Electron-beam modification of coating - aluminum substrate systems

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Abstract. Multiphase surface alloys with improved strength and tribological characteristics have been synthesized by exposing coating/A\textsubscript{7} substrate systems to a pulsed electron beam. Optimum modes of electron-ion-plasma treatment of commercially pure aluminum have been found at which the wear resistance and hardness of the surface layer were observed to increase by a factor of about 7.5 and up to 18, respectively.

1. Introduction

Aluminum and aluminum-based alloys have reasonable costs and are accessible for various applications. They have such advantages as high thermal conductivity, machinability, low cost, etc. In order to extend the application of aluminum products further, to endow them with high wear resistance, increased hardness, etc., a reasonable increase in costs is required. One of the modern and promising methods of modification of aluminum-based alloys is a complex electron-ion-plasma treatment of products, which combines deposition of thin one-component or multicomponent coatings followed by exposure to an electron beam to provide mixing of the coating/substrate system or to melt the hard coating in the low-melting substrate [1, 2]. In this case, in addition to the strengthening thin layer, whose properties are determined by the coating deposition conditions, an extended near-surface modified layer is formed which can consist of sublayers possessing different structure-phase characteristics and unique properties [3, 4].

Coating/substrate systems are exposed to an intense pulsed electron beam of submillisecond (up to 200 \textmu s) duration, which provides ultrahigh rates of heating (up to 10\textsuperscript{6} deg/s) of a surface layer of thickness tens micrometers to temperatures at which a melt can exists. This makes it possible to attain very high temperature gradients (10\textsuperscript{7}–10\textsuperscript{8} deg/m) in the surface layer that ensure cooling of the surface layer due to heat removal to the cold bulk material at a rate of 10\textsuperscript{4}–10\textsuperscript{6} deg/s [5-6]. Fast cooling of the surface layer conserves its non-equilibrium structure-phase state which is characterized by submicrometer and nanometer sizes of crystallites, high concentration gradients of alloying elements, and multiply increased values of physic-mechanical, tribological, electrical, and other parameters [7-8].

The goal of the study presented in this paper was to produce strengthened layers in coating/substrate systems by electron-beam treatment, to optimize the modes of complex electron-ion-plasma modification, and to examine the strengthened layers by up- to-date methods of material science.
2. Materials and procedures

The substrate material was commercially pure A7 aluminum alloy (99.7% Al, max 0.16% Fe, max 0.16% Si, max 0.02% Ti, max 0.01% Cu, max 0.01% Zn). At the first stage of electron-ion-plasma treatment thin (0.5–1 µm) Ti and Ti–Cu coatings were produced by plasma-assisted vacuum-arc deposition with the use of the QUINTA automated facility [9]. Commercially pure VT1-0 titanium and Ti–Cu (12 at. %) sintered powder [10] were used as materials for the evaporable cathode. The gas-metal plasma, which promoted the synthesis of coatings, was generated with the use of a DI-100 vacuum arc evaporator and the PINK plasma source with a hybrid (filament and hollow) cathode [11, 12].

The conditions for preliminary cleaning of the substrates with argon ions were chosen to minimize the aluminum surface heating and etching. The ion current density at the substrate was ≤1.5 mA/cm² and the temperature during the ion bombardment was not above 75°C. The coating deposition modes were optimized so that the coating growth rate would be high but the maximum sizes of the macroparticles present in the plasma flow would be not greater than the thickness of the coating.

The metal coatings were produced in argon used as the working gas medium with the working gas pressure p ~ 0.1 Pa and the evaporator arc current I_d = 60–100 A. The substrates were at a floating potential (U_b ≈ 15 V). Under these conditions, the coating growth rate was 1.5–2 µm/h. The temperature of the aluminum substrates at the stage of coating deposition was not over 150°C.

After deposition of a titanium-containing coating on an aluminum substrate, the coating/substrate system was irradiated with an electron beam in the SOLO automated electron-beam facility [13]. The irradiation parameters were the following: pulse repetition rate f = 0.3 Hz, electron beam energy density E_s = 10–20 J/cm², pulse duration τ = 50–200 µs, and number of pulses N = 3–50.

Examination of the modified samples was carried out using optical microscopy (µVizo-MET-221 metallographic microvisor), scanning electron microscopy combined with x-ray spectral analysis (Philips SEM-515 scanning electron microscope equipped with an EDAX Genesis XM 260 SEM microanalyzer), x-ray diffraction analysis (Shimadzu XRD 6000 x-ray diffractometer), micro- and nanoindentation (PMT-3 microhardness tester and NHT-S-AX-000X Nano Hardness Tester), and tribological examinations (THT-S-AX0000 PC-Operated High Temperature Tribometer).

3. Results and discussion

3.1. The Ti /A7 coating/substrate system

Experimentally it has been found that the coating/substrate system was not melted at W = E_s·N/τ ≤ 1·10^6 W/cm² per pulse (E_s – electron beam energy density; N – number of pulses; τ – pulse duration).

In this case, the coating survived, but pronounced cracking was observed, resulting in fragmentation of the coating (Figure 1 a, b). The material separating the coating fragments was aluminum. When W was in the range (1–5)·10^6 W/cm² per pulse, an island-type structure was observed to form (the coating islands were separated by regions where cellular crystallization of the coating/substrate system had occurred) (Figure 1 c, d). At greater values of W, the coating/substrate system was inconvertibly melted (Figure 1 e–h).

The structurally non-uniform surface layer contained, conventionally speaking, three types of regions different in substructure: (i) polycrystalline regions with the grain size ranging between 1.0 and 1.5 µm (Figure 1 h) in which the concentration of aluminum and titanium was 95 and 5 wt. %, respectively; (ii) regions of preferentially rounded shape in the bulk of which crystallization cells 150–700 nm in size were observed (Figure 1 g) and the concentration of aluminum and titanium was 90 and 10 wt. %, respectively, and (iii) irregularly shaped regions formed as a result of cellular crystallization which contained numerous micropores whose size ranged from 0.2 to 1.8 µm (Figure 1 h); according to x-ray spectral analysis data, the concentration of aluminum and titanium in these regions was 80 and 20 wt. %, respectively.
Figure 1. Surface structure of the Ti/A7 coating/substrate system treated with an intense pulsed electron beam under the following conditions: $E_s = 10 \text{ J/cm}^2$, $N = 5$, $\tau = 50 \mu\text{s}$ (a, b); $E_s = 15 \text{ J/cm}^2$, $N = 3$, $\tau = 50 \mu\text{s}$ (c, d), and $E_s = 15 \text{ J/cm}^2$, $N = 30$, $\tau = 50 \mu\text{s}$ (e–h).

X-ray diffraction analysis has revealed that the surface layer of thickness $\sim 10 \mu\text{m}$ in the Ti/A7 coating/substrate system is multiphase and its composition depends both on the system elemental composition and on the mode of electron-beam treatment. The following phases have been detected: aluminum-based solid solutions, titanium-based solid solutions, and titanium aluminide $\text{Al}_3\text{Ti}$, whose volume fraction was a maximum ($\sim 20\%$) when the irradiation parameters were $E_s = 10 \text{ J/cm}^2$, $\tau = 50 \mu\text{s}$, $N = 10$ pulses, and $f = 0.3 \text{ Hz}$.

The formation of surface alloys is accompanied by a manifold increase in hardness and wear resistance of commercially pure aluminum. The maximum increase in hardness has been attained for the electron-beam treatment modes with $E_s = 15 \text{ J/cm}^2$, $\tau = 50 \mu\text{s}$, $N = 3$ and 30 pulses (Figures 2).

Figure 2. Microhardness depth distribution for the Ti/A7 coating/substrate system after electron-beam treatment: $E_s = 15 \text{ J/cm}^2$, $\tau = 50 \mu\text{s}$, $N = 3$ (curve 1) and $N = 30$ (curve 2).

After three irradiation pulses, the maximum hardness, which was greater than the hardness of the original aluminum A7 by a factor of 40, was achieved at the irradiated surface. The hardness of the
coating/substrate system exposed to 30 pulses increased in going from the surface and, at a depth of about 10 µm, it became three times greater than the hardness of the original aluminum A7 (Figure 2).

In wear resistance tests, the best result (increase in wear resistance of the original aluminum by a factor of about 7.5) has been attained for the treatment mode with $E_s = 15$ J/cm$^2$, $\tau = 50$ µs, $N = 10$ pulses, and $f = 0.3$ Hz. In this case, the friction coefficient decreased by a factor of 1.4.

3.2. The Ti–Cu/A7 coating/substrate system

The Ti–Cu/A7 coating/substrate system, like the Ti/A7 coating/substrate system, was not melted at $W \leq 1 \cdot 10^6$ W/cm$^2$ per pulse. When $W$ was in the range $(1-6) \cdot 10^6$ W/cm$^2$ per pulse, an island-type structure was observed to form (Figure 3 a, b). At $W = 15 \cdot 10^6$ W/cm$^2$ per pulse, the coating/substrate system was inconvertibly melted (Figure 3 c, d). The surface layer became polycrystalline with the grain size ranging from 5 to 40 µm (Figure 3 d). The structure formed in the grain bulk as a result of cellular crystallization consisted of cells whose size ranged from 0.4 to 2.0 µm (inset in Figure 3 d).

X-ray spectral analysis has detected Al–Ti–Cu surface alloys with the element concentration strongly depending on the electron-beam irradiation parameters and ranging over wide limits (from 52 to 2.5 wt. %) (Figure 4). Thus, irradiation of the coating/substrate system with an electron beam makes it possible to vary the elemental and, hence, the phase composition of the surface layer of the material over wide limits.

X-ray diffraction analysis performed in Bragg–Brentano geometry has revealed a multiphase structure of the surface layer (~10 µm) whose qualitative and quantitative composition depended on the mode of electron-beam treatment. It has been found that the total volume fraction of the second phases (Al$_3$Ti, Ti$_3$Al, and Ti$_3$Cu) was a maximum (~40%) for the irradiation mode with $E_s = 15$ J/cm$^2$, $\tau = 100$ µs, $N = 20$ pulses, $f = 0.3$ Hz in which a surface alloy of composition 79Al–16Ti–5Cu (wt. %) was formed (Figure 4).
Figure 4. Concentration of aluminum (curve 1), titanium (curve 2) and copper (curve 3) in the surface layer of the Ti–Cu/A7 coating/substrate system versus irradiation parameters.

Figure 5. Hardness of the surface alloys versus load: $E_s = 15 \text{ J/cm}^2$; the pulse duration and the number of pulses are specified in the respective figures.

Modification of the phase and elemental composition and of the defect substructure of the aluminum surface layer should affect the physicomechanical and tribological properties of the material. To qualify the surface alloy, the hardness, Young modulus, and wear resistance of the coating/substrate system have been examined before and after exposure to an electron beam. The results of analyses on the surface layer hardness are given in Figures 5.

It can clearly be seen that the maximum hardness (5–6 GPa) and the maximum Young modulus (200–250 GPa) are achieved at the exposed surface. Taking into account that the Young modulus of aluminum oxide $\text{Al}_2\text{O}_3$ ranges between 200 and 400 GPa and the Young modulus of aluminum is not above 70 GPa, it can be said that a thin oxide film was formed on the system surface at the stage of cooling. For the indenter loads ranging between 20 and 70 mN, a sublayer of hardness ~2 GPa (~7 times that of the original material) and Young modulus ~110 GPa (~1.8 times that of the original material) was detected. As the indenter load was further increased, both the hardness and the Young modulus decreased, approaching the characteristics of the original material. It should however be
noted that in the coating/substrate system exposed to an electron beam with $E_s = 15 \text{ J/cm}^2$, $f = 0.3 \text{ Hz}$, $\tau = 50 \mu\text{s}$, and $N = 20$ pulses, an extended layer was formed whose hardness was more than three times and the Young modulus was 1.5 times greater than the respective values for the original aluminum.

The improvement of the strength properties of the surface layer was accompanied by an increase in wear resistance by a factor of ~1.2, which was found for the coating/substrate system exposed to an electron beam with $E_s = 15 \text{ J/cm}^2$, $f = 0.3 \text{ Hz}$, $\tau = 100 \mu\text{s}$, and $N = 20$ pulses.

4. Conclusion
For the Ti/A7 and Ti–Cu/A7 coating/substrate systems irradiated with an intense electron beam, multiphase alloys have been produced on the surface of the commercially pure aluminum. The concentrations of alloying elements in these alloys ranged up to 50 wt. %. Structural examinations have shown that the improvement of the physicomechanical characteristics of the aluminum was due to the multiphase submicrostructure and nanostructure state resulting from melting and fast crystallization of the coating/substrate systems.

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References
[1] Koval N et al 2012 Russian Physics Journal 54 1024
[2] Rotshtein V et al 2011 Technical Physics Letters 37 226
[3] Иванов Ю Ф и др. 2013 Известия ВУЗов. Физика. 56 98
[4] Ласковнев А.П. и др. 2013 Модификация структуры и свойств эвтектического силумина электронно-ионно-плазменной обработкой.(Беларусь, Минск: Белорусская наука)
[5] Koval N and Ivanov Yu 2008 Russian Physics Journal 51 505
[6] Глезер А М и др. 2012 Наноматериалы: структура, свойства, применение (Россия, Новокузнецк: Интер-Кузбасс)
[7] Rotshtein V et al 2006 Charter 6 in Book Materials surface processing by directed energy techniques (USA, New York: Elsevier)
[8] Иванов Ю.Ф. и др. 2011 Усталостная долговечность стали мартенситного класса, модифицированной высокоинтенсивными электронными пучками (Россия, Новокузнецк: Интер-Кузбасс)
[9] Shugurov V et al 2012 Izv. Vyssh. Ucheb. Zaved. Fizika 118
[10] Gurskikh A et al 2006 Izv. Vyssh. Ucheb. Zaved. Fizika. Supplement №8 400
[11] Koval N et al 2012 Proceedings of the 25th International Symposium on Discharges and Electrical Insulation in Vacuum (Russia, Tomsk) 2 537
[12] Vintizenko L et al 2001 Russian Physics Journal 44 927
[13] Koval N et al 2009 IEEE Trans. Plasma Sci. 37 1890