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Aluminum surface modification by electron-ion-plasma methods

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Abstract. The paper focuses on detection and structural-phase justification of the modes of combined electron-ion plasma treatment of commercially pure A7 grade aluminum carried out in a single vacuum cycle and enabling to enhance mechanical (microhardness) and tribological (wear resistance) properties of the material. Commercially pure A7 grade aluminum underwent combined surface treatment, including deposition of titanium coating by means of vacuum-arc technique and further mixing of the coating/substrate system by intense pulsed electron beam. The varied parameters were energy density of the electron beam (10, 15, 20) J/cm^2 and the number of impact pulses (3-100); the thickness of titanium coating was 0.5 μm. Electron-ion plasma treatment of aluminum was carried out in a single vacuum cycle. Optical and scanning electron microscope investigations, measuring of microhardness and tribological tests allowed defining the modes when hardness and wear resistance of the modified surface layer increases manifold in comparison to the initial properties of commercially pure aluminum.

Introduction

Aluminum and its alloys are widely used in industry due to their relatively high specific strength, satisfactory corrosion resistance and good processing qualities for mechanical treatment methods [1-3]. However, along with those advantages aluminum is also characterized by low hardness and wear resistance [1-4]. Various surface modification techniques are often used to enhance the above mentioned properties of metals and alloys (including aluminum), as well as sintered metal powder materials, such as deposition of hard, superhard and wear resistant coatings, surface treatment with concentrated energy flows, surface saturation with metals and gases atoms, etc. [1-14].

Deposition of various coatings is considered as an advanced way to increase dramatically the strength and tribological properties of metals and alloys. It can be found in recent studies that coatings with complex multi-phase nanocrystalline or amorphous structure possess unique properties, such as superhardness (≥40 GPa) [15, 16], oxidation stability at high temperatures (>1000°C) [17, 18], and low friction coefficient (≤0.1) [19]. Special interest is gained by traditional wear resistant materials coatings based on titanium

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nitride, possessing nanocrystalline structure by introduction of dopants into composition (Si, Al, Cr, Cu etc.). The interest to these systems is conditioned by their high wear resistance and hardness (Ti-Cu-N – up to 45 GPa, Ti-Si-N – up to 80 GPa) while being relatively easy to obtain. The research [20] shows that in coatings of Ti-Si-N system basic phase nanosized crystalline grains (TiN) are incorporated into amorphous silicon nitride matrix (Si_3N_4). In other case when introducing metal coatings that do not form compounds with nitrogen into MeN composition, such as Cu, Ni, Y, Au etc. (the coating of nc-MeN/soft phase system is formed (Me=Ti, Zr, Cr, Ta etc.)), atoms of dopants encircle nitride crystalline grains of the basic element thus restricting their growth in nanometer range [21].

The basic disadvantage of the coating deposition technique is not high enough properties of the coating/substrate system provided by large difference in physical and mechanical properties of the substrate and the coating being formed. The mentioned drawback is compensated by preliminary modification of the surface layer of the substrate by leaving the structure and properties of the material bulk unchanged [22]. Electron-ion plasma treatment is distinctive with high effectiveness level of modifying the structure and properties of the material surface layer. This is especially true for complex processes combining surface impacts of plasma flows, accelerated electron and ion beams [23].

Methods of combined electron-ion plasma treatment implemented so far include consequent modification of the structure and properties of metals and alloys surface layer using the combination of a several number of experimental setups [23, 24]. Drawbacks of the mentioned approach are obvious: high cost of maintenance of a series of separate setups, each of them having duplicating devices (vacuum system, working chamber, power supply and control board), relatively large durability of the cycle vacuuming – de-vacuuming, heating and cooling of the components, violation of purity of the treated surface (pollution of modified surface with atmospheric gases, etc. during samples placement from one setup to the other). The basic criterion in development of complex electron-ion plasma treatment is combination of its processes in a single vacuum cycle. For that purpose researchers of the Institute of High Current Electronics within the framework of the research upon the grant of the Russian Science Foundation (project No.14-29-00091) developed, designed and commissioned the COMPLEX setup of laboratory type. This setup enables to carry out material surface irradiation by intense pulsed electron beam in any sequence in a single vacuum cycle and saturates material with incorporation elements, deposit metal coatings and hard cermet and ceramic coatings. COMPLEX setup is unique in its combination of parameters and possibility of implemented processes and currently has no analogs both in Russia, and abroad. This fact defines undoubted research novelty and practical significance of the obtained results.

The present research focuses on detection and structural-phase justification of the modes of combined electron-ion plasma treatment of commercially pure A7 grade aluminum performed in a single vacuum cycle (COMPLEX setup) and enabling to enhance manifold the material mechanical (microhardness) and tribological (wear resistance) properties.

Materials and methods

Commercially pure A7 grade aluminum (Al – 99.7%; Fe – up to 0.16%; Si – up to 0.16%; Ti – up to 0.02%; Cu – up to 0.01%; Zn – up to 0.01%) was used as a modified material [25]. Combined modification of the structure and properties of commercially pure A7 grade aluminum was carried out on a COMPLEX laboratory setup [26]. The setup is intended for electron-ion plasma finishing modification of metals and alloys in a single vacuum cycle. The basic setup units are gas plasma source based on low pressure non-self-sustained arc discharge with combined thermionic and hollow cathode [27], source of electrons of submillisecond duration based on plasma cathode with grid stabilization of plasma boundary [28], arc evaporation source based on arc discharge with cold cathode [29].

The first stage of electron-ion plasma treatment included deposition of thin titanium coating 0.5 µm thick by vacuum arc method on the substrate made from commercially pure A7 grade aluminum. The second stage included electron-beam mixing of the coating/substrate system. The irradiation parameters were as follows: accelerated electrons energy 18 keV, the energy density of electron beam (10, 15, 20) J/cm^2, pulse duration of 50 µs, repetition rate and the number of impact pulses 0.3 s^{-1}, (3-100) pulses, respectively. Justification of selecting electron-ion plasma treatment for modification of commercially pure aluminum is defined by positive results of earlier studies performed on Al-12% Si alloy [23, 30].

Composition and structure of aluminum samples before and after modification were investigated by optical microscopy (µVizo-MET-221 metallographic microvisor), scanning electron microscopy and X-ray energy-dispersive analysis (Philips SEM-515 scanning electron microscope with EDAX ECON IV microanalyzer). Microhardness was measured using PMT-3 microhardness tester at the loading on the indenter 0.1 N. Tribological studies were carried out using Pin on Disc and Oscillating TRIBOtester (TRIBOtechnic, France) with the following parameters: a ball from steel 100Cr6, with the diameter 6 mm, track radius – 2 mm, load – 1 N, distance – 10 m. The chosen techniques and methodologies are well proved and widely used in material physics to study the structure and properties of metals and alloys. Therefore the validity of the obtained results is proved.

Results

It was established that microhardness of the system "coating (Ti) / (A7) substrate" significantly depends on the mode of intense pulsed electron beam irradiation (Fig. 1*a*). At the energy density of electron beam equal to 10 J/cm^2, microhardness of the surface layer increases with the growth of irradiation pulses number. Maximum value of microhardness was defined at irradiation of the coating/substrate system by electron beam with the following parameters: E_S = 10 J/cm^2, τ=50 µs, n = 50 pulses (Fig. 1*a*). Microhardness was increased by more than 4 times compared to that of the initial samples.

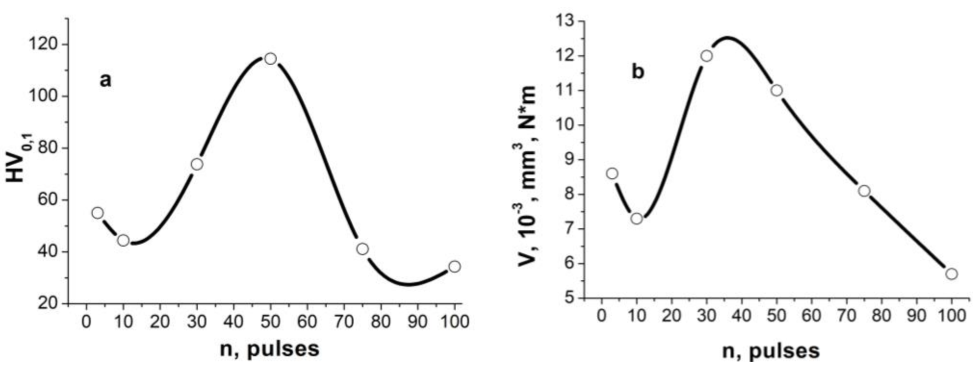

Fig. 1. Dependence of microhardness $HV_{0,1}$ (a) and wear parameter V (b) of modified surface of the commercially pure A7 grade aluminum on the number of irradiation pulses *n* by intense pulsed electron beam of the system "coating (Ti) / (A7) substrate" at the energy density of 10 J/cm^2.

During irradiation of samples by electron beam with energy density of 15 J/cm^2 microhardness is maximum at three impact pulses (it exceeds aluminum microhardness by more than 3.5 times) and it is reduced with the growth of the number of electron beam pulses. During irradiation of the system "coating (Ti) / (A7) substrate" by intense electron beam with energy density of 20 J/cm^2 microhardness of samples almost does not depend on the number of impact pulses and exceeds aluminum microhardness by 1.7 times.

Wear parameter (the value which is reverse to material wear resistance) is changed the similar way. Figure 1*b* presents dependence of the wear parameter on the number of impact pulses of electron beam by the energy density equal to 10 J/cm^2. As following from the results presented in Figure 1*b* it can be concluded that the maximum wear resistance, exceeding the value of the reference samples of commercially pure A7 grade aluminum by 2.3 times is observed in the samples treated by 100 pulses.

It is obvious that microhardness and wear resistance of material are defined by the state of substructure of modified layer [31-33]. Figure 2 illustrates electron-microscope images of structure formed at irradiating the system "coating (Ti) / (A7) substrate" by electron beam with the energy density of 10 J/cm^2. It is clearly seen that by three irradion pulses the titanium coating on the surface of aluminum sample remains unchanged (Fig. 2*a*). Resulting from thermoelastic stresses the coating is fragmented with microcracks; folded structure is formed on the surface. Increasing the number of irradiation pulses up to 50 results in formation of nanocrystalline structure in the sample surface layer; crystalline grains size being ≈70 nm (Fig. 2*d*). The grain size of the surface layer of these samples varies within the range of 15-20 μm.

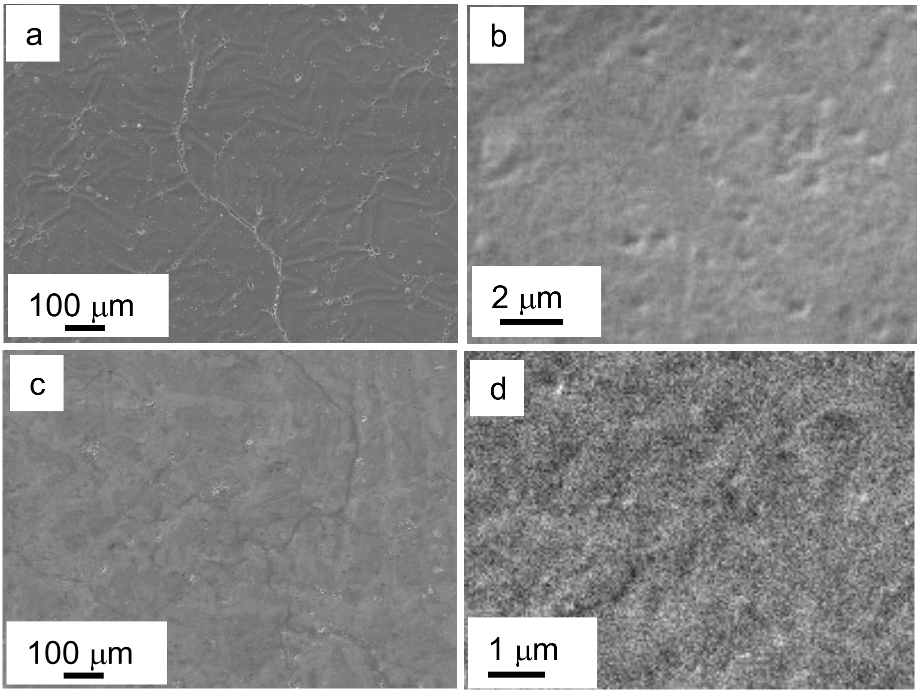

Fig. 2. SEM images: surface structure of the system "coating (Ti) / (A7) substrate" formed resulting from irradiation by intense pulsed electron beam at pulse duration of 50 μs and energy density of 10 J/cm^2; a, b – 3 pulses, c,d – 50 pulses; the thickness of titanium coating of 0.5 μm.

Increasing the number of irradiation pulses up to 100 at the energy density of electron beam of 10 J/cm^2 results in formation of fine-grained structure in the surface layer of commercially pure aluminum; the grain size varies within the range of 2.5-5 μm (Fig. 3*a*). Substructure of cellular crystallization is revealed in grain bulk; it is generally formed in alloys under conditions of ultrahigh speed crystallization [33]. The sizes of crystallization cells vary within the range of 250-500 nm (Fig. 3*b*).

Elemental composition of the surface layer of commercially pure aluminum was defined by electron probe microanalysis. It was established that irrespective of the energy density of electron beam, increasing the number of irradiation pulses leads to reduction of relative concentration of titanium atoms in the aluminum surface layer. It is obviously conditioned by titanium atoms leaving into the bulk of aluminum sample as a consequence of ongoing process of leveling diffusion. Growth of energy density of electron beams stimulates the process of titanium atoms rearrangement in the surface layer of the alloy.

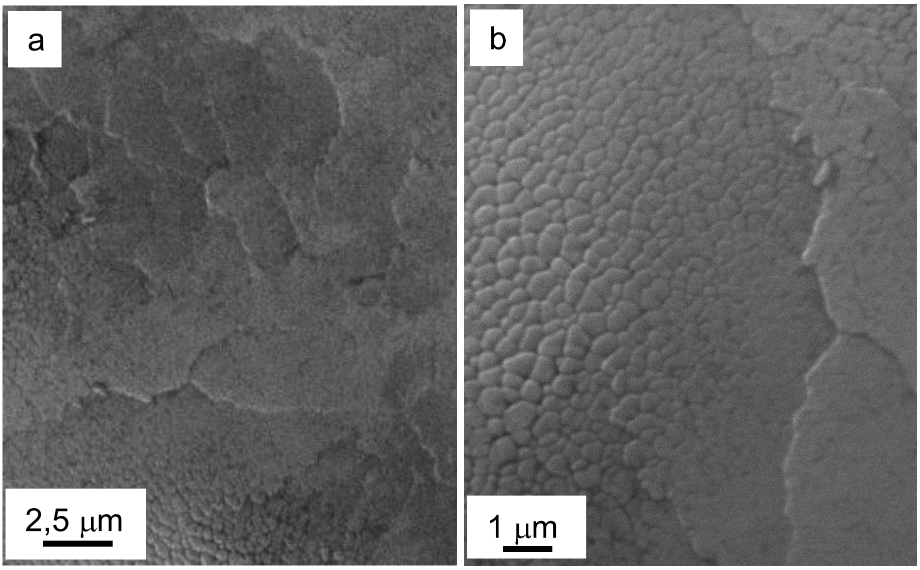

Fig. 3. SEM images: surface structure of the system "coating (Ti) / (A7) substrate" formed resulting from irradiation by intense pulsed electron beam at pulse duration of 50 μs and energy density of 10 J/cm^2; number of irradiation pulses – 100; the thickness of titanium coating of 0.5 μm.

Scanning electron microscopy investigations allow making the following assumptions. Relatively high microhardness of the surface layer of modified aluminum samples is conditioned by the formation of nanocrystalline structure (optimal irradiation mode by electron beam 18 keV, 10 J/cm^2, 50 μs, 50 pulses, 0.3 s^{-1}). Comparatively high wear resistance values taking place during melting of the system "coating (Ti, 0.5 μm) / (A7) substrate" (parameters of electron beam: 18 keV, 10 J/cm^2, 50 μs, 100 pulses, 0.3 s^{-1}) are conditioned by the formation of fine-grained polycrystalline structure with substructure of cellular crystallization.

Conclusion

Modification of the surface layer of commercially pure A7 grade aluminum was for the first time carried out on a COMPLEX laboratory setup in a single vacuum cycle. The process included formation of the system "coating (Ti) / (A7) substrate" and its further irradiation by intense pulsed electron beam. Modification modes and parameters of the formed material structure enabling to enhance microhardness and wear resistance of the modified layer manifold were defined, thus proving successful completion of the set objective of the present study.

The obtained results possess practical and economical significance as they justify new effective direction for forming high operational properties of metals and alloys. The method is based on modifying some surface layer of component or a product by leaving the structure and bulk properties generally unchanged. Further research in this direction will be devoted to search and justification of choosing alloying elements allowing controlling effectively the structure and properties of the component on the whole when applying electron-ion plasma modification to comparatively thin surface layer.

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