Effect of Surface Modification of a Titanium Alloy by Copper Ions on the Structure and Properties of the Substrate-Coating Composition

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Received: 28 October 2020; Accepted: 24 November 2020; Published: 27 November 2020

Abstract: To improve the strength properties, adhesion, and the thermal cycling resistance of ceramic coatings, the titanium alloy surface was modified with copper ions under different processing times. It is found that at the maximum processing time, the thickness of the alloyed layer reaches 12 µm. It is shown that the modified layer has a multiphase structure in addition to the main α and β-titanium phases with the intermetallic compounds of the Ti-Cu system. The parameters of the fine structure of the material are investigated by the X-ray diffraction analysis. It has been found that when the surface of the titanium alloy is modified, depletion occurs in the main alloying elements, such as aluminum and vanadium, the crystal lattice parameter increases, the root-mean-square (rms) displacements of the atoms decrease, and the macrostresses of compression arise. A multilevel micro- and nanoporous nanocrystalline structure occurs, which leads to an increase in the adhesion and the thermal cyclic resistance of the ceramic coating based on Si-Al-N.

Keywords: phase composition; structure; surface modification; elemental distribution; ionic treatment; X-ray structural analysis; electron microscopy; multiscale structure

1. Introduction

The VT23 alloy is related to the Ti-Al-V-Mo-Cr-Fe system. This is a medium-alloyed (α + β) martensitic-class alloy, which gets the martensitic "α" structure after hardening from the β-region. This alloy has high ductility, which is an important property for technological applications such as drawing, flanging, and other pressure treatment operations [1].

This property of the titanium alloy allows using it as the basis for deposition of heat-shielding coatings such as Zr-Y-O, Si-Al-N [2–6]. However, in order to improve the thermocyclic resistance and the adhesion properties of the coating, it is necessary to prepare the titanium alloy for coating using different ion-beam technology [7–13].

It is known that across the substrate surface adjacent to the coating, there is a sharp jump in the change in the structural phase state and the physical and mechanical properties of the "heat-protective coating—substrate" system. In this interface region, there appears the maximum localization of the elastic stress. In addition, the state of the substrate surface can significantly affect the formation of the structure and the properties of the coating itself [14,15].

To prepare the surface for deposition of a coating, the surface hardening of metals and alloys is widely used by increasing the density of dislocations in a layer up to 10 microns in depth (a long-range effect [16]) or due to the formation of nanocrystalline intermetallic phases [17]. In the latter case,
the element pairs of the “ion beam—processed metal” are selected from those systems in which the formation of intermetallicides is possible. Thus, in [17], the ionic synthesis of the intermetallic phases based on the Ni-Ti, Ni-Al, Fe-Al, and TiAl systems was discovered. However, the ionic synthesis in these systems is poorly understood.

One of the effective methods of preparing a substrate for the deposition of coatings is the modification of their surface layer with high-energy beams of metal ions. In this case, treatment with ion beams can change the morphology, phase, and the elemental composition of the surface layer [18].

Therefore, an urgent task is to study the effect of the phase composition, the structural state of the surface layer of a titanium substrate on the structure, and the properties of the coating formed on it, as well as on the thermomechanical characteristics of the whole “coating—substrate” system. This article focuses on the study of the surface modification of the VT23 titanium alloy, which was carried out to improve the thermal cycling resistance and the adhesion strength of the Si-Al-N-based coating.

2. Materials and Methods

Samples were treated under a continuous titanium ion beam with accelerating voltage (1200 V ± 20 V) and ion current (about 15 mA) using the vacuum system KVANT-03MI (Techimplant Ltd., Tomsk, Russia), and the vacuum arc ion source with a copper cathode [19]. The samples were placed in the camera on the object table in front of the ion source for ion bombardment. The temperature of the samples during the ion bombardment was 900 ± 10 K. After the ion beam treatment of the substrate, a Si-Al-N coating was deposited using a magnetron sputtering technique. Parameters of treatment of the titanium alloy by copper ions Technological parameters of processing are shown in Table 1.

| Samples         | Bias, V | Treatment Time, min | Fluence, Ion/cm² |
|-----------------|---------|---------------------|-----------------|
| Initial Ti alloy| -       | -                   | -               |
| Treated Ti      | -900    | 3                   | 0.9 × 10¹⁸      |
| Treated Ti      | -900    | 6                   | 1.8 × 10¹⁸      |
| Treated Ti      | -900    | 7.5                 | 2.3 × 10¹⁸      |

The structural phase state of the ion-modified layers of the samples was investigated by the Transmission Electron Microscope TEM method using a JEOL-2100 device (Jeol Ltd., Tokyo, Japan). Foils for the TEM studies were prepared by the cross-section method using an Ion Slicer EM-09100IS (Jeol Ltd., Tokyo, Japan). To classify the structures, the grain size, and the phase composition, the bright-field images together with the corresponding microdiffraction patterns and the dark-field images were used. The phase composition, the crystalline lattice parameters, the root-mean-square atomic displacement (rms), the macrostresses of the surface layer were determined by X-ray using the DRON-7 device St. (UED-Lab, Petersburg, Russia) [20,21]. X-ray investigation of the modified titanium alloy was carried out under continuous 2θ-scanning with the Bragg–Brentano focusing at Co Kα radiation. The data base JCPDS and PDF-2 (International Centre for Diffraction Data, Campus Blvd, PA, USA) was used for interpretation of the diffractograms.

The symmetric and the asymmetric Bragg–Brentano schemes of X-ray investigation were used. The X-ray diffraction (XRD) registration in an asymmetric mode was carried out at grazing angles of X-ray radiation incidence \( \alpha = 3^\circ \). The chemical composition and the element distribution in the titanium surface were determined by the energy dispersive X-ray (EDS) analysis using a microanalyzer INCA-Energy (Oxford Instruments) with the built-in TEM JEOL-2100 and scanning electron microscopy (SEM) LEO EVO-50XVP. The thermal cycling procedure was carried out by heating the samples to 1000 °K in air, followed by holding the sample at this temperature for 1 min and cooling to room temperature.
The VT23 titanium alloy was selected as the material for the study. It contains elements such as Fe, Cr, Mo, V, Al, as shown in Table 2.

Table 2. The chemical composition of the VT23 alloy (weight %).

|   | Fe    | Cr    | Mo    | V     | Ti    | Al    |
|---|-------|-------|-------|-------|-------|-------|
|   | 0.4–0.8 | 0.8–1.4 | 1.5–2.5 | 4–5  | 84–89.3 | 4–6.3 |

3. Results and Discussion

The VT23 alloy modified with copper ions at different processing times is investigated by X-ray diffraction analysis. Figure 1 shows the diffraction patterns of the titanium alloy modified with copper ions treated for different times (3, 6, and 7.5 min) and the diffraction pattern of the initial titanium alloy VT23. It is seen that the X-ray diffraction patterns of the initial titanium alloy contain the lines of α and β-phases of titanium, which are characteristic of the quenched VT23 alloy. In the composition of the titanium alloy treated with copper ions, in addition to the main phases of α and β-titanium, there are intermetallic phases of the equilibrium state diagram of Ti-Cu [22].

![Figure 1](image-url)  
**Figure 1.** Fragments of the X-ray diffraction patterns of the VT23 alloy in the initial state (1) and upon treatment with copper ions at different processing times (the processing time is indicated on the X-ray diffraction pattern).

It can be seen in the diffraction patterns obtained using the asymmetric X-ray investigation. Figure 1 shows that in the modified layer with a processing time of 7.5 min under the asymmetric X-ray investigation, the intensity of the (111) line of the CuTi$_3$ phase exceeds the intensity of the main peak of the α-phase by several times. This means that the surface layer 1 µm deep mainly consists of the CuTi$_3$ intermetallic compound.
It is interesting to note that at the same processing time, the peak is more extended than all the others. The broadening of the peak can be due to several reasons. First, it is the presence of other phases. At this temperature, in accordance with the phase diagram, the existence of other intermetallic phases, such as Cu_4Ti, Cu_2Ti, is possible, which were subsequently discovered by TEM. Their peaks are close in reflection angles and may overlap. The second reason is a significant grain refinement during more intense bombardment, which we also discovered by the TEM. Concentration inhomogeneity leads to broadening of peaks, since we are dealing with a nonequilibrium process, and the last reason is the creation of higher internal stresses due to defect formation, relaxation and annealing of defects, and accumulation and segregation of impurities. All these reasons can lead to significant peak broadening at maximum processing time.

The crystalline lattice parameter of the α-titanium can be estimated from the average angles of 2θ for the maxima corresponding to this phase (Table 3). The table shows the values of the crystalline lattice parameters of the α-titanium and the c/a ratio for all the investigated alloys.

Table 3. The crystalline lattice parameters, the compressing macrostresses σ //, the rms displacements of atoms $\sqrt{\langle u^2 \rangle}$ for direction <002> of the surface layer at different treatment durations of the titanium alloy with copper ions.

| The Structure Parameters | Initial VT23 | Treatment Time 3 min | Treatment Time 6 min | Treatment Time 7.5 min |
|--------------------------|-------------|----------------------|----------------------|------------------------|
| a, nm                    | 0.2893      | 0.2904               | 0.2899               | 0.2918                 |
| c, nm                    | 0.4731      | 0.4705               | 0.4726               | 0.4687                 |
| c/a                      | 1.63        | 1.62                 | 1.63                 | 1.61                   |
| $\sqrt{\langle u^2 \rangle}$, nm | 0.031 | 0.023 | 0.016 | 0.010 |
| σ //, GPa                | -           | -1.6                 | -3.0                 | -                      |

One can see that the crystalline lattice parameter in the modified titanium is higher than in the VT23 alloy in the initial state. The c/a ratio for this alloy is also higher than for the tabular values of α-titanium (c/a = 1.58). This fact indicates the deformation of the crystal lattice of the titanium alloy during standard heat treatment. The fact that the crystalline lattice parameter of the titanium alloy increases with the ion treatment time suggests that the main dopants, such as aluminum and vanadium, leave the surface layer. At the same time, the rms displacements of the atoms in the modified layer decrease uniformly with increasing ion treatment.

It is shown that the rms displacements of the atoms depend, to a large extent, on the concentration of the alloying elements. As a rule, a decrease in the concentration of the doping atoms in a solid solution leads to a decrease in the rms atomic displacements, which, most likely, is observed in this case with an increase in the duration of the ion treatment. For copper-based solid solutions, it was found that the atomic displacements decrease with a decrease in the concentration of the solid solution [23]. Our assumption has been confirmed by the pattern of the distribution of the elements across the depth of the modified layer.

Figure 2g–i shows that the content of all substitutional elements, such as Al, V, Cr, Mo, first decreases from its initial concentration (table of the composition of the VT23 alloy) in the modified layer, and then gradually reaches its original composition.

The depth of the layer depleted in the alloying elements correlates with the thickness of the modified layer in the first case. With a processing time of 3 min, it is about 150 nm, and then, down to a depth of 540 nm, the content of the alloying elements gradually returns to the previous level (Figure 2g). When the time of the ion treatment is 6 min, the depletion in the alloying elements reaches a depth of about 1 µm and the initial composition, with the thickness of the ion-modified layer being 3.5 µm (Figure 2h). At the maximum processing time, the thickness of the depleted layer is about 1.5 µm and down to 7 µm, with the content of the alloying elements gradually restoring to the initial concentration (Figure 2i). Compressive macrostresses arise in the treated surface, whose magnitudes increase with
an increase in the treatment duration of the titanium alloy by an ion beam (Table 3). A similar effect was observed in the work [24], where the authors believe that the stress distribution over the sample depth is such that the alloyed layer is strongly compressed across the surface. The following processes contribute to the formation of a stressed layer (region) upon surface modification: defect formation, relaxation and annealing of defects, accumulation and segregation of impurities, diffusion (thermal and radiation-stimulated), and sputtering.

Figure 2. Surface morphology of the treated titanium alloy: 3 min (a), 6 min (b), 7.5 min (c). TEM images of the cross-section of the titanium alloy modified with copper ions with different processing times (d-f) and the distribution of the elements in depth: the processing time is 3 min, (g) 6 min, (h) 7.5 min (i).

Figure 2b,c shows the surface morphology of the titanium alloy treated with copper ions at different processing times. It can be seen that even at a processing time of 3 min, the surface is etched, but the martensite plates are still visible. Upon further processing for 6 min, the structural elements become smaller, the martensitic structure disappears. However, at a processing time of 7.5 min, a structure with a more developed surface takes place; voids are visible between the formations, which should be filled with the material of the deposited coating. In this case, the adhesive properties of the coating are significantly improved, as shown in [25–27].

TEM studies (Figure 3) have confirmed the results of the X-ray phase analysis. It has been established that depending on the processing time, the intermetallic phases of the Cu-Ti equilibrium phase diagram appear in the modified layer. Figure 3a–c shows the cross section of the titanium alloy modified with copper ions for 3 min. One can see that in the upper modified layer, in addition to the main α-Ti phase, there are intermetallic phases of Cu$_3$Ti, Cu$_4$Ti$_3$, and CuTi. The intermetallic phases are identified at a depth of no more than 300 nm (Table 4). The maximum copper content up to 30% is at a depth of 50 nm. Further, in the modified layer, only α-Ti is identified. The depth distribution of the elements shows (Figure 2g) that copper penetrates down to a depth of 600 nm and its amount is not more than 5 at.%. Apparently, it is in solid solution.
Figure 3. TEM images of the cross-section of the titanium alloy modified with copper ions: during 3 min (a–c), bright-field images, microdiffraction, and indication schemes; during 6 min (d–f), bright-field images and indication schemes; within 7.5 min (g–l). The white arrows show the indicated phases, the black ones—the pores.
Table 4. Phase composition and thickness of Ti modified by Cu ions.

| Ion Treatment | Thickness, nm | Phases | Ion Treatment | Thickness, nm | Phases | Ion Treatment | Thickness, nm | Phases |
|---------------|---------------|--------|---------------|---------------|--------|---------------|---------------|--------|
| 3 min         | 0–150         | α-Ti, CuTi | 0–150         | α-Ti, Cu3Ti | Cu4Ti | 0–150         | α-Ti, Cu3Ti | Cu4Ti |
|               | 150–500       | α-Ti    |               | 150–500       | α-Ti   | 150–500       | α-Ti, Cu3Ti | Cu4Ti |
| 6 min         | 0–150         | α-Ti, Cu4Ti, CuTi3 | 0–250         | α-Ti, Cu3Ti | Cu4Ti | 0–150         | α-Ti, Cu3Ti | Cu4Ti |
|               | 150–500       | α-Ti    |               | 150–500       | α-Ti   | 150–500       | α-Ti, Cu3Ti | Cu4Ti |
| 7.5 min       | 0–150         | α-Ti, Cu4Ti, CuTi3 | 0–250         | α-Ti, Cu3Ti | Cu4Ti | 0–150         | α-Ti, Cu3Ti | Cu4Ti |
|               | 150–500       | α-Ti    |               | 150–500       | α-Ti   | 150–500       | α-Ti, Cu3Ti | Cu4Ti |

For a sample treated with titanium ions for 6 min, the phase formation was found to take place at a depth of 250 nm (Table 4). We can see such phases as Cu3Ti, Cu4Ti, CuTi3, and then titanium is observed in the initial state. The maximum amount of copper up to 35 at% is observed at a distance of 800 nm from the surface, and then it sharply decreases down to 10 at% and further decreases down to 5 at% at a distance of 6.5 µm (Figure 2h). In the TEM image, the modified layer is visible up to 3.5 µm from the surface (Figure 3b). In a sample modified during 7.5 min, the pattern is significantly different from the previous ones. The intermetallic phases are observed here almost down to a depth of 4.0 µm. The phases such as Cu2Ti, Cu4Ti, CuTi have been identified. Interestingly, the particles of Cu3Ti within the α-titanium plates are observed in the modified layer at a distance of 6.0 µm from the surface. The maximum amount of copper is observed at a depth of about 1.0 µm, but its concentration at this distance from the surface reaches only 25 at%, then the copper concentration is 10–12 at% at a distance of 6.0 µm and down to 12.0 µm the copper concentration remains in the amount of 5 at% (Figure 2i). It is interesting to note that in this sample, the Cu3Ti phase is in the α-Ti base phase layer inside the martensite plates at a distance of 7.5 µm from the surface (Table 4).

Figure 3b,e,h shows the pores indicated by black arrows. If in a sample with a short processing time they are only in the upper layer in a small amount, with longer processing times the pores are located everywhere in large quantities. In the sample with a treatment time of 7.5 min, the pore size becomes significantly larger (marked with black arrows). The intermetallic phases present in the modified layer are shown by white arrows.

After a comprehensive study of the titanium alloy modified with copper ions, a Si-Al-N-based coating was applied by magnetron sputtering. For this, the titanium alloy VT 23 is taken in its original state and modified for 7.5 min. Thermal cycling tests were carried out after deposition of the coating. The resistance of the coatings to cracking and peeling under changing temperature was determined from the results of the thermal cycling of the samples according to the following regime: heating the sample up to 1000 °C for 1 min, then cooling for 1 min to 20 °C. For the criterion of the thermal stability of the coatings, the number of the cycles before the destruction of 30% of the coating area of the sample surface was selected [14,28]. After that, the tests were stopped.

The coating, deposited on the initial surface, looks like one containing rectangular hollow cracks. The maximum number of cycles of this coating until catastrophic failure is not more than 500 as shown in Figure 4b. The coating applied to the treated surface contains rounded cracks, which are immediately filled with titanium oxide (in Figure 4d marked with numbers 1 and 2). The amount of oxygen in the cracks (indicated by the number 1) significantly exceeds its value in the coating (number 2). Using the EDS method it was shown that in (1) the oxygen value is about 60 at% and in the coating (2) its amount does not exceed 20 at%. This contributes to the healing of the cracks and prevents their further propagation, which, in turn leads to a high thermal cycling resistance of the coating. It was this coating that withstood 1500 cycles in our investigation (Figure 4d).
Figure 4. SEM images of coatings on the basis of Si-Al-N: coatings deposited on the initial surface of the titanium alloy: in initial state (a), after 500 cycles (b). Coating applied to titanium alloy treated with copper ions in initial state (c) and after 1500 cycles (d).

4. Conclusions

The titanium alloy modified with copper ions at different processing times has been comprehensively studied at various structural levels by the methods of X-ray diffraction analysis and electron and scanning microscopy.

1. It has been established by SEM that the modification of the titanium alloy by copper ions results in the refinement of the structure and the formation of developed micropores.

2. It has been shown by X-ray that the phase composition of the modified surface depends on the processing time. At short times of ionic treatment, the phases rich in titanium (CuTi$_3$) appear. With an increase in the duration of the treatment up to 7.5 min, the reflections of the CuTi$_3$ phase become more intense than those of the titanium substrate, i.e., almost the entire surface consists of an intermetallic compound. The structure parameters of the modified layer change: the crystalline lattice parameters of the titanium alloy increase, the rms displacements of the atom decrease, the compressive macrostresses occur.

3. It has been shown that the depth of the modified layer depends on the processing time. With a minimum processing time of 3 min, the depth of the modified layer is about 150 nm. With a processing time of 6 min, this it is about 3 µm, with a maximum processing time of 7.5 min, it is 7.5 µm, with the copper ions penetrating much deeper (0.6 µm, 7.5 µm, and 12 µm, respectively).

4. It has been found that the intermetallic compounds of the Cu-Ti system are formed not only in the surface layer of the treated surface, but also at a distance of 7.5 µm from the surface located inside the martensite plates, the so-called second-level phases. In the modified surface, the pores are found everywhere for all processing times. As a result, of the above treatment, the multiscale micro- and nanoporous nanocrystalline structure has been produced.

5. The thermocyclic resistance of the Si-Al-N-based coating increases several times if the coating is applied to the surface of the titanium alloy modified with copper ions, which is directly related to an increase in adhesion.

Author Contributions: Conceptualization, V.S. and M.F.; methodology, M.F.; validation, V.S. and O.P.; investigation, M.K., I.B. and M.F.; resources, V.S.; writing—original draft preparation, O.P.; writing—review and editing, M.F., O.P.; funding acquisition, V.S. All authors have read and agreed to the published version of the manuscript.
**Funding:** This research was supported by Tomsk Polytechnic University Competitiveness Enhancement Program, as well as its part was performed under the government statement of work for ISPMS Project No. III.23.1.1.

**Conflicts of Interest:** The authors declare no conflict of interest.

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