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Effect of Irradiation with Si^+ Ions on Phase Transformations in Ti–Al System during Thermal Annealing

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Abstract: The article deals with the effect of irradiation with Si^+ ions on phase transformations in the Ti–Al system during thermal annealing. An aluminum film with a thickness of 500 nm was deposited on VT1-00 titanium samples by magnetron sputtering, followed by ion implantation. Samples before and after irradiation with Si ions were annealed in a vacuum of 10^{-4} Pa in the temperature range 600–1000 °C. It was established that ion implantation reduces the dissolution of Al in α-Ti with the formation of titanium silicides ($TiSi_2$, Ti_5Si_3) and stabilizes aluminide phases Ti_3Al rich in aluminum. As a result, a composite structure based on titanium silicide/aluminide was obtained on the surface of the sample synthesized by complex treatment: deposition, irradiation with Si^+, and thermal annealing at the near-surface layers. The formation of the phase-structural state of the implanted layers is associated with the displacement of atoms of the crystal lattice, a result that is reflected in an increase in the size of the crystal lattice and a decrease in microdistortion of the lattice. The opposite effect is observed with increasing temperature. This fact is explained by the relaxation of unstable large grains with an excess of internal energies. At the annealing temperature of 900–1000 °C, a significant increase in microhardness was observed due to silicide phases.

Keywords: Ti–Al system; magnetron sputtering; ion implantation; coating; structure

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1. Introduction

Intermetallic compounds of the Ti–Al system have high melting point, low density, high modulus of elasticity, resistance to oxidation and fire, and high specific heat resistance [1]. Intermetallic alloys of the Ti–Al system are distinguished by unique structural properties and are considered very promising for aerospace engineering products. The main disadvantages of these alloys are low plasticity at low temperatures and low fracture toughness, which complicate their technological processing and industrial use [2–4]. Consequently, methods of increasing their ductility while maintaining their strength remain serious problems.

In recent years, composite coatings based on the Ti–Al–Si system, obtained by combined methods, have become attractive for many industrial applications due to their properties, such as low friction coefficient, increased hardness, and heat and oxidation resistance, which significantly increase the service life of the products [5–7]. The combination of ion-plasma and ion-beam technologies opens up new possibilities in the formation of effective composite nanostructured and nanolayer films. The prospects of such technologies are due to the possibility of creating various new surface structures with improved physical and mechanical properties [8]. At the same time, the study of the formation regularities of the structure and properties of composite coatings obtained by combining the methods of magnetron sputtering and ion implantation are important problems. One of the most promising ways of development of modern materials science is the creation of new combined methods of material processing using ion implantation [9–11]. During ion implantation, radiation and thermal and shock-mechanical effects are carried out simultaneously. The structural rearrangement processes occur under conditions far from thermodynamic equilibrium states, and make it possible to obtain surface layers with a unique set of physical and mechanical properties [12–14]. In this light, studying the mechanisms and features of changes in structural-phase states during heating of implanted materials is of great scientific and practical interest. Therefore, in this work, the effect of irradiation with Si^+ ions on phase transformations in the Ti–Al system during thermal annealing was studied.

2. Materials and Methods

A layer of aluminum (99.9999% pure) 500 nm thick was deposited by magnetron sputtering on VT1-00 titanium samples, which were used as a substrate. The substrate temperature during deposition did not exceed 100 °C. The implantation was carried out with Si ions with an energy of 1 MeV and a dose of 10^{17} ions/cm^2. The irradiation energy was selected from the calculation of the average ion path in order to mix the Al film with the Ti substrate to obtain a composite structure on the titanium silicide/aluminide interface. Samples of titanium coated with Al before and after ion implantation were annealed in a vacuum of 10^{-4} Pa in the temperature range of 600–1000 °C for 2 h, followed by cooling in a furnace. The phase composition and crystal structure of the samples were investigated by X-ray diffraction analysis using D8 ADVANCE diffractometer (Bruker AXS, Karlsruhe, Germany) in CuKα radiation using a Grazing Incidence Attachment device [15]. Surface morphology was studied using an atomic force microscope JSPM-5200 (JEOL Ltd., Tokyo, Japan). The microhardness of the surface layers was measured by the Vickers method on PMT-3 (LOMO, St. Petersburg, Russia) device at a load of 50 g.

3. Results and Discussion

The modification of the physical properties of the surface is associated with structural and phase changes in the surface layer of the substrate, the thickness of which is commensurate with the penetration depth of X-rays when recording diffractograms. Taking into account the thickness of the film (df = 500 nm) and the path length of Si^+ to a complete stop in the element (for λTi = 739 nm and for λAlTi = 843 nm according to the SRIM-2006 program data), the study was carried out using a small-angle incidence device (Grazing Incidence Attachment). Preliminarily, the values of x(m) (the maximum thickness of the near-surface layer of the sample, corresponding to 99% of the contribution to the intensity of the diffracted beam) and x(e) (the thickness of the near-surface layer of the sample, corresponding to the e times attenuation of the intensity of the primary beam, contribution to the intensity of the diffracted beam is 63.2%) were calculated [16]. These results are presented in Table 1.

Table 1. Dependence of the penetration depth on the absorption of Cu–Kα radiation in the titanium sample under grazing irradiation of the sample surface (Grazing Incidence Attachment).

Absorber	Cu-Kα Radiation						
Ti	φ, degrees	0.5	1.0	1.5	2.0	2.5	3.0
	x(m), μm	0.44	0.87	1.31	1.74	2.18	2.61
	x(e), μm	0.09	0.19	0.28	0.38	0.47	0.57

The use of the Grazing Incidence Attachment device makes it possible to examine thin-layer coatings with an X-ray beam penetration depth of 0.1–0.5 μm. At a glancing angle of 2°, the intensity of the beam diffracted from layers located deeper than 0.4 μm decreases by more than e times (CuKα radiation, sample—Ti).

Figure 1 shows diffractograms of Ti–Al samples during heat treatment before and after ion implantation. During heat treatment, aluminide phases on the titanium surface are formed sequentially in accordance with the equilibrium state diagram of Ti–Al (Al_3Ti, Al_2Ti, AlTi, and Ti_3Al) as a result of reactions between the Ti substrate and the Al film.

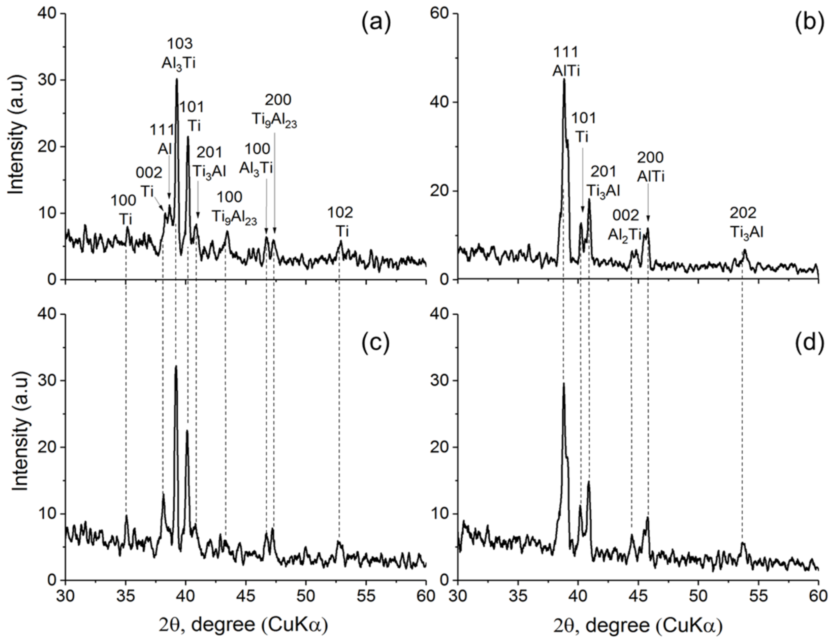

Figure 1. XRD patterns of Ti–Al samples before (**a**,**b**) and after Si^+ implantation (**c**,**d**) after annealing at 600 °C (**a**,**c**) and 700 °C (**b**,**d**).

It can be seen that, upon heating to 600 °C, the reaction of interaction between Ti and Al leads to the formation of Al_3Ti, Ti_9Al_{23}. In the samples implanted with Si^+ ions, annealing at 600 °C leads to the formation of Al_3Ti, Ti_9Al_{23}, and AlTi phases. The formation of AlTi phases only in the implanted samples is explained by the fact that Si^+ ions irradiation of Al-coated titanium samples accelerates the process of Al–Ti interaction.

When the annealing temperature rises to 700 °C, the reaction of interaction between Al and Ti occurs with the formation of Al_2Ti and AlTi phases at the interface between Ti substrate and Al coating. At the same time, after annealing at 700 °C, the phase composition of the Ti–Al samples before and after irradiation is the same.

Formation of the phase-structural state of the implanted layers is associated with the processes atom–atom collisions caused by irradiation of internal deformation, structural changes with the formation of numerous defects, and so forth [17,18]. Tables 2 and 3 show the calculations of the crystallite size and microdistortion of the crystal lattice from the integral width of the diffraction maxima after annealing at 600 °C and 700 °C from the reflections of Al_3Ti (103) and AlTi (111), respectively. According to the results of the analysis, it was found that after annealing at 600 °C in the sample implanted with Si^+ ions, the microdistortion decreases slightly. With decreasing microdistortions, the average effective crystallite size increases, which makes a direct contribution to the increase in the intensity of diffraction lines.

Table 2. Results of X-ray structural analysis after annealing at 600 °C; along the Al_3Ti plane (103).

Sample	Crystallite Size, D (A)		Microdistortion, Δd/d	
	Before Si^+ Implantation	After Si^+ Implantation	Before Si^+ Implantation	After Si^+ Implantation
Al film with the Ti substrate	491	911	0.00283	0.00064

Table 3. Results of X-ray structural analysis after annealing at 700 °C; along the AlTi (111) plane.

Sample	Crystallite Size, D (A)		Microdistortion, Δd/d	
	Before Si^+ Implantation	**After Si^+ Implantation**	**Before Si^+ Implantation**	**After Si^+ Implantation**
Al film with the Ti substrate	498	422	0.00334	0.00289

Thus, from the calculation results, it can be deduced that ion irradiation increases the mobility of lattice atoms and contributes to the decrease in microdistortions. Currently, the thermal stability of implanted systems remains key when introducing this technology to strengthen products operating at high temperatures.

Figure 2 shows XRD patterns of samples after heat treatment at 900 °C. The study of the phase composition of the sample showed that ion implantation reduces the dissolution of Al in α-Ti, forming titanium disilicide $TiSi_2$. The phase formation of titanium silicides in the Ti–Al–Si system was studied in the work [19]. The diffractogram also shows the lines of a solid solution based on the intermetallic compound Ti_3Al. This is explained by the fact that diffusion saturation occurs gradually as the aluminide is saturated with titanium, resulting in the formation of titanium-rich aluminides, such as Ti_3Al. In the presence of silicon, the titanium substrate begins to diffuse with silicon, resulting in the formation of titanium silicides. The formation of titanium silicides is thermodynamically more favorable and the diffusion saturated aluminide phases are stabilized.

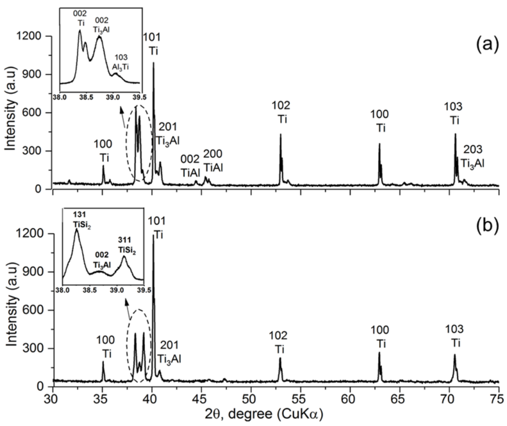

Figure 2. XRD patterns of Ti–Al samples before (**a**) and after Si^+ implantation (**b**) after annealing at 900 °C.

After annealing at 1000 °C, the formation of metastable phases with HCP lattice (Ti_5Si_3, Ti_3Al, Ti) is observed (Figure 3). Diffraction lines of Ti_3Al are stabilized, and the system passes into a more stable state.

Figure 4 shows the atomic force microscopy (AFM) results of the Ti–Al surface during heat treatment at 600–1000 °C before and after ion implantation. Before annealing, the sample surface has a granular structure. After annealing at 600 °C, the surface morphology differs sharply. After irradiation, coarsening of grains is observed; the average size is 0.4–0.5 µm. The observed regularity of grain growth during annealing is traditionally explained by two main reasons: first, the dissolution of dispersed inclusions blocking the boundaries; second, by different amounts of volumetric energy stored in different grains in the form of lattice defects. In this case, the abnormal grain growth cannot be associated with the dissolution of inclusions, since the solubility of silicon in titanium is very low (0.3–0.4%). The role of the second reason can be determined by the calculations of the crystallite sizes and microdistortions given in Tables 2 and 3. It can be assumed that during the implantation process, silicon ions caused the field to displace the atoms of the crystal lattice, a result that is reflected in an increase in crystallite size and a decrease in lattice microdistortions. With increasing temperature, the opposite effect is observed: the surface morphology is covered with grains with an average size of 0.05–0.3 μm. This fact is explained by the relaxation of unstable large grains with an excess of internal energies.

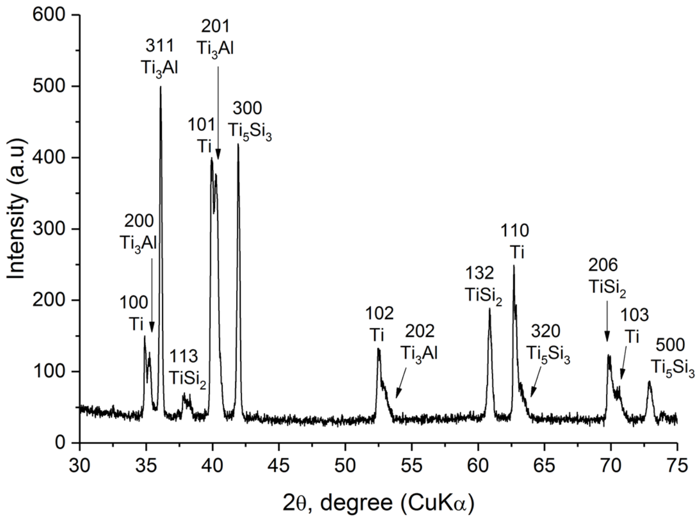

Figure 3. XRD patterns of Ti–Al samples after Si^{+} implantation after annealing at 1000 °C.

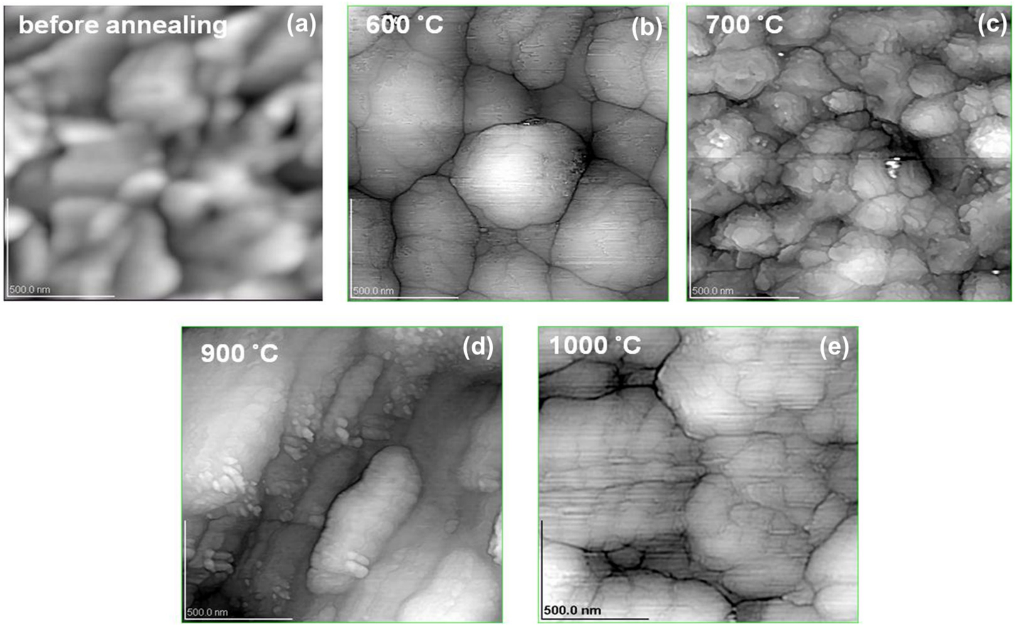

Figure 4. AFM image of the Ti–Al samples after Si^{+} implantation during heat treatment: (**a**) before annealing; (**b**) 600°C; (**c**) 700°C; (**d**) 900°C; (**e**) 1000 °C.

The presented results clearly illustrate the fact that, upon implantation of ions, the grain size changes depending on the annealing temperature. For example, after annealing at 600 °C, the average grain size is 0.52 μm, and after annealing at 700 °C, grains appear with an average size of 0.05 μm. With an increase in the annealing temperature to 900 °C, the microstructure of the sample surface differs sharply. Because of the unification of individual grains, stretched grain shapes are observed in the form of ordered cavities and tops; the average size is 0.84 μm. After annealing at 1000 °C, an accumulation of grains ~0.16 μm in size is observed, in one close-packed system, 0.8 μm in size. With an increase in temperature, coarse grains with elongated shapes in the form of ordered depressions and peaks disintegrate. This fact is explained by the relaxation of unstable large grains with an excess of internal energies. The elongated shape of the texture of the surface layers after annealing at 900 °C is associated with the growth of crystallites along a certain direction.

All structural changes occurring on the surface of the Ti–Al samples after Si^+ implantation are accompanied by significant changes in microhardness, in accordance with Figure 5. With high-temperature annealing, a significant increase in microhardness is observed due to silicide phases. In the works of many researchers, it has already been established that siliconizing significantly increases the hardness and wear resistance of titanium [20].

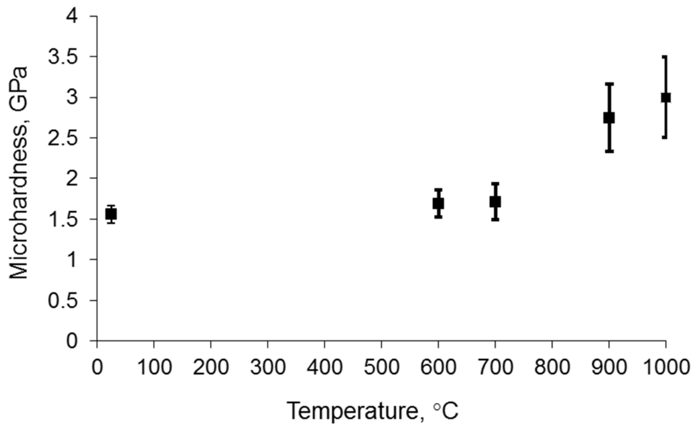

Figure 5. Change in the microhardness of the Ti–Al samples after Si^+ implantation during heat treatment 600–1000 °C.

However, it is very difficult to draw a conclusion based on this. At present, the thermal stability of implanted systems remains key when introducing this technology to strengthen products operating at elevated temperatures. For the successful application of these technologies, it is necessary, first, to find out the temperature regimes of operation of ion-modified products.

4. Conclusions

Ion implantation allows mixing the Al film with Ti substrate. As a result of the synthesis at the interface of the near-surface layers, it was possible to obtain a composite structure of silicide/titanium aluminide. The formation of the phase-structural state of the implanted layers is associated with the displacement of atoms of the crystal lattice, a result that is reflected in an increase in the size of the crystal lattice and a decrease in microdistortion of the lattice. The opposite effect is observed with increasing temperature. This fact is explained by the relaxation of unstable large grains with an excess of internal energies.

Ionic implantation reduces the dissolution of Al in α-Ti with the formation of titanium silicides ($TiSi_2$, Ti_5Si_3) and stabilizes Ti_3Al aluminide phases rich in aluminum. After annealing at 900–1000 °C, metastable phases based on the Ti_3Al and Ti_5Si_3 are formed. All structural changes that occur on the surface after implantation are accompanied by significant changes in microhardness. Significant increase in microhardness is observed due to silicide phases.

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