Formation of the titanium-aluminum intermetallic compounds by ion-beam mixing

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Abstract. The results of studying the X-ray photoelectron spectroscopy of the chemical composition formation of titanium surface layers with a deposited aluminum film after ion-beam mixing are presented. At the selected parameters of ion irradiation, the aluminum films 10 and 20 nm thick are mixed with a titanium substrate. TiAl compounds are formed during mixing.

1. Introduction
Intermetallic phases, in particular, Ni–Al and Ti–Al systems possess unique physical and mechanical characteristics [1]. They retain structure and strength at high temperatures and are superior to conventional materials in terms of their anticorrosion and antifriction characteristics. The formation of intermetallic structures in the nanocrystalline state in the surface layers of metallic materials can be successfully implemented upon the exposure of high intensity beams of metal ions on a surface [2]. In addition, ion mixing, which is based on the incorporation of a required impurity from the surface layers after transfer of the primary-beam kinetic energy to this impurity, is very promising for the fabrication of new structures and compounds with specified characteristics [3].

This work aims to study the chemical composition formation of titanium surface layers with a deposited aluminum film after ion-beam mixing.

2. Samples and research methods
The titanium samples had the form of 10×10 mm plates with a thickness of 2 mm. The thickness of the deposited aluminum films were 10, 20, 30, and 40 nm. The ion-beam mixing of the aluminum films was carried out by bombardment with Ar⁺ ions in the pulse-periodic mode with the duration of the pulses of 1 ms and a repetition rate of 200 Hz, with the energy of ions of 40 keV and irradiation dose of 10¹⁶ ion/cm². The average current density was 40 μA/cm². Irradiation was carried out on an ion-beam installation “Pion-1M”.

Studies of the elemental and chemical composition of the samples were carried out on an X-ray photoelectron spectrometer SPECS using MgKα-radiation (1253.6 eV). The vacuum in the chamber of the spectrometer was less than 10⁻⁶ Pa. The measurement error of the bond energy is ±0.1 eV. The relative measurement error of the concentration of elements is ±3 at %. The layer-by-layer analysis was carried out by etching the surface of the samples with argon ions with an energy of 4 keV and a
current density of 30 μA/cm². The calculated rate of etching was 1–1.2 nm/min. The experimental data were processed using a CasaXPS license program.

3. Results and discussion
Analysis of the X-ray photoelectron (XPE) spectra of Ti2p, as well as the Auger lines and valence bands of TiAl and Ti reference samples, showed that the positions of the maxima of these spectra coincide with an accuracy of up to ±0.1 eV. Therefore, it is impossible to identify compounds of aluminum with titanium from these spectra. However, the comparison of Al2p spectra recorded from the surface of Al and TiAl intermetallic reference samples revealed a difference of 0.4 eV in the position of the maxima shown in figure 1. The bond energy corresponds to 72.8 and 72.4 eV, respectively, in these samples. The shift of the maximum of the Al2p aluminum spectra by 0.4 eV to lower bond energies indicates the formation of a compound of aluminum with titanium [4].

![Figure 1. Experimental X-ray photoelectron Al2p spectra of the samples of Al and TiAl.](image)

The distribution of elements in the surface layers of titanium samples after ion-beam mixing of aluminum with different thicknesses of the deposited film is given in figure 2. On the surface of the samples, there is mainly oxygen in the amount of 40–50 at. % and aluminum in the amount of 30–40 at. %. The XPS spectrum of oxygen O1s indicates that oxygen is in a state corresponding to the chemical compound Al₂O₃, since the oxygen spectrum is practically completely described by the reference oxygen spectrum in Al₂O₃. This is also confirmed by the presence of a peak with a binding energy of 76 eV in the Al2p spectrum (figure 3, a). The second peak with a binding energy of 72.8 eV in the Al2p spectrum corresponds to unbound aluminum [5]. The position of the spectrum from the reference aluminum sample is shown by the solid line in figure 3. After ion-beam mixing of aluminum with a thickness of ~10 nm, starting from the surface (~1 nm) and further, the maximum of the Al2p spectrum shifts to the region with lower binding energies – 72.4–72.6 eV (relative to the binding energy corresponding to Al in an unbound state – 72.8 eV). This is shown in figure 3, a. This indicates the formation of a chemical compound Al-Ti. A similar shift was found in the sample after ion-beam mixing of an Al film ~20 nm thick, but starting from a depth of ~10 nm (figure 3, b).

In a sample with a deposited aluminum film 30 nm thick, after ion-beam mixing, the Al state corresponding to the Ti-Al bond does not appear up to a depth of ~25 nm. This depth corresponds to
the film-substrate interface (figure 4, a). Up to this depth, Al is in an unbound state. The state of aluminum in the sample after ion-beam mixing of an Al film ~40 nm thick similarly manifests itself. At least at a depth of ~30 nm, aluminum is still in an unbound state (figure 4, b).

**Figure 2.** Distribution of elements in the surface layers of samples after ion-beam mixing of aluminium films with a thickness of ~10 a), ~20 b), ~30 c), and ~40 d) nm, respectively.

**Figure 3.** Al2p spectra of titanium samples after ion-beam mixing of aluminum films with a thickness of ~10 nm a), ~20 nm b), respectively.
Figure 4. Al2p spectra of titanium samples after ion-beam mixing of aluminum films with a thickness of \(~30\text{ nm} \ a\), \(~40\text{ nm} \ b\), respectively.

Analysis of the O1s oxygen spectra made it possible to reveal the depth distribution of the Al-O and Ti-O bonds. On the surface and near it (\(~1–5\text{ nm}\)), first of all, the aluminum oxide \(\text{Al}_2\text{O}_3\) is formed [5]. However, in deeper layers, from a depth of \(5–10\text{ nm}\), a bond corresponding to titanium oxide \(\text{TiO}_2\) begins to appear. \(\text{TiO}_2\) bonds become predominant already at a depth of \(25\text{ nm}\). This order of formation of bonds in depth from \(\text{Al}_2\text{O}_3\) to \(\text{TiO}_2\) was also found in the initial samples with a deposited aluminum film (without any mixing).

Figure 5. Model of the chemical composition formation of the titanium surface layers with a deposited layer of aluminum by mixing with argon ions.

Based on the experimental data obtained by X-ray photoelectron spectroscopy, we can assume the following mechanism for the chemical composition formation of the titanium surface layers with a
deposited aluminum layer as a result of mixing with argon ions (figure 5). The surface layer of the deposited film consists mainly of Al₂O₃ with a small amount of pure aluminum. This layer has a strong effect on the energy loss of incident argon ions. The projective range of 40 keV argon ions in Al₂O₃ is ≈ 22 nm, which is significantly less than in pure aluminum (Rp ≈ 36 nm). In this case, a layer 3 nm thick is etched away during the ion irradiation [6]. As a result, the formation of TiAl intermetallics occurs in samples with deposited aluminum films ~10 and ~20 nm thick. The ion energies are insufficient for the formation of TiAl intermetallics in samples with deposited aluminum films ~30 and ~40 nm thick, despite the high concentration of embedded aluminum (up to 20 at.%).

4. Conclusions
At the selected parameters of ion irradiation, aluminum films 10 and 20 nm thick are mixed with a titanium substrate, accompanied by the formation of Ti-Al compounds. However, with an increase in the thickness of the films to 30 and 40 nm, the selected parameters of ion irradiation are insufficient for mixing the films with the substrate. In this work, a mechanism of the chemical composition formation of the titanium surface layers with a deposited layer of aluminum, as a result of ionic mixing by argon ions, is proposed.

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