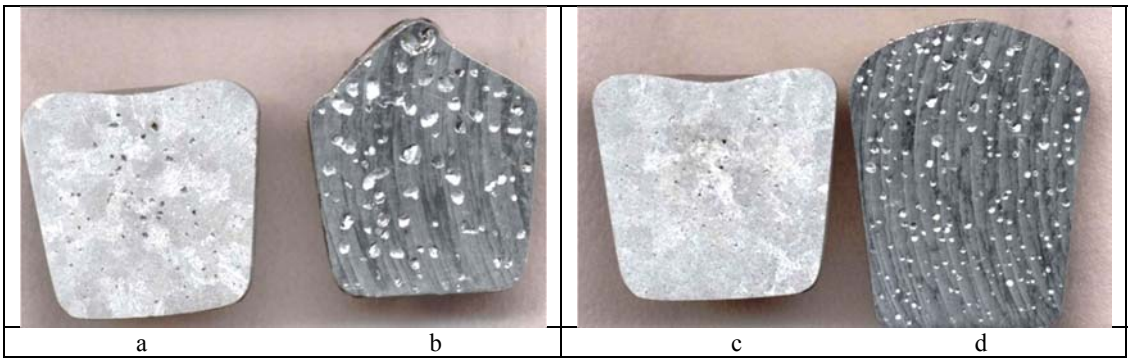

Figure-3. Control samples with results of density, density index and hydrogen content: *a, b* - density index 14.7%, hydrogen content for solid sample 0.38 cm3/100g; *c, d* - density index 12.4%, hydrogen content for solid sample 0.30 cm3/100g. Density, g/cm3: *a* - 2.601; *b* - 2.213; *c* - 2.579; *d* - 2.26.

The experimental work showed good reproducibility of measurement results by three different ways: density index method, vacuum heating method and Alspek H mini portable device (Figure-5). In this case, location of density index graph above rest is explained by the fact that this method evaluates purity of metal, including content of hydrogen and oxide films.

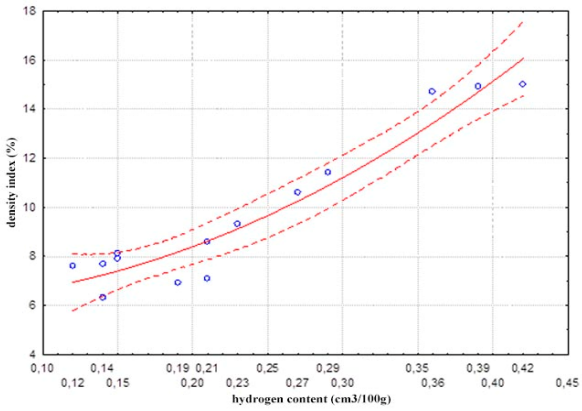

Figure-4. Scatter diagram for density index (%) and hydrogen content (cm3/100g)

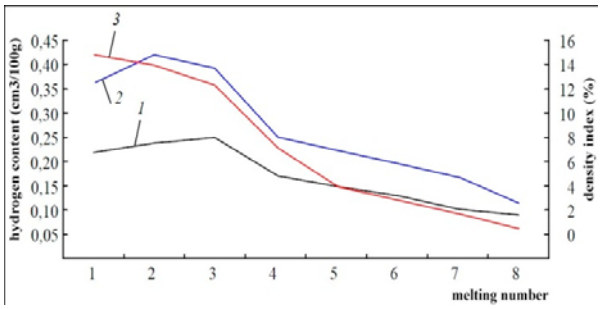

Figure-5. Metal hydrogen content and density index: Alspek H mini method (1), density index (2) and solid sample (3).

The contamination assessment of metal with oxide films was carried out using well-known method - dependence of grain size and purity of metal [20]. The method consists in the following: sample in form of a cylinder (diameter 60 mm, high 15 mm) is cast into an open mold. The surface of the sample is etched with special reagents to identify macrograins. Coarse-grained structure is obtained on metal samples slightly contaminated with oxide inclusions. Fine-grained structure indicates a greater contamination of metal with oxides. The effect is explained by presence in melt suspension of Al2O3 in various concentrations, which in turn is the center of alloy crystallization (Figure-6).

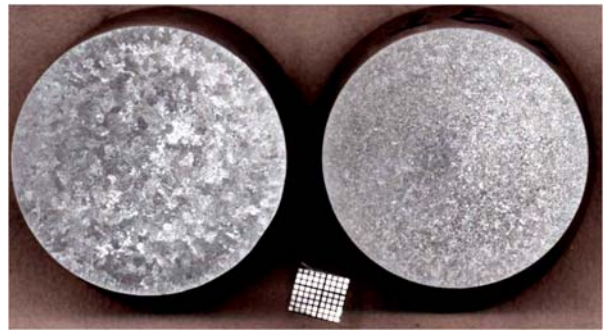

Figure-6. Macrostructure of samples with different density index, %: *left* – 9.1; *right* - 14.

As a result of using the density index method, it was found that when metal is smelted in induction crucible furnaces, an excess of melt temperature over the liquidus temperature for every 10 ºC leads to saturation with hydrogen and a change in density index (Figure-7).

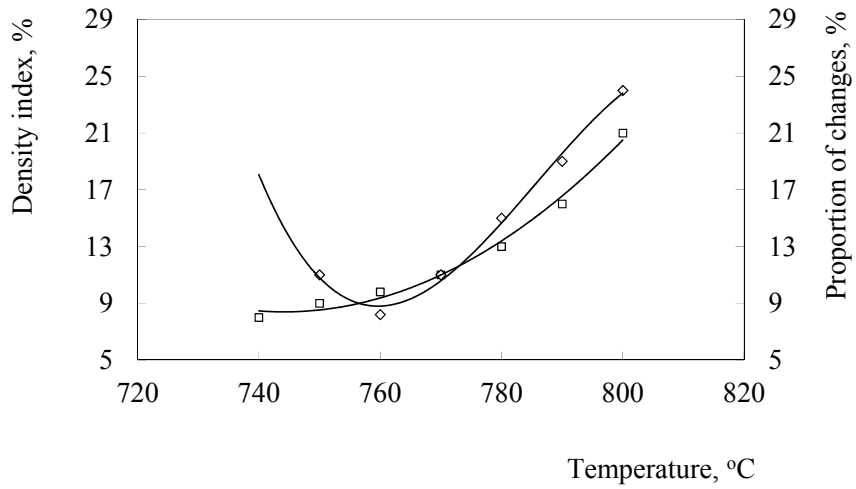

Figure-7. Change in the density index depending on melt temperature: 1 (□) - density index; 2 (◇) - proportion of changes in density index.

The studies carried out to assess the effect of charge materials on hydrogen content made it possible to establish that a change in the share of mechanical processing waste from 0 to 100% leads to an increase in metal density index by a factor of 5 - from 3 to 15% (Figure-8).

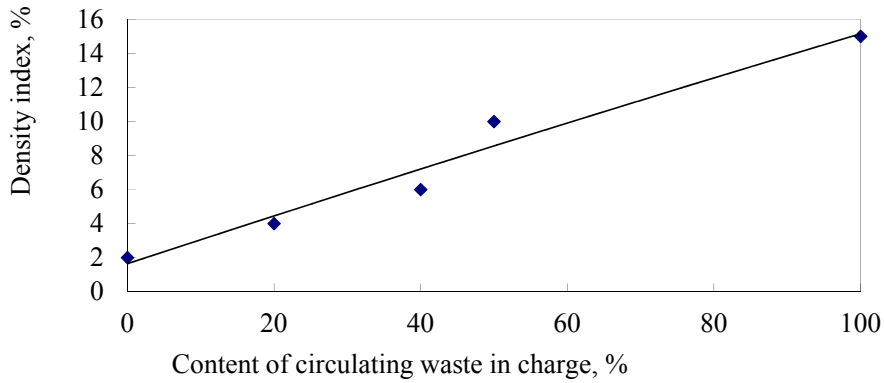

Figure-8. Change in the density index of alloy depending on content of circulating waste and "refreshing" in composition of charge (rest - content of primary charge materials).

Thus, the results of study showed the possibility of using density index method as a reliable and effective express method for controlling melt purity in production conditions, monitoring compliance with technological parameters of alloy preparation and stability of its composition.

Statistical analysis of the results on influence of melt temperature and relative humidity on density index (Figures 9, 10) showed that the density index values increase with an increase in the melt temperature and relative humidity of environment. The increase in density index with increasing temperature is explained by the fact that process of gas dissolution is accompanied by an endothermic reaction and can be described for aluminum by solubility equation [21, 22].

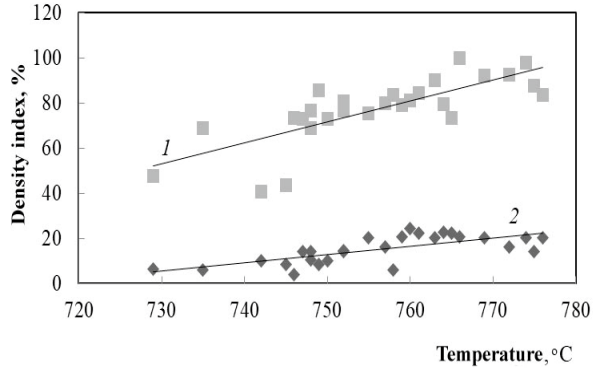

Figure-9. Density index versus melt temperature: 1 - before refining; 2 - after refining.

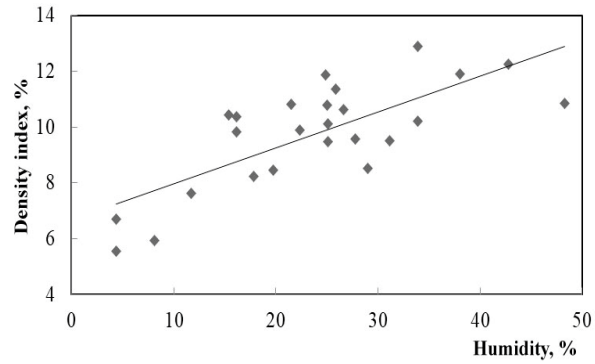

Figure-10. Dependence of density index on ambient humidity.

An increase in density index value with increasing ambient humidity is due to the fact that aluminum melt interacts with atmospheric moisture, and the following reaction occurs

$$3H_2O + 2Al = Al_2O_3 + 3H_3$$

Thus, refining the AK12 melt makes it possible to reduce density index by 90%. It should be note that in the studied interval, density index decreases with decreasing temperatures.

In parallel with sampling density index, hydrogen content in the AK12 (DIN AlSi11, ISO AlSi12) melt was measured by a direct method using an ALSPEK H MINI device before and after refining, and a statistical analysis of obtained data was carried out. Based on the measurement results a graphical dependence is plotted (Figure-11).

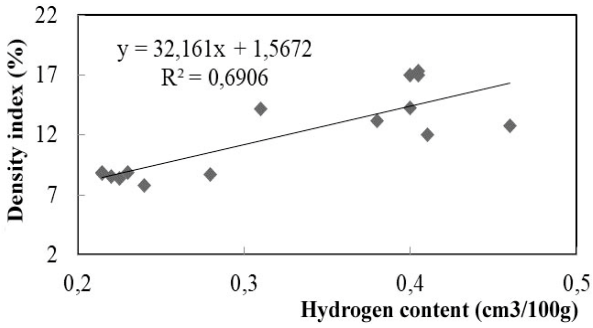

Figure-11. Dependence of density index on hydrogen content.

Theoretically, the correlation dependence of density index and hydrogen content should tend to unity if they vary proportionally to each other. The experimental results show that the coefficient of determination R2 determines the average relationship between the values of density index and hydrogen content. Consequently, density index shows not only change in hydrogen content, but also contamination of melt with non-metallic inclusions.

During melt preparation, intense gas saturation with hydrogen, nitrogen, oxygen occurs. Because of this interaction, Al2O3 oxides are formed in form of films and suspensions, which are a strong adsorbent of hydrogen. Being loose, surface of oxide films largely adsorbs hydrogen and creates conditions for formation of pores during solidification of sample under low pressure. The density index of sample, in this case, depends on amount of absorbed hydrogen and amount of suspensions of oxide films that got into melt during its preparation. The results of study are consistent with the data presented in [23], which shows difference between actual hydrogen content and its relative content according to density index. Therefore, density index is a qualitative method for assessing contamination with non-metallic inclusions and hydrogen.

CONCLUSIONS

Thus, the results of the study showed that most promising methods for assessing the hydrogen content in aluminum alloys are density index method and measurement by a solid sample (vacuum extraction). Application of Alspek H mini method is limited to use of expensive sensors.

Measurement of density index can be used as a reliable and effective express method for monitoring melt purity by hydrogen and oxide inclusions in production conditions. The control of hydrogen on a solid sample is most reliable, but cannot be recommended as an express method in production because of its considerable duration.

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