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Formation of Hydrides in the Surface Layer of Aluminum in Non-Equilibrium Conditions of Electrolyte Plasma

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In this paper, the formation of a diffusion layer on aluminum, which includes aluminum hydrides, in non-equilibrium conditions of electrolyte plasma with high local temperatures, high heating and cooling rates were studied. As a result of the research it was obtained that in the diffusion layer formed complex nanosized inclusions of polymorphic modifications $(AlH_3)_n$ and AlB_3H_{12}. The diffusion in the non-equilibrium conditions of the electrolyte plasma is carried out in hydrogen environment, where the hydrogen atoms have the greatest energy and is one of the main forces that activate the diffusion process and influence the structure, composition and micromechanical characteristics of the diffusion layer.

Keywords: electrolyte plasma, aluminum hydrides, diffusion layer, non-equilibrium conditions, nanosized inclusions.

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Introduction

According to the scientific statement [1-4], hydrogen is a universal external agent and alloying element which provides the opportunity for new and effective methods of metal materials treatment. Hydrogen action on materials, as it has been established, is one of the fundamental controlled impacts, along with such influences as, for example, temperature, pressure, fields and particle flows. It has been established [1-6] that the influence of hydrogen is multifactorial and is determined by the superposition of a number of factors depending on the conditions of treatment (type of energy source, the nature of the heating source, composition of the gas environment, duration of exposure), composition and structure of the metal. In the conditions of electrolyte plasma, which is formed as a result of discharges in an aqueous electrolyte solution [7], a hydrogen atmosphere is formed around the cathode, in which the diffusion of elements forming cathode space into the cathode proceeds.

In this paper, the formation of a diffusion layer on the aluminum surface in non-equilibrium conditions of electrolyte plasma with high local temperatures, high heating and cooling rates of metals were studied.

I. Method and materials

The treatment of aluminum and its alloys in electrolyte plasma was carried out in laboratory conditions in electrolysis mode: U = 30 - 80 V, j = 0,3 - 1,8 A/sm2, t = 10 - 30 min. An aqueous solution of alkali metal carbonate, glycerin, boron carbide powder were used as an electrolyte. The stainless steel electrode was used as anode, and samples of aluminum and its alloys were cathode.

For the purpose of research, the influence of temperature on the structure of diffusion zone treated in electrolyte plasma, the aluminum specimens were annealed in a vacuum for two hours at temperatures: 473 K, 623 K, 773 K, 973 K.

The phase and structural components of the diffusion layer were determined by micro X-ray spectral analysis on JSM-6490 microscope, X-ray diffractometer analysis on DRON-3 diffractometer in monochromatic radiation of Fe-Kα. The metallographic analysis of the diffusion layer was carried out using an optical microscope "Neofot-21", a microhardness meter PMT-3.

II. Results and discussion

A layer of white color on the surface of aluminum and its alloys with a thickness of 30 to 80 microns with microhardness, which varies in depth from 10 GPa to 4 GPa depending on the treatment and composition of the aluminum alloy are found as a result of metallographic analysis. The microhardness of the sample bases increased on average of 2-3 times.

The results of the X-ray diffraction analysis

presented in Table 1 shows the distribution of the boride

nanosized structures, are distributed mainly on the

Table 1

Summarized results of layer by layer X-ray analysis of aluminum samples treated in electrolyte plasma

Depth of layer, μm	Phase composition
10	α, β-AlB$_3$H$_{12}$, NaAlH$_4$, a , b , g - AlB$_{12}$, a , b , d , e , γ, ξ –AlH$_3$, AlB$_{10}$.
50	α, β-AlB$_3$H$_{12}$, AlB$_{10}$, d , e , ξ –AlH$_3$, NaAlH$_4$
100	α, β-AlB$_3$H$_{12}$, d , e , ξ –AlH$_3$.
150	α-AlB$_3$H$_{12}$, e , ξ –AlH$_3$.

and hydride phases on the depth of the diffusion layer. Among them, the most probable triple compounds α, β-AlB$_3$H$_{12}$, NaAlH$_4$ and hydrides AlH$_3$ are practically all known modifications depending on the conditions of aluminum treatment.

Results of the X-ray analysis of the diffusion layer obtained on the aluminum surface in the electrolyte plasma showed the lines of polymorphic modifications (AlH$_3$)$_n$ are identified when small-angle scattering of radiation, while the triple AlB$_3$H$_{12}$ compounds are basically identified at large angles.

In addition, the influence of the electrolysis mode on the composition of the diffusion layer is investigated. Thus, with increasing current density, the number of lines that are identified with triple AlB$_3$H$_{12}$ and NaAlH$_4$ is increased. Thus, with increasing current density, the number of lines that are identified with triple AlB$_3$H$_{12}$ and NaAlH$_4$ is increased. According to layer by layer X-ray and spectral analysis carried out on samples treated in electrolyte plasma in the regime with a current density ≥ 1.2 A/sm^2 (Table 1), the presence of these compounds and their depth of their occurrence depend on the boron and sodium distribution [7]. At low current density, boron diffuses to a lesser depth, and sodium practically does not diffuse into metal. Therefore, in the case of low-current regime, there is no triple compound NaAlH$_4$.

Aluminum hydrides formed in non-equilibrium electrolyte plasma conditions have a polymeric molecular structure (AlH$_3$)$_n$ whose crystalline form can exist in seven polymorphic modifications: a -(AlH$_3$)$_n$, a' -(AlH$_3$)$_n$, b -(AlH$_3$)$_n$, d -(AlH$_3$)$_n$, e -(AlH$_3$)$_n$, g -(AlH$_3$)$_n$, z -(AlH$_3$)$_n$ [6]. A1H$_3$ hydride is stable under normal conditions, non-toxic and at the same time contains about twice as many hydrogen atoms per unit volume than liquid hydrogen. In this regard, A1H$_3$ is one of the most promising materials for storage and transport of hydrogen, and its comprehensive experimental and theoretical study is actively practiced in almost all industrialized countries.

It is known that NaAlH$_4$ decomposes at a temperature of 493 K, AlB$_3$H$_{12}$ – a complex mixed aluminum hydride and boron having a boiling point of 317.5 K. That is, at temperatures above, they are not formed. However, in non-equilibrium conditions of electrolyte plasma at high heating and cooling rates the decomposition processes do not have time to happen, and the formation of these compounds has a high probability. In the diffusion layer on the aluminum surface treated in electrolyte plasma, complex inclusions are formed from two - three elements and their modifications, forming

boundaries of grains, phases, microdefects, estimating the size of which is about 6 - 22 microns.

At annealing in vacuum in isothermal conditions of treated aluminum samples, according to the results of X-ray analysis, presented in Table. 2, the amount of hydrides and their modifications are significantly reduced with increasing annealing temperature. Thus, annealing at 773K, the number of NaAlH$_4$ lines is reduced and practically absent AlH lines, but the triple compound β-AlB$_3$H$_{12}$ is retained. At annealing temperature of 973 K, the number and intensity of the β-AlB$_3$H$_{12}$, NaAlH$_4$ lines decreases and α-AlB$_{12}$ increases. At lower annealing temperatures 473 K and 623 K the most stable phases of the aluminum hydride α, β-AlH$_3$ are remained. It can be assumed that with increasing temperature the hydrogen from the form of iodine hydride passes into the state of the proton gas dissolved in the metal, and then degassed from the crystalline metal lattice.

To understand the diffusion processes at the treatment of aluminum in electrolyte plasma, it is necessary to consider the processes occurring around the cathode zone.

Analysis of the dependence of energy transferred to ions by electrons from the concentration of plasma and atomic mass of the ion, shows that the ions of hydrogen have the greatest energy [7, 8].

At the moment of contact hydrogen atom with a metal surface the energy that passes mainly into the oscillatory energy of the surface metal atoms is released. It is more than the value of potential barrier on the surface, and hydrogen atoms without activated transition from the gas phase to the near-surface layers of the metal. Particles whose speed is such that allows them to pass through the cathode without interference leave behind the line of inhomogeneities, thereby increasing the strength of the aluminum alloy.

According to [8], plasmochemical reactions around the cathode zone lead to the formation of compounds containing hydrogen. By binding energy of the dipole moments hydrogen first forms Na-H, B-H, and then Al-H. The absorption of hydrogen by sodium begins at 473 K and goes at a high speed at 573 – 623 K [6]. Hydrogen diffusion is inhibited by oxygen adsorbed on the aluminum surface, or by cations of sodium and boron. Reducing the solubility of hydrogen under these conditions is also due to the competition of boron, which has increased solubility in electrolysis and, unlike hydrogen, forms more stable bonds with aluminum atoms. For such physicochemical processes around the cathode the inhibition of hydrogenation metal is

occurred.

2. Complex compounds containing hydrogen and

The phase composition of the diffusion layer on aluminum before and after annealing

№	Regime of electrolysis	Composition of the diffusion layer	
		before annealing	after annealing for 2 hours
		at 473 K	
1	U = 85 V, j= 0.52 A/sm^2, t = 15 min	β- AlB_{12}, β-AlB_3H_{12}, $NaAlH_4$, γ, β, ε, ξ -AlH_3	α- AlB_{12}, β-AlB_3H_{12}, $NaAlH_4$, α, β -AlH_3
		at 623K	
2	U = 85 V, j = 0.26 A/sm^2, t = 15 min	β- AlB_{12}, β-AlB_3H_{12}, $NaAlH_4$, α, ξ, ε -AlH_3	α- AlB_{12}, α-AlB_3H_{12}, $NaAlH_4$, α -AlH_3
		at 773K	
3	U = 45V, j = 0.1 A/sm^2, t = 15 min	β- AlB_{12}, β-AlB_3H_{12}, $NaAlH_4$, δ, β -AlH_3	α-AlB_{12}, β-AlB_3H_{12}, $NaAlH_4$
		at 973K	
4	U = 80-90 V, j = 0.12 A/sm^2, t = 15 min	β- AlB_{12}, α, β-AlB_3H_{12}, $NaAlH_4$, α, β, ε -AlH_3	α-AlB_{12}, β-AlB_3H_{12}, $NaAlH_4$

However, in the process of diffusion under conditions of electrolyte plasma boron on one side prevents the hydrogenation of aluminum, because it has high solubility in electrolysis and, unlike hydrogen, forms more stable bonds with aluminum atoms, and on the other side, promotes to hydrogen retention even with increasing temperature up to the melting point of aluminum. Consequently, the conditions for the treatment of aluminum and its alloys promote the regulation of metal hydrogenation process.

Conclusions

1. Diffusion of the elements forming an electrolyte is carried out in non-equilibrium conditions of electrolyte plasma in hydrogen environment, with high heating and cooling rates.

their modifications that form nanoscale structures, distributed mainly along the boundaries of grains, phases, microdefects and affect the structure and micromechanical characteristics of the diffusion layer are formed in the diffusion layer, on the aluminum surface.

3. A characteristic feature of the aluminum hydrides formation in non-equilibrium electrolyte plasma conditions is to obtain almost all polymorphic modifications $(AlH_3)_n$ and AlB_3H_{12}.

4. In the diffusion process under electrolyte plasma conditions, boron on one side prevents hydrogen saturation of aluminum, since it has increased solubility in electrolysis and forms more stable bonds with aluminum atoms, and on the other side, it promotes hydrogen retention even when the temperature rises to the melting point of aluminum.

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Утворення гідридів в поверхневому шарі алюмінію в нерівноважних умовах електролітної плазми

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У даній роботі вивчали процес утворення дифузійного шару на алюмінії, до складу якого входять гідриди алюмінію, в нерівноважних умовах електролітної плазми з високими локальними температурами, більшими швидкостями нагріву та охолодження. В результаті досліджень отримано, що в дифузійному шарі формуються складні нанорозмірні включення поліморфних модифікацій $(AlH_3)_n$ та AlB_3H_{12}. Дифузія в нерівноважних умовах електролітної плазми здійснюється у водневому середовищі, де атоми водню мають найбільшу енергію і є однією з основних активуючих процес дифузії сил, що впливають на структуру, склад та мікромеханічні характеристики дифузійного шару.

Ключові слова: електролітна плазма, гідриди алюмінію, дифузійний шар, нерівноважні умови, нанорозмірні включення.