

## THE INFLUENCE OF ALLOYING ADDITIONS ON INTERACTION OF ALUMINUM ALLOYS WITH AQUEOUS MEDIA

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### Abstract

The influence of strontium, bismuth, lead and tin alloy, magnesium and other alloying components on the microstructure evolution of superficial films of aluminum and its alloys was researched using an X-ray electron spectroscopy. It was established that the alloying additives are surface-active materials and concentrate mainly in the surface layer, with partial oxidation together with aluminum. The chemical composition and properties of the formed film influence the properties of products based on doped alloys, in particular, powders, when used for different purposes. The correlation was determined between the level of hydrogen discharge from the alloy composition as well as the solution pH during interaction of aluminum, magnesium powders and their alloys with water, NaOH solution (pH = 11) and HCl (pH = 3). It was established that the aluminum powders alloyed with bismuth are the most reactive ones, and the powders alloyed with strontium are the least reactive ones.

### Introduction

Aluminum is quite similar to oxygen, it is an electronegative metal, and therefore it should not exist in the metallic form in air and water. But due to a quick formation of a protective oxide film on the surface, aluminum and aluminum-based alloys are quite stable and widely used both in the compact and in the powder form.

When preparing the aluminum powder, it is possible to vary the level of protection of its particles, by varying the permeability of the surface film to desired level. Most often, powders and products made from powders are needed that can sustain long storage and operation without a considerable oxidation. But in separate cases when powders are used as reagents, for instance, in production of hydrogen, and when high reacting capacity of powder in aqueous medium is needed, the surface film should have lower protection properties [1,2].

The physical properties are also dependant on the nature of the surface film: adhesion, slope of repose, fluidity, compression rate, compactibility, reflecting capacity and other.

Aluminum powders activated by alloying additives with interaction with alkali liquor and acids can be the basis of operation of cheap heat generators used in all kinds of areas and in everyday life.

### Experimental

The influence of alloying additives on the properties of surface films of aluminum powders were subject to researches. Strontium, bismuth and lead and tin alloy in 1:1 proportion were used for alloying. These alloying metals have a low surface tension, low melting temperature and do not form solid solutions with

aluminum. The alloying element content was 0,5 % w/w, except for magnesium.

In equilibrium conditions, magnesium and aluminum form a solid solution and two congruently melting compounds - Mg<sub>5</sub>Al<sub>8</sub> and Mg<sub>17</sub>Al<sub>12</sub> [3], and in unbalance conditions, for instance, during quick cooling when producing powders by atomisation, spherical particles are formed consisting of a homogenous solid solution only [4].

The aluminum-containing powders with different proportion of aluminum and magnesium in them were used for researches (Table 1).

Researches of the atomic and phase composition of the surface layer of powder particles were performed using an X-ray photoelectronic spectroscopy with SPECS unit. The analyser sensitivity is 0,1 % (at.), the penetration distance during the analysis – 0,5 to 10 nm (depending on the sample material and the angle of photoelectron flux), the analysis surface is 0.1 mm<sup>2</sup> [5,6]. Chemical activity of powders of aluminum, magnesium and their alloys in relation to distilled water and HCl and NaOH solutions was determined by the amount of discharged hydrogen. When analysing the information, the hydrogen amount was reduced to 1 cm<sup>2</sup> of the source powder surface. During the tests, the flask was put into the thermostat, and after the necessary temperature was reached, the powder sample was thrown to the aqueous environment without breaking impermeability. The amount of produced hydrogen was measured with the accuracy of up to 0.1 cm<sup>3</sup> using a temperature-controlled dropping glass. The tests were performed at a temperature of 50 °C.

In order to create equal conditions for the tests, the samples with an even specific surface of 200 m<sup>2</sup>/kg were prepared by mixing different fractions of powders. The powder particle size was below 50 μm.

Protective properties of oxide films on metals and alloys are characterised by the value of the Pilling-Bedworth ratio (α):

$$\alpha = \frac{M_{ox} \cdot \rho_{Me}}{A_{Me} \cdot \rho_{ox} \cdot n}$$

where M – molecular mass, A – atomic mass, ρ – density, n – number of metal atoms in the oxide formula, «ox» and «Me» indexes mean "oxide" and "metal", accordingly.

At α > 1 the oxide film protects the metal from oxidation, at α < 1 the oxide layer has a loose structure and does not provide adequate protection of the metal. Based on calculations, for aluminum α = 1,45, for magnesium α = 0,81, therefore, the magnesium surface film can prevent oxidation in air and corrosion in aqueous environment. In contrast, the surface film of compact aluminum is dens and it is not a reliable protection from interaction with gases and liquids.

**Table 1. Characteristics used in the study of aluminum and magnesium powders**

NN	Content of Mg+MgO, % wt.	Specific surface area, cm <sup>2</sup> /g	Density, g/cm <sup>3</sup>
1	99,95	1634	1,74
2	50±2	913	2,11
3	30±1	1075	2,31
4	10±0,5	926	2,55
5	trace	1287	2,69

Aluminum powders were produced by gas atomisation with nitrogen and oxygen addition. When producing powder, the metal temperature was 930 °C, that of nitrogen – up to 400 °C. In these conditions, oxidation of drip surface takes place until they are crystallised. When solidifying, the metal loses 17 % of its volume relative to the size of the source melt drop, that is why the oxide film for the metal core is quite big, and corrugations and cracks are formed on it decreasing protection properties of the superficial layer [4].

### Results and discussion

The results demonstrate that the surface of particles consists of oxides, and in separate cases metal particles are present (bismuth and tin).

An amorphous matrix was formed on the particle surface, with local groups of crystals  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> of small size.

It was established that in production of powders by spraying, during crystallisation of aluminum particles the atoms of alloying metals were expelled to the surface, and this influenced the chemical composition and properties of the film formed on the particles.

The results of chemical analysis of aluminum powder containing 0,5 % Sr demonstrated that the surface of powder particles contained 14 times more Sr compared to the source melt. All strontium turned out to be oxidated, besides, 90 % rel. of its total amount in the oxides layer was as SrAlO<sub>4</sub> aluminate having a dense structure of a spinel type. Since strontium forms an intermetallic compound with aluminum, it is most likely that they were mutually oxidised.

In the aluminum powder containing 0,5 % Bi, the surface layer of particles was enriched with bismuth by 8,5 times; over 80 % of bismuth is present as  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub>, dissolved in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. These oxides of bismuth and aluminum have an equal crystal lattice, but the size of the cube edge of  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> lattice is 1,07 Å, and this is considerably less than for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> – 7,7 Å, which makes the superficial film insufficiently dens and permeable for oxidants. The remaining 20 % of the total bismuth in the superficial film are in the metallic condition and form fine inclusions. Being an electropositive metal, bismuth ( $E_H = +0,226$  V) in contact with an electronegative aluminum ( $E_H = -1,66$  V) forms a short-circuited galvanic pair, causing an intense corrosion in the aqueous environment and, accordingly resulting in hydrogen discharge.

In the aluminum powder containing 0,5% (Pb+Sn) the surface layer is enriched with lead and tin by 10-12 times. As this takes place, the oxides of metals with different valence were formed: tin

is present as SnO<sub>2</sub> and SnO in equal proportion, lead is present predominantly as PbO, aluminum forms Al<sub>2</sub>O<sub>3</sub>. Lower oxides of lead and tin with aluminum should form aluminates, but it was not possible to determine this. Higher oxides of these metals form separate crystals. The oxide layer in this case has a dense mass free of defects, as in case with aluminum alloyed with strontium.

The correlation of the rate of hydrogen discharge and time during interaction of aluminum powders alloyed with different metals and aqueous medium is shown in Fig. 1.

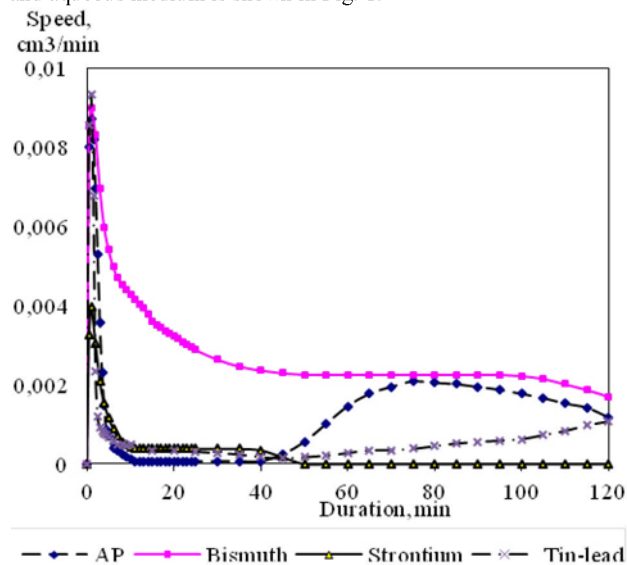


Figure 1. Dependence of the rate of hydrogen evolution with time at 50 °C

From Fig. 1 it follows that all samples demonstrate the maximum intensive but quickly finishing interaction directly after contact with water. This is explained by the presence of defects in the film formed during crystallisation, followed by quick "healing" of these defects by the reaction products, mainly by aluminum hydroxide.

At a later stage, the pattern of interaction for different alloys is different depending on the oxides film structure.

Aluminum alloyed with strontium, due to the presence of a defectless, dense and watertight film of spinel and counterdiffusion of aluminum ions, becomes passive; it discharges a small amount of hydrogen only at the beginning, at the rate that is considerably lower compared to other samples.

Aluminum alloyed with bismuth demonstrates high activity throughout the interaction. At the beginning, as with other samples, there is a peak of dependence of rate and time, but later on the process is quite intensive. This is due to a porous structure of the surface layer of particles and the presence of electropositive metallic bismuth in it.

Aluminum alloyed with the fusion of lead and tin is considerably less active compared to aluminum alloyed with bismuth and pure aluminum. After an initial intensive interaction, there is an induction period, after completion of which the rate continuously but insignificantly increases. The oxides layer is a substantial obstruction for water penetration into the reaction area, but it does not fully isolate the metal. In time the oxides layer becomes more permeable.

Unalloyed aluminum demonstrates a considerable activity in relation water only after a very long induction period.

Therefore, with the help of alloying additions of metals, it is possible to influence the structure and properties of the protective film on the surface of aluminum alloys.

In order to produce items made of powders intended for long operation in humid conditions, the powder alloyed with strontium is the most suitable. If it is necessary to use aluminum powder to produce hydrogen, it is optimal to use the powder alloyed with bismuth or other electropositive metal. In this case, no solid solutions or intermetallic compounds with aluminum are formed. If a long operation and a small amount of gas are needed, in particular, for electrochemical source of current, it is possible to use the aluminum powder alloyed with lead that forms intermetallic compounds with aluminum.

During the researches of magnesium-containing powders (Table 1) it was established that the surface layer contains much more metal compared to the alloy from which the powder was produced. For instance, the surface film on the particles of the powder produced from the fusion with almost equal atomic contents of magnesium and aluminum, had 86,6 at. % Mg and 18,9 at. % Al from the total of metals (less oxygen). This is explained by the fact that magnesium is a surface-active component in relation to aluminum, therefore, it enriches the surface layer of particles.

From the obtained photoelectron spectra and the results of decomposition of spectrum lines of Mg2s and Al2s by components, it is established that in the surface layer of the alloy particles with the correlation of atomic concentrations of Mg:Al  $\approx$  1:2, a superficial film consisting of magnesium aluminate  $MgAl_2O_4$  is formed as a result of a joint oxidation of liquid metals.

The correlation of the escape depth of photoelectrons and the amounts of oxide and metallic phases makes it possible to evaluate the superficial film thickness as 4,2 - 4,5 nm.

The results of analyses of other samples demonstrate that in case of deviation from this correlation, a two-phase structure is formed in the surface layer, consisting of magnesium aluminate with excess aluminum oxide or magnesium oxide.

Fig. 2 shows correlation of time for the reduced amount of hydrogen discharge during interaction of aluminum and its alloys with distilled water at 40 °C. The reaction was started without the

induction period. The active discharge of hydrogen during the first minutes of the test is due to the presence of defects in the superficial film of powder particles.

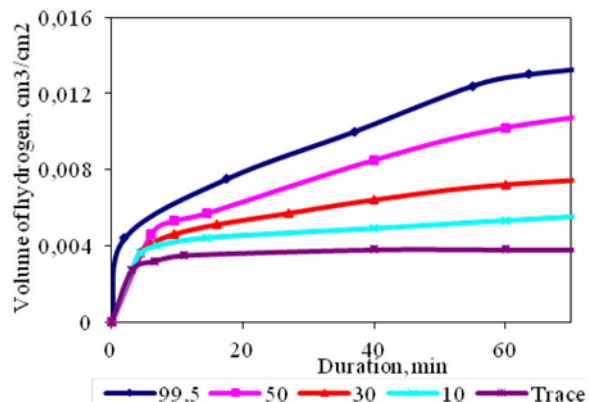


Figure 2. The dependence of the reduced volume of hydrogen vs; the interaction time with distilled water (pH = 7) при 40 °C

Magnesium-containing alloys have a loose superficial film, its permeability to water increases in proportion to the increased magnesium content. Moreover, the standard electrochemical potential of magnesium is more electronegative compared to aluminum, therefore in the tests with alloys hydrogen is discharged more intensively in proportion to the increase of magnesium content in them.

Fig. 3A shows the correlation of the amount of discharged hydrogen and the time of interaction of the researched powders with hydrochloric acid (pH = 3) at a temperature of 40 °C.

Aluminum is stable in HCl solution due to a dense surface film of the hydroxide salt  $AlCl_n(OH)_m$  which is insoluble in hydrochloric acid [7]. Magnesium and its alloys with aluminum having a porous superficial film containing magnesium oxide soluble in HCl, actively reacts with the hydrochloric acid solution. With the increase of magnesium content, intensity of the hydrogen discharge rate is increased.

Fig. 3B shows a similar correlation, but aluminum reports to NaOH solution (pH = 11). Magnesium reacts with it only slightly. Powders of pure aluminum and its alloys with magnesium actively interact with the solution.  $Al_2O_3$  and  $Al(OH)_3$  contained in surface films are dissolved, juvenile surfaces of the metal are revealed and it begins to react with hydroxyl ions.

Fig. 4 shows correlations of the amount of discharged hydrogen in water, alkaline and acid environments and the magnesium content in Al-Mg alloys at the 45th minute of the test at 40°C. The time was selected randomly, supposing that the process stabilised at that moment and no side effects were present.

The scheme of aluminum and magnesium interaction with solutions is similar: the protective superficial film breaks, the access to the metal opens for the reagent, and the alloy interacts with one of the following constituents: in the alkaline solution – with aluminum, in the acid solution – with magnesium.

The results of tests shown in Fig. 4 prove that it is possible to produce the maximum amount of hydrogen using pure metals. Application of alloys decreases intensity of hydrogen discharge.

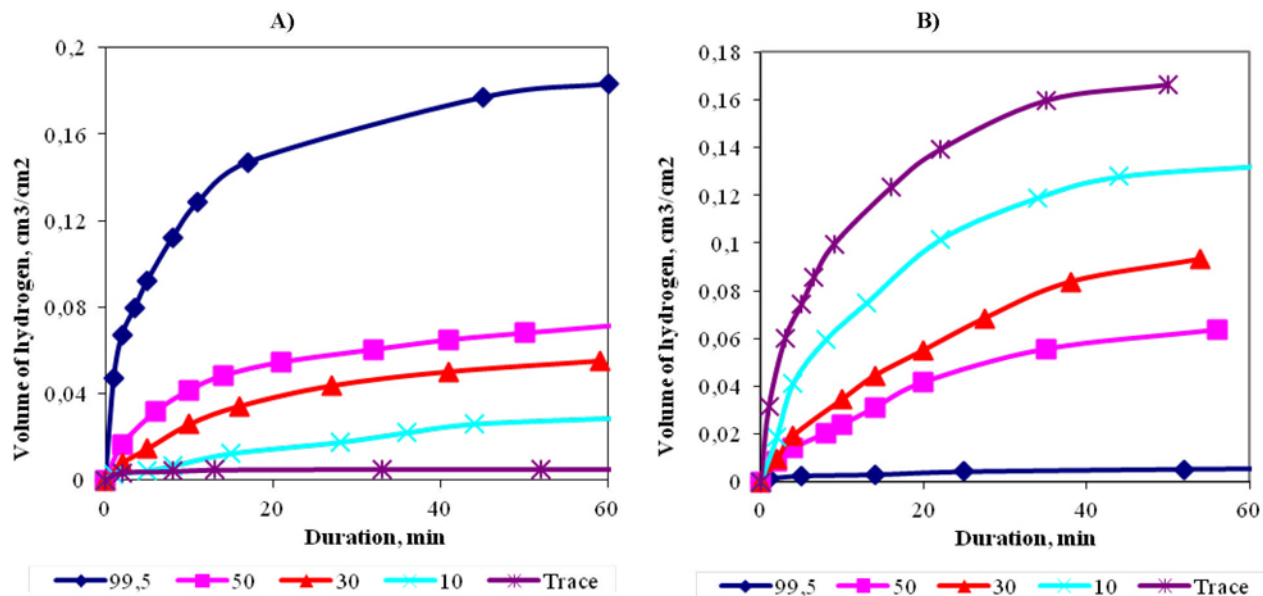


Figure 3. The dependence of the reduced volume of hydrogen from powders vs interaction time at 40 ° C in solutions: A – HCl (pH = 3) and B – NaOH (pH = 11)

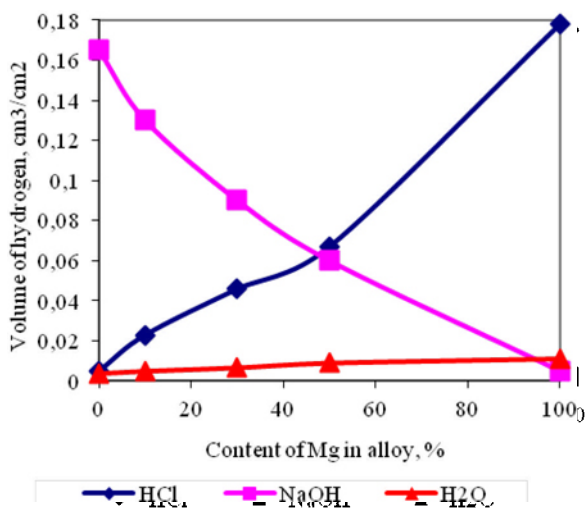


Figure 4. Dependence of the reduced amount of hydrogen evolved in different environments vs the magnesium content of the alloy in the 45th minute of the experiment

For practical use in hydrogen generators, it is more efficient to use the aluminum powder that reacts with NaOH solution.

### Conclusion

1. It is possible to change the properties of the surface film of the aluminum powder by microalloying of source powder with surface-active additives.

2. The aluminum powder alloyed with strontium has the densest impermeable surface film of a spinel type, and the items made of it can operate in water and in humid environment for a long time.

3. The aluminum powder microalloyed with bismuth is the most reactive in an aqueous solution. The surface film of such powder has inclusions of metallic bismuth, which is an electropositive metal, creating a short-circuited galvanic microelement with aluminum. Such powder can be used to produce large amounts of hydrogen.

4. Microalloying with fusions of lead and tin decreases the reaction capacity of the aluminum powder but does not create a full corrosion protection. Such powder can demonstrate a long lifetime with an even discharge of hydrogen, for instance for chemical sources of current.

5. The surface of particles of the powder produced by atomisation of the aluminum-magnesium alloy is rich in magnesium, which is a surface-active metal in combination with aluminum.

6. As a result of a joint oxidation of aluminum and magnesium during atomisation, the magnesium aluminate is formed in the oxide film of the powder.

7. The results of tests using powders of aluminum and its alloys in the solutions of hydrochloric acid and sodium hydroxide demonstrated a decisive role of the properties of metal oxides forming the superficial film.

8. In order to produce hydrogen, it is possible to use interaction of aluminum with NaOH solution; using powders of Al-Mg alloy for production of hydrogen both in the alkaline and in the acid environment is inadvisable.

## References

1. Joseph R. Davies. ASM Specialty Handbook: Aluminium and Aluminium Alloys, ASM International, 1993. 784 p.
2. Edward Ghali. Corrosion Resistance of Aluminum and Magnesium Alloys: Understanding, Performance, and Testing. John Wiley & Sons, Inc., 2010. 719 p.
3. L.F. Mondolfo. Aluminum alloys: structure and properties. Butterworths, 1976. 971 p.
4. Gopienko V.G., Cherepanov V.P., Zotikova A.N. and Kuryashkin L.V. "Chemical heat and effervescing mixtures based powders of aluminum, magnesium and their alloys" Russian Journal of Non-Ferrous Metals (Tsvetnye Metally), (1)(2000), 65-68.
5. J.F. Moulder, W.F. Stickle, P.E. Sobol, and K.D. Bomben, Handbook of X-Ray Photoelectron Spectroscopy (Physical Electronics, Eden Prairie, MN, 1995. 262 p.
6. <http://srdata.nist.gov/xps>
7. US Patent 4944933, Preparation of basic aluminium halides, C01F/56, 1990.