COMPOSITE CERAMIC-GRAPHITE SURFACE LAYER CREATED BY DUPLEX METHOD AT ALUMINIUM ALLOYS SURFACE

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Abstract:

In the paper authors propose the new method of creation the composite surface layer at the aluminium alloy substrate. The surface layer was obtained using the duplex technology – electrochemical oxidation of the surface alloy EN-AW-5251 and carburization of oxide layers, as the thermo-chemical treatment. Composite layers were examined using transmission electron microscope JEM 2010 ARP, spectrometer PHI 5700/660 and scanning microscope Philips XL30 with EDS attachment. During result analysis also the layer thickness and microhardness of the composite layers were measured. The new proposed method enables the creation of unique surface layers that characterize the higher carbon content and higher microhardness level. As the final effect the improvement of tribological properties was stated.

Key words: composite surface layer, aluminium carburization, tribological properties

1. INTRODUCTION

Among a number of materials applied in modern technologies, aluminium alloys are more and more frequently used due to their very good strength properties, low densities and low production costs. In recent years, research has been largely focused on enhancing strength properties of upper layers of materials, manifesting by the fabrication of composite coatings, with simultaneously preserving the original properties of the base material. Electrolytic anodizing of aluminium alloys leads to producing an oxide layer on their surface, which layer is characterized with a microhardness significantly higher than the input material [1,2]. The presence of an oxide layer on the surface of an aluminium alloy enables its use in sliding couples of kinematic parts of machines, owing to good adhesion to the substrate and high abrasion resistance. The properties of oxide layers may change within a wide spectrum and they depend mainly on the conditions of fabrication [3-7]. Owing to its characteristic porous structure, a hard oxide layer may serve as an appropriate material in the fabrication of composite surface layers [8-10]. Where the reinforcement phase of the oxide layer is a material with excellent lubricating properties, a newly formed layer will have good lubricating properties as well, and the material may be used for sliding couples in dry friction conditions [11]. The surface layer for sliding couples should ensure good adhesion to the substrate, proper hardness and durability, and good tribological properties. Therefore, an assumption has been made that it is reasonable to modify the oxide layer by incorporating graphite into its matrix, as the structure of graphite shows high resistance to pressure and low shear strength. So far, the modification of the anodic oxide layer has been performed using various techniques, from the electrolytic method to ion implantation or thermal spraying [8-10, 12, 13]. The authors of the paper studied the possibility of fabricating ceramic-graphite surface layers on aluminium alloys by the duplex technology consisting in the application of two surface engineering technologies. The aluminium oxide layers obtained using the electrochemical method by means of hard anodizing of aluminium alloys were subjected to carbonization through thermochemical treatment in a solid medium consisting of graphite dust.
2. THE OBJECT OF THE STUDY

The oxide layers were fabricated by means of the direct-current electrolytic method, using a stabilized feeder, GPR-25H30D, through hard anodizing, on 5x10^{-4} m^2 samples made of aluminium alloy EN-AW-5251. The cathode consisted of a lead electrode with the same surface area as the aluminium alloy samples. Before anodizing, the surfaces of the samples were purified in a 5% KOH solution and a 10% HNO_3 solution. The electrolyte used to produce the oxide layers was a water solution of sulphuric, phthalic and oxalic acids at 303 K. The use of carboxylic acids in the electrolyte composition enables anodization at a room temperature and causes adsorption of carbon from the electrolyte to the oxide layer, where carbon is used as a diffusion activator in the subsequent thermochemical treatment. The anodization was performed at a constant current density of 3 A/dm^2 for 1 h. Such conditions are the most optimal for the fabrication of oxide layers destined for a tribological interaction [14]. After anodizing, the oxide layers were rinsed for 1 h in distilled water in order to rinse out the electrolyte from the aluminium oxide pores. Carbonization of the oxide layers was conducted in a solid medium consisting of graphite dust of 99% purity and a grain size below 1 \( \mu \)m. The selection of the carbonizing medium was made with taking into account the degree of purity and a specific structure of the crystalline lattice of graphite, which accounts for its excellent lubrication properties. The depth of the carbonized layer depends primarily on the time and temperature of carbonization. In practice, however, it is more frequent to manipulate the time rather than temperature, since a change of the latter has a significant impact on the carbon concentration at the surface, which may lead to an unfavourable distribution of graphite. The carbonizing process is conducted below the substrate metal recrystallization temperature, which for the aluminium alloy amounts to 403 K. The oxide layers were placed in ceramic boxes and sprinkled with graphite powder. Next, the boxes were closed tightly and soaked in an electric furnace at 343-403 K for 24-48 h. During thermochemical treatment, the graphite dust reacts with the oxide contained in the box between the powder grains, forming carbon monoxide and dioxide. Depending on the content of CO and CO_2, the mixture undergoes a reaction to achieve a state of equilibrium. Carbon dioxide formed disturbs the balance of the CO-CO_2 mixture, causing carbon absorption from the environment and formation of CO, until the equilibrium between the oxides is reestablished. Since other CO molecules release atomic carbon at the same time, the reaction proceeds in two directions simultaneously, with absorption of carbon from the environment and its release on the surfaces of the carbonized layers.

3. EXPERIMENTAL

The composite layers obtained by means of the duplex technology were subjected to microstructure examination using an electron transmission microscope JEM 2010 ARP JEOL with the accelerating voltage of 200 kV and a high resolution of 0.194 nm. The microscope equipped with an EDS microanalyzer enabled a chemical analysis of the precipitates visible on microscopic images. The investigations were performed on cross-sections of samples prepared by the "cross" method. The identification of the chemical elements and a quantitative analysis of the chemical composition of the composite layers were performed with a PHI 5700/660 spectrometer by the XPS method and using the technique of X-ray induced photoelectrons. For ion etching, Ar^+ ions of 4 keV were used. The examination was conducted to the depth of 8 \( \mu \)m from the surface of the layers, taking measurements after each 10 min sputtering cycle. The analyses of chemical compositions were also made using a scanning microscope Philips XL30 with an EDS attachment. The thicknesses of the composite layers were measured with a Dualscope thickness gauge by means of the eddy current method. Microhardness was determined from cross-sections of the layers impressed with a Hanemann's microhardness tester in 3 zones under the load of 0.3 N. The analyses of the microhardness were performed based on the photographs of the indentations taken with a digital camera of the Neophot 2 microscope at the magnification of 1000x. For each indentation, the microhardness and the distance of the indentation centre from the substrate of the layer were calculated. Afterwards, the trend lines were determined for the dependence of microhardness on the measuring point.
4. RESULTS AND ANALYSES

The results of examination of the microstructure of surface layers showed a columnar-fibrous structure oriented along the direction of its growth (Fig. 1). Individual adjacent fibres create columnar bundles propagating from the substrate to the outer part of the layer, forming characteristic pores on its surface.

![Fig. 1. Initial microstructure of a non-carbonized surface layer; a – morphology of Al₂O₃ surface, b - columnar-fibrous layer structure](image)

Fig. 2. Microstructure of a composite layer carbonized for 36 h at 383 K with carbon precipitates; a – the cross section, b – lengthwise section.

![Fig. 2. Microstructure of a composite layer carbonized for 36 h at 383 K with carbon precipitates; a – the cross section, b – lengthwise section.](image)

Fig. 3. Atomic element concentration of the composite layer carbonized before sputtering for 36 h at 383 K
Carbon precipitates, settled between the oxide layer fibres, are visible in the carbonized layers (Fig. 2). These precipitates have a relatively weak connection with the matrix, as an envelope with numerous discontinuities forms around each carbon precipitate. They have micrometric dimensions, occur in groups and are composed of small grouped nanometric particles making agglomerates. Carbon and aluminium compounds were also identified in the carbonized layers as well as precipitations of intermetallic compounds of aluminium with elements acting as alloying additions for the EN-AW-5251 alloy. XPS detection of the chemical composition of the composite layer surface carbonized for 36 h at 383 K, before sputtering (Fig. 3), revealed the presence of 26.07% of carbon, 0.66% of nitrogen, 52.92% of oxygen and 20.36% of aluminium. A detailed analysis of spectra after the first sputtering cycles performed for the composite layer (Fig. 4), has shown the presence of carbon in 4 chemical states. The main line of spectrum C1 s occurred at f 285.2 eV, which corresponds to a single C-H type carbon bonds and is associated with the adsorption of carboxylic acids from the electrolyte. After 10 min of sputtering, a line with a bond energy of 284.6 eV, characteristic of C-C bonds, emerged. This line can be associated with the carbon adsorbed in the process of thermochemical treatment. A carbon-oxygen bond occurs for this line at 289.2 eV, as well. After another 10 min of sputtering, a line of bond energy of 282 eV emerged. This bond energy can be attributed to the compounds of carbon with metals present in the layer substrate. A detailed analysis of the spectra in the last sputtering cycles demonstrated only the presence of carbon with the C-A1 bond.

**Fig. 4.** Detailed analysis of spectra of the composite layer carbonized for 36 h at 383 K hafter the first sputtering cycle

The examination of chemical composition carried out with an EDS spectrometer on cross-sections of the layers revealed a varied carbon content, depending on the conditions of thermochemical treatment (Figs. 5, 6). The carbon content in the composite layers is twice higher than the carbon content in the non-carbonized layer. The layer after thermochemical treatment at 403 K had the highest content of carbon. EDS examinations at the cross-sections of the layers also showed that the carbon content in a layer depends on the distance from the substrate of the layer. The examination of thickness consisted of 10 measurements taken on the length of a layer before and after thermochemical treatment. The measured values were averaged afterwards. The maximum difference in thickness resulting from a comparison of the results before and after thermochemical treatment amounted to 0.4 µm. The differences in the thickness of the layers after anodizing conducted in identical conditions for all the samples result from slight roughness of the substrate and from the presence of alloy precipitates which affect the rate of the oxide layer formation.
Fig. 5. The influence of temperature of thermochemical treatment on the carbon content in the cross-section of surface layers carbonized for a constant time of 36 h.

Fig. 6. The influence of duration of thermochemical treatment on the carbon content in the cross-section of surface layers carbonized at a constant temperature of 383 K.

Fig. 7. Dependence of the microhardness of a carbonized layer (36 h) on the temperature (1 - 343, 2 - 363, 3 - 383, 4 - 403K) and time (383K; 1 - 24, 2 - 36, 3 - 48h) of thermochemical treatment, determined at the cross-sections at the distance of 20 µm from the layer substrate.
The examination of microhardness, carried out on cross-sections of the composite layers, showed a linear decrease of its values from the substrate to the surface of the layers. The values calculated for the distance of 20 µm from the layer substrate ranged from 4000 to 5350 MPa. The investigation has shown that the layers carbonized by the duplex method have microhardness higher by 20% than the non-carbonized layers. The highest microhardness was obtained by the layers carbonized for 36 h at 403 K and for 48 h at 383 K. The dependence of the microhardness of the layer on temperature of the thermochemical treatment (Fig. 7), shows that the higher the temperature, the higher the microhardness. A similar dependence is observed when analyzing the influence of time of thermochemical treatment on the layers microhardness. In this case, the slope of the curve is higher than in the case of the microhardness/carbonization temperature dependence, which implies that an extended time of thermochemical treatment has a greater impact on the layer microhardness than an increase of temperature.

5. CONCLUSIONS

Carbonization of aluminium oxide layers formed on a substrate of the EN-AW-5251 alloy allows obtaining ceramic-graphite surface layers. The layers obtained by the duplex method are characterized by an increased content of carbon compounds. The carbon content in the carbonized layers is the highest at the surface (26%) and decreases to 2% along the cross-section of the layer. The process of thermochemical treatment does not significantly influence the thickness of the composite layers, although it leads to microhardness increase. Through manipulating the parameters of thermochemical treatment (time, temperature), it is possible to exert impact, within certain limits, on both the microhardness of the layers and the amount of graphite incorporated into the composite layer.

LITERATURE


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