

Effects of Doping of Composite Ti–TiC Coatings with Transition and Valve Metals on Their Structure and Mechanical Properties

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Abstract—This study presents the results of an examination of the mechanical properties and structure of wear-resistant composite Ti–TiC-based coatings, which were formed on commercially pure titanium by electric-arc processing in an aqueous electrolyte, with transition and valve metals (Al, Ni, Cr, and Si) introduced into their composition. This study demonstrated that the change in mechanical properties can be attributed to the formation of the martensitic phase at the titanium–TiC interface, which is induced by hardening phenomena associated with electric-arc processing.

Keywords: titanium alloys, titanium carbide, composite materials, electric-arc processing

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INTRODUCTION

Features such as high specific strength and corrosion resistance, non-magnetization, and low density have ensured that titanium alloys are widely used in aeronautical engineering, shipbuilding, aerospace engineering, and other industries [1, 2].

One of the specific features of titanium alloys is their high surface reactivity, which translates, on the one hand, into low frictional seizure load and high values of the friction coefficient and the wear rate [3–6] and, on the other hand, into high oxygen affinity and the consequent formation of a thin oxide film that prevents the adhesion of common lubricants [3, 7–9]. These natural features of titanium hinder the use of titanium-based alloys in the manufacture of parts to be used under friction load [1, 2].

At least three approaches can be distinguished in studies focused on reducing the friction coefficient and enhancing the antifriction properties of titanium and its alloys: (1) the search for efficient lubricants for titanium alloys [8–10]; (2) the adjustment of the alloy composition by doping with various metals [11, 12]; and (3) the treatment of titanium alloy surfaces with the synthesis of protective coatings. The third approach is currently of great interest. Methods involving plasma processing [18–20], which are efficient and relatively simple, hold a special place among the techniques for surface treatment of titanium alloys [13–17].

The method of the electric-arc processing of titanium surface with an employment of a graphite anode in an aqueous electrolyte [21] is one of those that belong to the aforementioned group of plasma techniques. The surface layer of a titanium alloy subjected to such treatment is a composite material based on the Ti–TiC binary system: finely dispersed particles of titanium carbide arranged chaotically in the titanium matrix enhance the antifriction properties of the surface and its resistance to oxidation [22].

Ternary carbide or nitride systems (MAX phases such as Ti₂AlC, Ti₃AlC₂, Ti₃SiC₂, etc. [23, 24]) have attracted much attention in recent years. The Ti₃SiC₂ phase offers high ductility, which is uncharacteristic of common carbides, and fine wear resistance [25, 26]. The introduction of elements such as Cr, Si, and Al into coatings based on amorphous carbon leads to a reduction in the fraction of diamond-like *sp*³ bonds and an increase in the fraction of graphite-like *sp*² bonds, relieving internal stresses [27]. Therefore, the layer of a Ti–TiC-based carbide system modified by these elements should become somewhat more ductile, and its hardness should decrease. However, an increase in hardness and wear resistance of alloys based on titanium carbide was noted in [28, 29] after chromium was introduced into the binder material. It is clear that the introduction of another component into the Ti–TiC binary system affects its properties. It

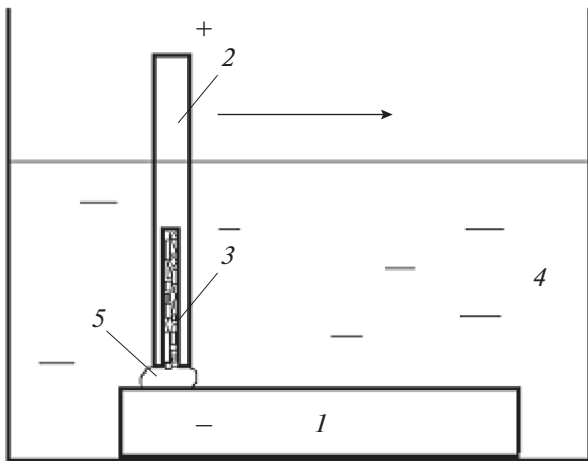


Fig. 1. Schematic diagram of electric-arc processing. Titanium sample 1, graphite electrode 2, metallic insert 3, electrolyte 4, and arc 5 are indicated.

is of interest in this context to modify this system with transition and valve metals (Al, Ni, Cr, and Si).

EXPERIMENTAL

A channel with $d = 3$ mm to be filled with a metallic insert (wire, foil, or metal granules) was drilled in cylindrical graphite electrodes ($d = 6$ mm) along their axis. We used the obtained composite graphite–metal anodes for electric-arc processing of VT1-0 titanium alloy samples $150 \times 20 \times 3$ mm in size (cathodes) in an aqueous 0.1–0.2% NaCl solution. The movable anode formed carbide tracks on the surface of samples. Figure 1 presents a schematic diagram of this process: graphite electrode 2 with metallic insert 3 was moved relative to stationary titanium sample 1 in a vessel filled with electrolyte 4. We performed electric-arc processing at an initial current strength of 70–90 A in accordance with the polarity indicated in Fig. 1; the direction of movement of the electrode is marked with an arrow. A TiG 200AC/DC welder was used as a source of electric current.

We then used selected titanium samples to prepare polished specimens for the examination of the composition and the structure of composite layers and work out specimens for static tension tests (type XIIIa, GOST 6996-66 [30]) with the carbide track-strip located in the middle (Fig. 2). The width of the track-strip was 5.0–5.5 mm, and the cross-section area of the neck of these specimens was $S_{cs} = 38$ mm². Each composite electrode was used to process a series of three specimens with subsequent calculation of the arithmetic mean of surface microhardness HV and breaking stress σ_u .

We conducted X-ray phase analysis using a Bruker D8 ADVANCE diffractometer in Cu $K\alpha$ radiation. The surface microhardness was determined by the Vickers method using a PMT-3M microhardness tester under a load of 50 g. We studied the strength properties of titanium alloys with a carbide-containing layer in tension tests. We performed these static tension tests at a rate of 0.5 mm/min using a Shimadzu Autograph AG-X plus 50 kN testing machine.

Selective etching of polished specimens prepared for microstructure studies was performed in concentrated nitric acid (chemically pure) for 72 h to completely remove the TiC phase. We examined surface microstructure using a high-resolution Hitachi S5500 scanning electron microscope with a Thermo Scientific EDS attachment.

RESULTS AND DISCUSSION

Figure 3 presents the X-ray patterns of titanium samples subjected to electric-arc processing with an unmodified graphite anode. We can identify the following phases: titanium, rutile, and titanium carbide (Fig. 3a). The thin rutile layer was removed in the process of subsequent polishing, and only titanium and titanium carbide remained (Fig. 3b).

When anodes containing various elements were used, we found oxidized forms of the corresponding element (alongside the primary Ti, TiO₂, and TiC phases) on the treated surface; we observed in certain cases the formation of intermetallics based on tita-

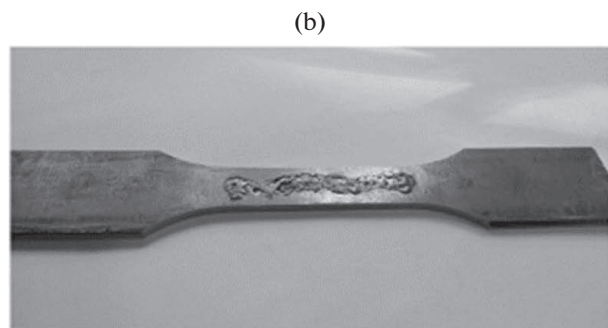
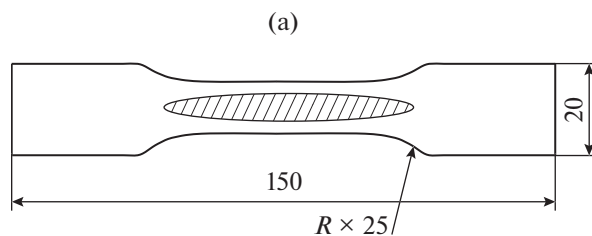


Fig. 2. (a) Schematic diagram of specimens for static tension tests and (b) photographic image of such a specimen.

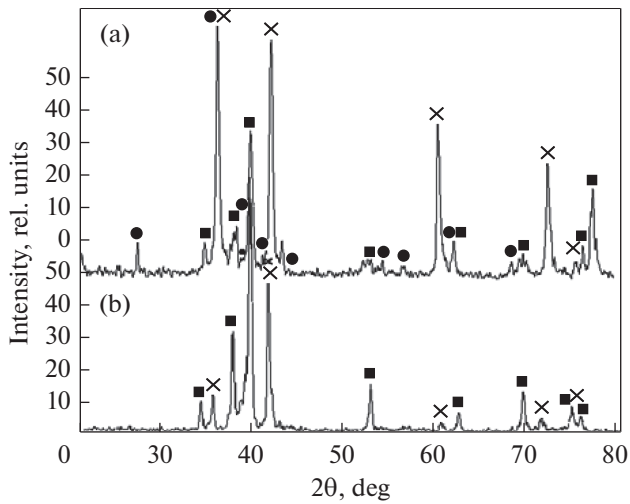


Fig. 3. X-ray patterns of titanium specimens processed with a graphite anode: (a) before polishing and (b) after polishing (● TiO_2 (rutile), ■ Ti, × TiC).

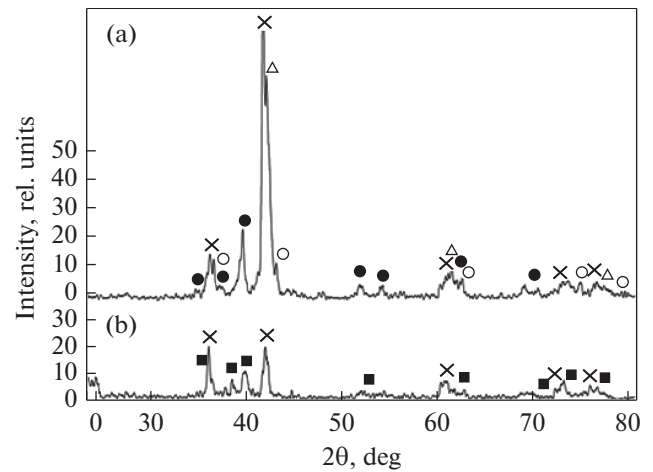


Fig. 4. X-ray patterns of titanium specimens processed with a graphite–Ni anode: (a) before polishing and (b) after polishing (● TiO_2 (rutile), ■ Ti, × TiC, ○ NiO, Δ NiTi).

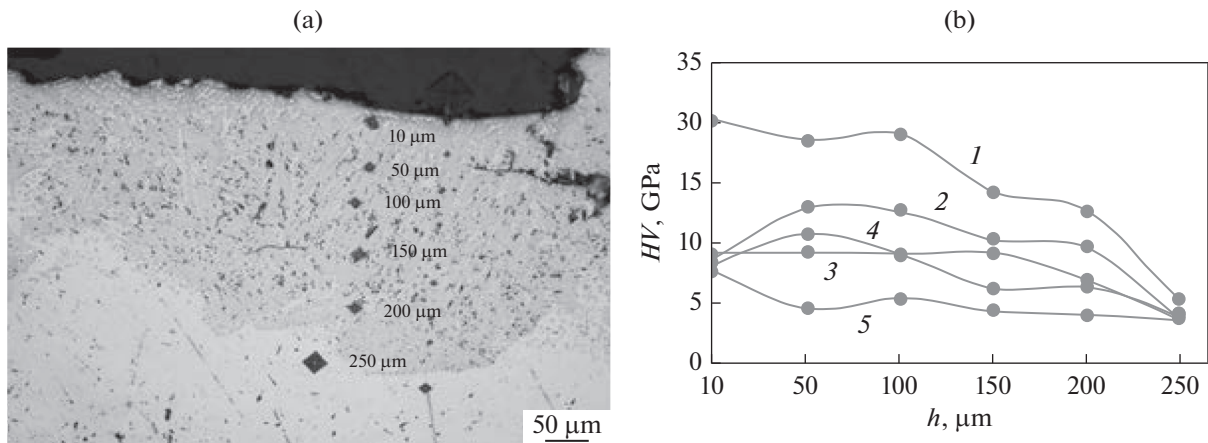


Fig. 5. Variation of microhardness with thickness of the composite coating with different added elements on titanium specimens: initial Ti–TiC coating (1), Cr (2), Ni (3), Al (4), and Si (5).

niium and the metal introduced into the anode (Fig. 4a). However, only the Ti and TiC phases remained after polishing in all cases (Fig. 4b). This is due to the fact that the processing conditions (carbon excess and high temperatures in the local region affected by the discharge) are conducive to the formation of the carbide phase in the bulk of the alloy, while oxides and intermetallics form on the surface as the sample cools down in the aqueous electrolyte after the arc treatment (in the short interval when the optimum conditions for their synthesis are established).

We plotted the curves of microhardness variation with the carbide-layer thickness after polishing based on the results of six measurements in the direction of the indenter motion from the surface to the substrate (Fig. 5a).

It follows from Fig. 5b that the curve of microhardness variation with the thickness of unmodified Ti–TiC coatings reaches a maximum of 13500 MPa and then decreases gradually to the microhardness values

Table 1. Average σ_u values (MPa) of titanium specimens with composite coatings synthesized with the addition of various metals

Metal in the Ti–TiC coating	Average σ_u values
Specimens with an unmodified carbide coating	358
Carbide coating with Cr	367
Carbide coating with Ni	360
Carbide coating with Al	348
Carbide coating with Si	352

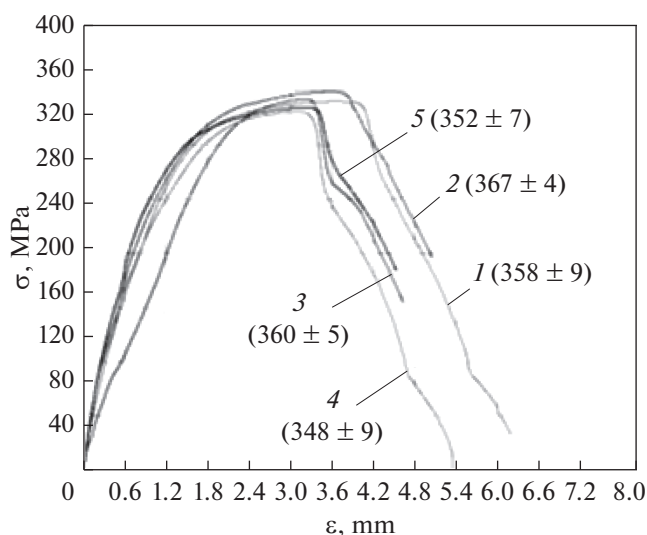


Fig. 6. Stress–elongation curves obtained in tension tests of specimens with composite coatings with different added elements: initial Ti–TiC coating (1), Cr (2), Ni (3), Al (4), and Si (5).

of the titanium substrate. The average microhardness values decrease considerably after the introduction of Ni, Al, and Si into the composite layer; in contrast, the introduction of chromium causes a significant enhancement of microhardness. The results of tension tests for specimens with Ti–TiC coatings with various added elements are presented in Fig. 6. The average values of σ_b and the maximum deviations from them for each series of specimens are indicated in brackets.

The trend observed in microhardness variations is also evident in the measurements of σ_u : when nickel, aluminum, or silicon are introduced into the composition of the Ti–TiC layer, both the average σ_u values of specimens and their elongation ϵ decrease, which indicates embrittlement. In contrast, if chromium is added to the composition, the ductility remains the same (judging by the elongation of specimens in tests (see curve 2 in Fig. 6)), while the average σ_u value increases somewhat relative to the initial one.

Therefore the highest values of microhardness and σ_u correspond to specimens with chromium-containing coatings. This may be attributed to the fact that chromium is a eutectoid-forming β stabilizer for titanium and reinforces the titanium matrix. Al- and Si-containing coatings have the lowest HV and σ_u values, which is likely related to the formation of intermetallics based on titanium and metastable martensitic phases, which emerge under rapid cooling in dilute titanium alloys and have an adverse effect on their mechanical properties [31], during processing. Al- and Si-containing specimens are also characterized by the smallest elongation, which agrees with the data from [32], where we noted the adverse effect of intermetallics based on these elements on the ductility of titanium alloys.

Figures 7–9 present the results of our examination of the microstructure of specimens after selective etching in nitric acid. Titanium-carbide particles are completely dissolved in the process of etching, while the titanium matrix is passivated in the HNO_3 solution and remains intact [33].

A porous microstructure (Fig. 7) forms after etching of the surface of the titanium alloy treated with unmodified graphite anodes. This microstructure allows us to determine the shapes and sizes and the distribution of the initial titanium-carbide particles. It is clear from the comparison of the results of X-ray phase analysis and SEM studies that a composite coating (TiC particles in the titanium matrix) forms under the indicated processing conditions in the titanium–graphite system.

If nickel-containing electrodes are used, needle-shaped grains of the martensitic phase occupying the sites of etched-out TiC dendrites are clearly visible (Fig. 8). The small size and the nonuniform distribution of these needles over the surface made it impossible to identify them in X-ray phase analysis. Since intermetallics based on Ni and Ti ($TiNi$, Ti_2Ni , $TiNi_3$, etc.), which form together with carbides, are, just as the TiC phase, freely soluble in nitric acid, these needle-shaped structures should be a titanium-based phase. This is confirmed by the results of energy-dis-

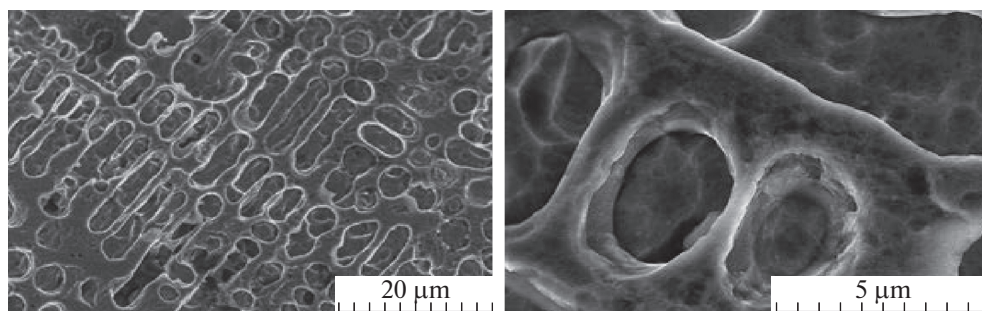


Fig. 7. Surface microstructure of the titanium alloy, which was processed using a graphite anode, after etching.

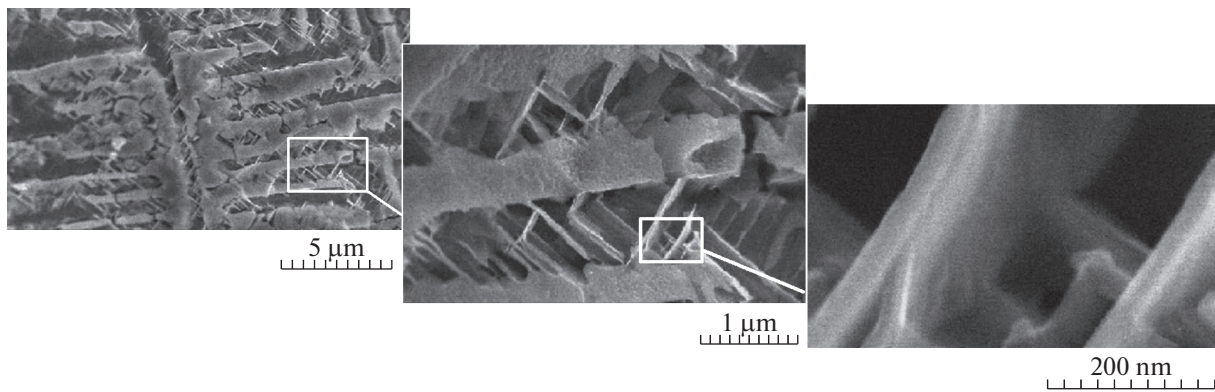


Fig. 8. Surface microstructure of the titanium alloy, which was processed using a graphite–Ni anode, after etching.

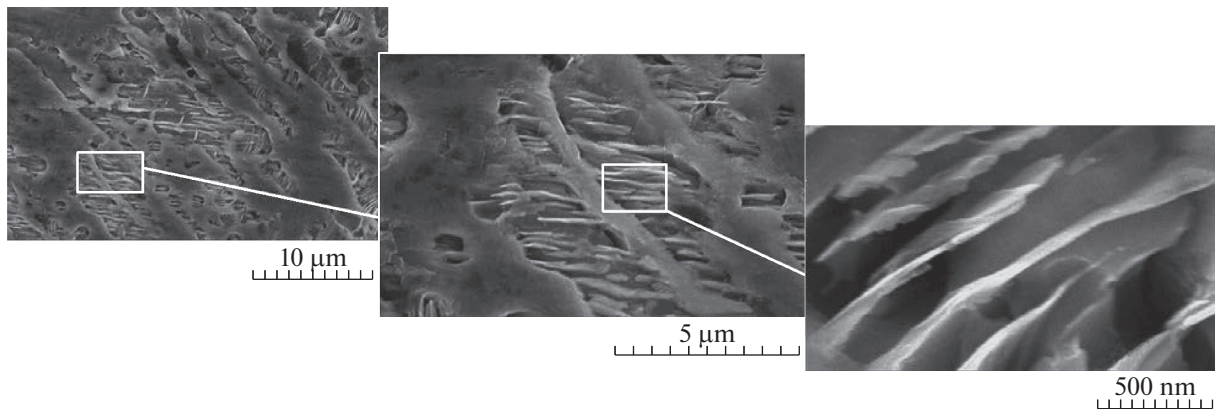


Fig. 9. Surface microstructure of the titanium alloy, which was processed using a graphite–Al anode, after etching.

persive analysis: 70–100 at % Ti are found in the elemental composition of needles.

As the processing conditions enable hardening, we can assume that needle-shaped structures are the metastable titanium α' -, α'' -, or ω -phase.

Similar needle-shaped structures form in specimens processed using Al- and Si-containing anodes (Fig. 9). The X-ray phase analysis did not reveal any new phases on the surface of these specimens after etching. Titanium-based needle-shaped grains form within etched-out TiC dendrites (i.e., at the TiC–titanium interface), thus naturally reducing the interfacial strength of carbide particles and the matrix and, consequently, negatively affecting the mechanical properties of the surface layer and the structure as a whole.

We already know that the processes of formation of the crystal structure are impeded by the rapid cooling of metal alloys [34, 35]. Microcrystalline or compositionally uniform metastable amorphous structures may form as a result. Many-component systems are more prone to forming an amorphous structure in metals [36]. This is the likely reason for the fact that needle-shaped structures were not found in the titanium–graphite two-component system but were

observed in three-component systems with various elements. We should note that although the mechanical properties of the formed surface deteriorate, this may help enhance the surface area in plasma synthesis of titanium-based porous materials [37, 38].

CONCLUSIONS

It is clear from the data that the introduction of Al, Si, Ni, or Cr in the process of formation of Ti–TiC-based composite coatings on titanium alloys alters the mechanical properties of these coatings.

These changes are induced, among other things, by the presence of particles of a martensitic structure in the coating. The formation of these needle-shaped titanium-based grains at the TiC–titanium matrix interface is induced by hardening phenomena associated with electric-arc processing. The coating microhardness and the breaking stress of specimens are somewhat reduced after processing with Al-, Si-, or Ni-containing anodes. If chromium-containing anodes are used, the values of these parameters increase, which may be due to the reinforcement of the titanium matrix because of the partial dissolution of chromium in it.

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