Formation of transition gradient layers in the process of creating a surface composite "steel-coating (Al, Al-N)" at VIP treatment

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Abstract. The regularities of the formation of gradient layers in the process of applying coatings on steel by the vacuum ion-plasma method when the ratios of the elements of the gas flow of a metallic plasma are studied. It was shown that the interaction of Al-based plasma flows with the sample surface produces single-layer and multi-layer coatings of Al and Al-N systems, in which the processes of direct and inverse diffusion of the coating and substrate elements occur.

1. Introduction

The method of vacuum ion-plasma (VIP) coating deposition allows you to form a wide range of gradient layers on the surface of the processed products. The method is based on a combination of the processes of direct diffusion of plasma flow elements into the substrate and inverse diffusion of the substrate elements into the coating being created. The formation of various gradient layers in the created coatings allows to obtain in practice a large variety of functional coatings used in mechanical engineering. The type of surface composites formed during processing allows you to create a new level of mechanical, optical, electrical, magnetic, thermal and chemical properties of the surface of processed products [1]. The layers formed on the basis of nitride and carbide compounds, have received the wide practical application in mechanical engineering.

Aluminum and its compounds are the most promising materials for creating coatings. Aluminum nitride, which has dielectric properties with a low coefficient of thermal expansion, corresponding to silicon, is a very promising material for the practical implementation of such composite coatings. Composites based on aluminum nitride are used as protective and impact resistant coatings with dielectric properties for electronic equipment elements [2]. Compounds based on aluminum nitride possess high chemical resistance in biological active media, which makes it possible to use them as a coating on traditional materials for implantation – titanium alloys, stainless steel, cobalt-chromium alloys, etc. [3]. Aluminum nitride can also be used as a cryo-stable coating resistant to shock loads. The quality of the composite formed on the products depends on the efficiency of the impact of the gas-metal plasma flows on the surface being processed and the subsequent interaction with it [4, 5]. As a rule, the presence of a diffusion zone at the metal – coating interface and its depth are a criterion for assessing the adhesive strength of the composite being created. Therefore, the present work was...
devoted to the study of the processes occurring at the metal-coating interface, depending on the ratio of the components of the flow of gas-metallic plasma and substrate elements during the formation of single-layer and multilayer coatings of Al and Al-N.

2. Method and methodology of the work

Experimental surface composites based on Me-Al, Me-Al-N systems were formed by vacuum ion-plasma deposition (VIP). Aluminum-based coatings were deposited on the surface of the product by deposition from a plasma stream created by an arc discharge from the surface of a cathode of aluminum alloy D16. Deposition was carried out on the VIP-installation "RAINBOW", developed at JSC "NIAT". Coating modes, differing in composition and pressure of the working gas in the installation chamber, are presented in table 1.

| Type of coverage | I, A | U, V | Pressure, Pa | Plasma gas | τ, min |
|-----------------|------|------|--------------|------------|--------|
| Mono-layer Al coating | 100 | 50 | 0,13 | Ar | 10 |
| Mono-layer AlN coating | 100 | 50 | 0,4 | N | 10 |
| Multi-layer Al-AlN-Al coating | 100 | 50 | 0,13 – 0,4 – 0,13 | Ar – N – Ar | 10 – 10 – 10 |
| Multi-layer AlN-Al-AlN coating | 100 | 50 | 0,4 – 0,13 – 0,4 | N – Ar – N | 10 – 10 – 10 |

Carbon structural steel (C-0.8%) was used as a substrate. The process of applying a gas-metal plasma coating on the treated surface was carried out with preliminary electron heating of the sample surface (up to 320 °C), its cleaning by ion etching, followed by deposition of plasma flow elements. Cleaning and activation of the treated surface was carried out by bombarding of the treated surface with argon plasma for 5 minutes. The surface heating temperature of the processed products in the vacuum chamber was controlled by an IP 140 digital infrared pyrometer.

The processes occurring in the deposited coating and on the substrate were investigated by the method of quantitative layer-by-layer analysis performed on a GDS850A LECO atomic emission spectrometer. The principle of operation of the spectrometer is based on the cathode sputtering of the sample followed by the excitation of sample atoms in a glow discharge plasma in a Grimm lamp in an argon atmosphere with controlled parameters of voltage, current and pressure.

Microhardness and hardness (HV) was measured on a Micromet 5101 microhardness meter according to GOST R ISO 6507-1-2007 in the load range from 0.1 to 5 N.

3. The results and discussions

Plasma flows generated by an arc discharge interact with the treated surface. As a result of interaction with the plasma, the substrate is heated, components are deposited on it from the plasma and processes of mutual diffusion of the coating elements and the substrate proceed. In this case, gradient layers are formed in the coating and in the substrate. A quantitative depth profile analysis of the coatings obtained showed that when plasma flows interact with the surface to be treated, a surface layer is formed consisting of the coating, the transitional diffusion zone and the base metal zone. A distinctive feature of the formed zones is the presence of gradients of the elemental composition. The thickness of the formed zones, the gradients of the composition of the substrate and coating depend on the energy and composition of the plasma.

The deposition of aluminum coating elements in argon plasma is accompanied by the primary adsorption of plasma flow elements with subsequent diffusion into the treated surface layer of the matrix. In this case, the formation of two diffusion processes is observed: direct diffusion of the coating elements into the substrate and inverse diffusion of the substrate elements into the coating. The
concentration of deposited elements on the surface of the coating determines the width of the diffusion zone: the greater the concentration of deposited elements on the surface, the greater the width of the diffusion layer, (figure 1). The process of back diffusion of the substrate elements into the coating is more complex and, apparently, depends both on the solubility of the substrate elements in the coating being created and on the structural state of the boundary layer.

The replacement of plasma gas from argon to nitrogen during the formation of an aluminum coating changes the conditions of the formation of gradient layers. The presence of nitrogen in the process of deposition of aluminum plasma flow to the substrate increases the intensity of surface diffusion of plasma flow elements into the substrate due to the formation of interstitial phases that change the character of concentration curves of gradient layers. At the same time, the appearance of copper in the formed coating was noted.

![Figure 1](image_url)

**Figure 1.** Results of the quantitative layer-by-layer analysis of single-layer aluminum coatings on a steel substrate, depending on the composition of the working gas in the chamber volume: (a) – working gas – Ar; (b) – N.

Tables 2 and 3 show the data of average values of the concentrations of the main elements of the coating deposited on the substrate. Coating zones characterized by a low ratio of copper to aluminum concentration (0.016–0.017) were deposited in a nitrogen atmosphere. Zones with a high ratio of copper to aluminum (0.020–0.027) correspond to the process of coating in argon. These ratios well characterize the process of VIP coating. It is known that the presence of nitrogen in the chamber significantly reduces the concentration of electrons and helps reduce the temperature on the surface of the sprayed sample. This, in turn, leads to a decrease in the deposition of copper from the plasma, whose concentration in the sputtered target of D16 alloy is 3.8–4.9%.

The low ratio of copper and aluminum concentrations in the first sample (figure 2(a)) 0.017 at a depth of 2.6–3.3 μm is explained by the initial stage of the deposition process, which is characterized by a low temperature on the substrate surface, which leads to a decrease in copper deposition on the surface. At the same time, at a depth of 0.1–1.1 μm, where the spraying process reached its final stage and most of the nitrogen was removed from the chamber, the ratio of copper to aluminum concentrations is 0.027 and speaks of almost complete precipitation (∼2.36%) of copper from the composition of the D16 alloy cathode.

The presence of nitrogen in the flow of aluminum plasma leads to a change in the nature of diffusion processes along the metal-coating interface, while the depth of the aluminum diffusion zone in the substrate remains almost unchanged. The process of back diffusion of the substrate elements into the coating increases the diffusion zone.

The intensity of mutual diffusion of the elements of the substrate being processed and the elements
of the plasma flow depends not only on their physicochemical interactions, but also on the concentration of the deposited coating. The deposition intensity can be determined from the quantitative change in the mass of the deposited plasma flow elements, Figure 2. The constancy of the parameters of the arc current and the parameters of the accelerating voltage implies the creation of identical conditions for the formation of the density of the plasma flow. Changes in the gas medium and pressure in the vacuum chamber, as well as the formation of functional layers: “a” Al – AlN – Al and “b” AlN - Al – AlN, influenced the composition of the surface layer formed.

![Figure 2](image)

**Figure 2.** Formation of diffusion zones in the processes of deposition of multilayer coatings on a steel substrate, depending on the pattern of formation of functional layers: (a) – Al – AlN – Al; (b) – AlN – Al – AlN.

| Table 2. The average values of the concentrations of the elements of the Al-AlN-Al coating. |
| The depth of the layer, microns | C\text{Al, avg.}, wt.% | C\text{N, avg.}, wt.% | C\text{Cu, avg.}, wt.% | C\text{Cu, avg} / C\text{Al, avg.} |
|----------------------------------|----------------------|----------------------|----------------------|----------------------|
| 0.1-1.1                          | 86.65                | 6.60                 | 2.36                 | 0.027                |
| 1.1-2.6                          | 69.43                | 22.05                | 1.09                 | 0.016                |
| 2.6-3.3                          | 70.09                | 6.86                 | 1.21                 | 0.017                |

Where is C\text{Cu, avg} / C\text{Al, avg} – the ratio of the average concentrations of copper and aluminum within the layer.

| Table 3. The average values of the concentrations of the elements of the AlN-Al-AlN coating. |
| The depth of the layer, microns | C\text{Al, avg.}, wt.% | C\text{N, avg.}, wt.% | C\text{Cu, avg.}, wt.% | C\text{Cu, avg} / C\text{Al, avg.} |
|----------------------------------|----------------------|----------------------|----------------------|----------------------|
| 0.1-1.6                          | 72.33                | 24.31                | 1.24                 | 0.017                |
| 1.6-3.5                          | 87.83                | 8.50                 | 1.78                 | 0.020                |
| 3.5-5.5                          | 58.22                | 18.77                | 0.95                 | 0.016                |

Despite the fact that nitrogen is practically insoluble in solid aluminum, increasing the temperature during the formation of AlN coatings leads to the diffusion of nitrogen to a certain depth, forming a layer of mutual diffusion of these elements in the coating. Thus, the diffusion of nitrogen from the AlN layer (scheme “a”) goes to the entire depth of the zone of pure Al and has a thickness of about 1 μm (figure 2(a)). Direct diffusion of nitrogen into the substrate is not observed, i.e. in this case, the zone of pure Al acts as a barrier, which is also observed in figure 2(b). With the formation of AlN compounds in the coating on the graphs of layer-by-layer analysis, this is expressed in relatively horizontal
sections. The flow of plasma-chemical reactions on the surface of the steel leads to the interaction of plasma flow elements with the treated surface with the formation of AlN compounds with a surface hardness of more than 8000 MPa (when the load on the indenter is 0.49 N), figure 3.

![Micro hardness of Al-AlN-Al and AlN-Al-AlN multilayer coating](image)

**Figure 3.** Change of micro hardness of Al – AlN – Al and AlN – Al – AlN multilayer coating.

**4. Conclusions**

It was shown that the interaction of Al-based plasma flows with the sample surface produces single-layer and multi-layer coatings of Al and Al-N systems, in which the processes of direct and inverse diffusion of the coating and substrate elements occur. It was found that changes in pressure and chemical composition of working media (nitrogen or argon) practically do not affect the change in the concentration of deposited aluminum when applying multilayer coatings of the Al-AlN-Al and AlN-Al-AlN systems. Thus, the effect of plasma flows on the treated surface when changing the concentrations of the deposited plasma flow elements and the chemical composition of the treated surface ensures the formation of a coating and diffusion zones that affect the formation of functional and operational properties of products.

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