THE EFFECT OF HEAT TREATMENT ON THE STRUCTURAL-PHASE STATES OF Ti-Al COATINGS SYNTHESIZED BY THE METHOD OF MECHANICAL ALLOYING

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Abstract

This article presents the results of studying the structural-phase state changes of Ti-Al coatings on the surface of titanium synthesized by mechanical alloying. The study of the substrate-coating boundary showed the practical absence of traces of diffusion of the coatings in the titanium substrate after the mechanical alloying process. The mechanism of formation of Ti-Al coatings is due to cold welding and due to deformation compaction of powder particles on the surface of titanium under the impact of ball hits. Stirring of coating components with the formation of diffusion zones at the interfaces is observed after annealing at 600 ºC. Al_3Ti is the first phase that forms in the coatings as a result of the interaction of Ti and Al. The compounds Al_2Ti and TiAl are formed as a result of subsequent reactions between Ti and Al_3Ti. After the process of mechanical alloying, heat treatment should be used as a complex treatment to accelerate the diffusion processes in the coating-substrate system.

Keywords: Coating, mechanical alloying, structural-phase state, intermetallic compound, heat treatment

1. INTRODUCTION

The use of the mechanical alloying method for the production of Ti-Al-based alloys attracted the attention of many researchers. However, considering that mechanical alloying is a complex process, since the number of parameters is very high (time, size of grinding bodies, mass ratio of balls to powder mass, temperature, ambient atmosphere, amplitude and frequency of oscillations), published research results are completely different.

Guo et al. [1] reported that in the powder mixture Ti40Al60, when treated in a planetary ball mill after achieving a high degree of amorphization (after 12 h), a further crystalline phase (27 h) appears on further grinding, which can be conditionally indexed as TiAl with fcc (face-centered cubic) lattice (a = 0.41 ± 0.05). In the next paper [2], where the formation of the metastable fcc phase in the Ti-Al system was studied during the mechanical alloying of pure powders, the fcc phase was attributed to the formation of (Ti, O) N. Oehring et al. [3] published an entirely different phase evolution of Ti-Al in the planetary ball mill called Fritsch pulverisette 5, where phase formation occurs due to the formation of a lamellar microstructure of the words Ti and Al, in which Al diffusion into Ti occurs. The final products of the synthesis in the Ti>60at.% Al system are γ-TiAlfct (face-centered tetragonal) and metastable solid solutions with hcp (hexagonal close-packed) lattice (α_2-Ti_3Al), and in the Ti-70 at.% Al system, metastable solid solutions of fcc lattice (D022-$TiAl_3$). In Bhattacharya's work [4], the solid solution was the only final product of mechanical alloying. And also, Fadeeva et al. [5] showed that the solid solution was the only final product of mechanical alloying and the metastable fcc phase is formed upon annealing of the solid solution Ti (Al).

Thus, when summing up the results of numerous studies of phase evolution in the Ti-Al system during the mechanical alloying process, it can be noted that the formation of the final product depends on the compositional composition of the Ti-Al mixture and the energy yield of the mechanical alloying process. To create chemical bonds of Ti-Al with the formation of new compounds, the leading role is played by diffusion accelerated by super equilibrium vacancies (generated during deformation), matter flows along the nucleus of dislocations and along the grain boundaries. This requires a large energy intensity (i.e., a large amount of energy that the working medium transfers to the processed material during machining), which cannot be achieved with mechanical activators in a short time. Proceeding from this, in this paper we studied the structural-phase transformation in the Ti37Al63 system (in wt.%) during mechanical alloying and subsequent heat treatment.

2. MATERIAL AND RESEARCH METHOD

The application of coatings by the method of mechanical alloying was carried out in the SVU-2 (stand vibration universal) vibrational mechanical activator. A plate made of technical pure titanium (Grade2) measuring 70 x 70 x 3 mm was used as the substrate. Ti powders (99 % pure, 45 μm fractions) and Al (99 % purity, 5 μm fractions) were used for coating. The powder composition in weight percent Ti is 37 % and Al is 63 %.

The parameters of the coating process for mechanical alloying are 50 Hz, the amplitude is 3.5 mm, the degree of filling of the chamber is 80 %, the coating time is 1 h, the diameter of the balls is 6 mm, the mass of the ball is 300 g, the ratio of the mass of the powder to the mass of the balls (m_p:m_b) = 1:50.

The following methods were used for the study of mechanical alloying process: the phase composition and structural parameters of the samples were studied on an XRD-6000 diffractometer on CuKα radiation using PDF4+ databases; the microstructure of the samples was examined using a scanning electron microscope JSM-6390; a qualitative analysis of the elemental composition of the samples was carried out using an Auger spectrometer "Schoona-2". The samples were heat treated in a vacuum of 10^{-4} Pa at 600 °C - 900 °C. The holding time at each temperature was 2 h. The samples were cooled with the furnace.

3. RESULTS AND DISCUSSIONS

The study of the formation of the structure of coatings is interrelated with the properties of the original components. If we consider the mechanism of formation of coatings depending on the physical properties of the alloyed components [6], the Ti-Al system refers to the system "plastic-plastic", and the components have the most optimal combination for mechanical alloying. According to the mechanism "plastic-plastic" during mechanical formation, a layered structure of a plurality of flattened particles of the alloyed metals is formed. On the cross section of the sample, the coating structure is clearly visible, which consists of a Ti particle in the Al matrix (**Figures 1a, 1b**). The titanium particles in the aluminium matrix are oblate and in the structure of the coatings are more ordered. The lines of Ti and Al were recorded on the diffractogram (**Figure 1c**). The formation of intermetallic, oxide, carbide compounds by X-ray phase analysis was not detected.

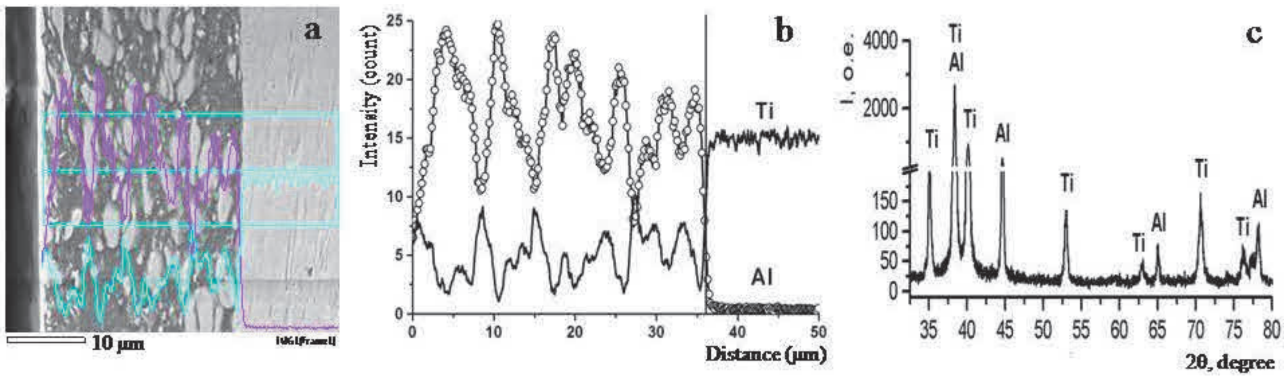

Figure 1 Ti-Al coating on the surface of titanium: a) cross section; b) distribution of elements along the cross section of the sample; c) diffractogram

Figure 2 shows the results of coating studies using layered electron Auger spectroscopy (AES). The elements were registered by moving the electron beam from the surface to the bottom along the wall of the ground crater (**Figure2 b**), then, in accordance with the profile, the depth was determined. For the reliability of the results, four spectra were recorded at each depth. It can be seen from the AES (**Figure 2c**) that the coating components (Ti, Al) are uniformly distributed over the thickness of the coatings. **Figure 3a** shows the concentration profile of the coatings. According to the AES data, the concentration of the detected elements remains constant. However, the aluminum content in the coating is at the level of 3.5 at.%. It is known that the AES method, like other methods of electron spectroscopy, makes it possible to obtain information on the composition of only the near-surface layers of the sample. The main advantage of AES in comparison with many other methods is the very small depth of analysis. Most of the information comes from a depth of 0.5 to 1.0 nm [7]. Because of this, the AES method is sensitive to the composition of atoms on the surface and several near-surface layers of the sample. Proceeding from this, it can be assumed that the Auger electrons carried information from most of the titanium conglomerates in the structure of the coatings.

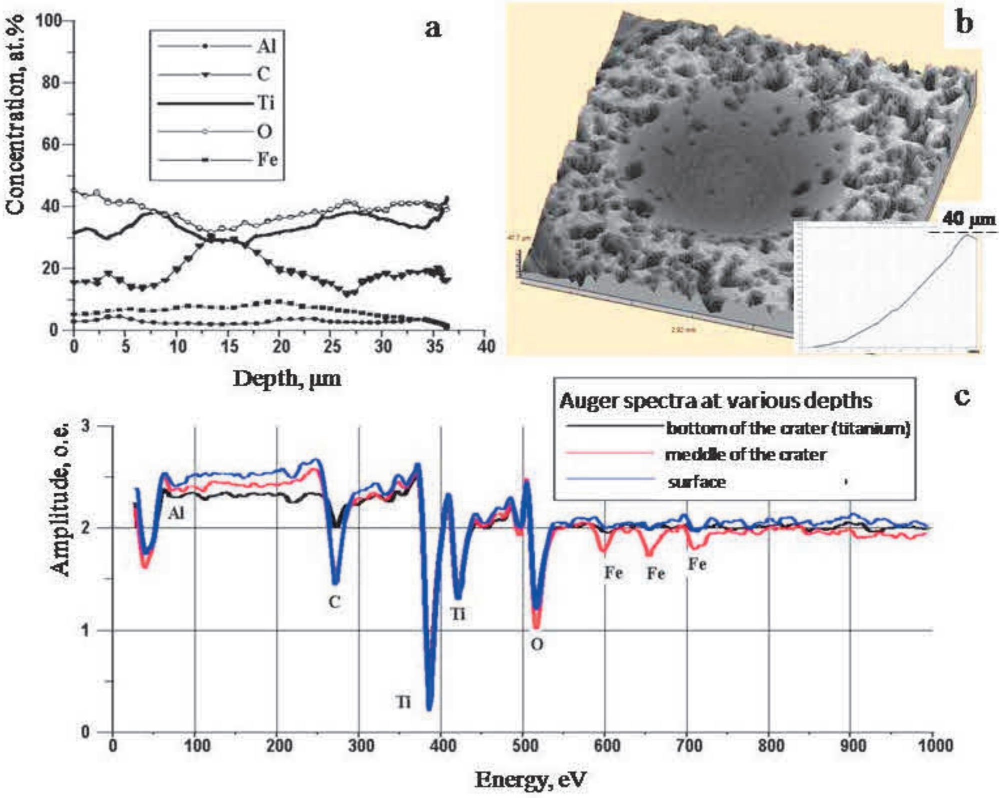

Figure 2 Results of AES: a) the distribution of elements over the thickness of the coatings; b) a crater with a profile image; c) Auger spectrum at different depths of the crater

On Auger spectra of near-surface layers, an increased content of carbon and oxygen is observed. In this work, the chamber was not sealed; the surrounding atmosphere penetrated the container during coating. Iron contamination is observed on the middle layers of the coatings. In the case of coatings inside the chamber, contamination was detected at the coating/substrate interface, and decreased towards the coating surface. Perhaps at the initial stages, the self-lining process favors a reduction in the level of contamination, and in the following stages, due to plastic deformation, the coating, which consists of a plurality of flattened particles of fused metals on the surface of the balls, becomes brittle and collapses leaving the surface of the working body (ball). Proceeding from this, on the near-surface layers of coatings, in case of fixing the sample on top of the chamber, the probability of contamination with iron is increased on the contrary.

Table 1 shows the X-ray phase analysis data of Ti-Al coatings after thermal treatment at temperatures of 600 - 900 °C. When decoding the diffractogram, possible "traces" of new compounds from the coating elements and contamination products were analyzed.

Table 1 Results of X-ray phase analysis of Ti-Al coatings on the surface of titanium

Annealing temperature	**Detected phases**	**The data of the phase structure in the PDF 4+**		**Structure type**	**Phase content, wt.%**
		lattice type	**simple group**		
600 °C	TiAl$_3$	tetragonal	I4/mmm (139)	D0$_{22}$	79
	Al	cubic	Fm-3m (225)	A1	8
	Ti	hexagonal	P63/mmc (194)	A3	5
	Ti$_{12.9}$Fe$_{7.2}$Al$_{9.9}$	cubic	Fm-3m (225)	A1	4
	Ti$_{0.15}$Al$_{0.85}$	cubic	Fm-3m (225)	A1	4
700 °C	TiAl$_3$	tetragonal	I4/mmm (139)	D0$_{22}$	87
	Al	cubic	Fm-3m (225)	A1	6
	AlTi3C	cubic	Pm-3m (221)	B2	4
	Ti	hexagonal	P63/mmc (194)	A3	3
900 °C	TiAl$_3$	tetragonal	I4/mmm (139)	D0$_{22}$	49
	TiAl	tetragonal	P4/mmm (123)	L1$_0$	19
	Al$_2$Ti	tetragonal	I4$_1$/amd (141)	-	18
	Ti$_{0.25}$Al$_{0.75}$	cubic	Fm-3m (225)	A1	13

The phase composition of the coatings after annealing at 600 °C mainly consists of the Al$_3$Ti phase and small trace lines of Al, Ti, Ti12.9Fe7.2Al9.9, Ti0.15Al0.85. Al$_3$Ti with the D022 structure is a stable phase in the system compared to the two modifications of L12 and D023 of this phase. Calculations of lattice dynamics of the crystals give the relative energy stability of the Al$_3$Ti phases in the form D022 <D023 <L12 [8]. The authors of Ref. [9] reported that when mechanical alloying of Al and Ti powders with a bulk composition of Al$_3$Ti leads to the formation of a fcc phase with lattice dimensions near the structure of L12. Restoration of the equilibrium of the system was shown by thermal analysis, which led to the formation of L12 phases (at 365 °C), D023 (at 454 °C) and D022 (at 637 °C). The mechanical alloying of powders with composition Al0.95Ti0.05, Al0.90Ti0.10, Al0.85Ti0.15, Al0.80Ti0.20 and Al0.75Ti0.2 was studied in [10] before and after annealing at temperatures of 600 °C-920 °C. The D022 phase was observed for all compositions at the corresponding highest temperatures. The temperature interval in which the D023 phase was observed increases with increasing Ti concentration. In our work, according to the data of the roentgen phase analysis, the coating consists of Al63.4Ti36.6 wt.%. The formation of D023-Al$_3$Ti was not detected; the D022-Al$_3$Ti phase is the only phase at all study temperatures.

The Ti0.15Al0.85 compound corresponds to the stoichiometric composition Al85.00Ti15.00 at.% (Al76.15Ti23.85 wt.%). Local formation of a composition corresponding to this composition is entirely possible, since the composite structure of the coatings is different, according to the result, the study of the distribution of elements along the thickness of the coatings.

The phase Ti12.9Fe7.2Al9.9 corresponds to the stoichiometric composition of Ti43Fe24Al33 at.% (Al20.76Fe31.25Ti48.00 wt.%). On the basis of the results of elemental analysis carried out by various methods, it can be said that in the coating composition the iron content is not sufficient for the formation of

Ti12.9Fe7.2Al9.9. It should be noted that the accuracy of the quantitative phase analysis is usually 5-10 % of the determined value. Based on this, we can say that the content of these phases is at the background level.

After annealing at 700 °C, the content of the Al_3Ti phase increases, Al, Ti reflexes are present. Small traces of $AlTi_3C$ compounds were found which correspond to the composition Al20C20Ti60 at.% (Al14.77C6.58Ti78.65 wt.%). The triple Al-Ti-C compound is formed as a result of in situ reaction between Al-Ti melts and various carbon sources, such as CH4, C-fibers or Al_2C_3 particles at temperatures usually above 900 °C [11]. And also in the samples of coatings after annealing, it was not possible to establish the presence of Al_2O_3, which was supposed to be higher in the form of an amorphous phase. In [12]at temperatures above 1123 K, the crystallization of Al_2O_3 from the amorphous phase in γ-Al_2O_3 was observed in the composition A1-25 at.% Ti. However, the formation of Al_2O_3 during annealing at 900 °C was not observed.

When the Ti-Al coating is annealed at 900 °C, the volume fraction of the Al_3Ti compound is reduced. The absence of aluminum and titanium in the final product shows complete dissolution of Al in Ti with the formation of new intermetallic compounds, which are the basis of the interaction product in the system under study. Form r-Al_2Ti (Pearson symbol tI24, space group I41/*amd*) and TiAl with L10 superstructure (Pearson symbol tP2, pg P4 / mmm) and Ti0.25Al0.75 connection (Pearson symbol cF4, prg Fm-3m). The formation of the Ti0.25Al0.75 composition can be due to periodic reordering of the atoms in the process of phase transitions. In [13], the alloy Ti-62 at.% Al annealed 4h at 900 °C, 950 °C and 1000 °C, the alloy consisted of TiAl and r-Al_2Ti, according to the Ti-Al state diagram. The presence of the phase Al_3Ti and Ti0.25Al0.75 indicates an incomplete phase transition after annealing for 2 h. However, after annealing at 1000 °C, the structure of the coatings consists of TiAl and Al_2Ti due to the complete recrystallization of the Al_3Ti phase [14].

The change in the phase composition of the coatings is accompanied by a change in the microstructure of the coating surface as a result of activation of the diffusion process between the Ti and Al coating components. **Figure 3** shows the cross-section of the coatings after annealing at 600 °C and 900 °C.

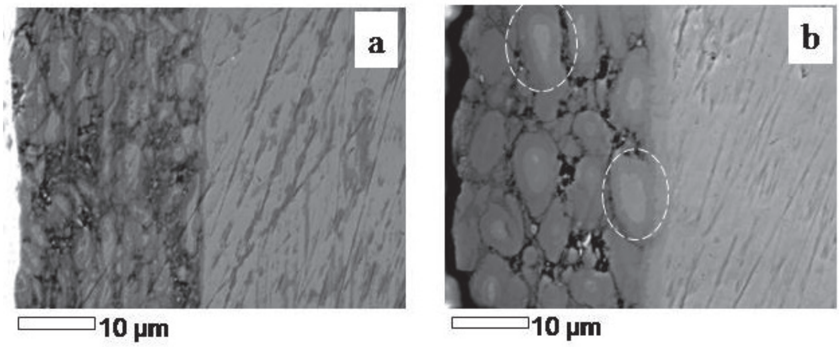

Figure 3 The structure of the cross section of the coatings after annealing a) 600 ºC; b) 900 ºC

Stirring of coating components with the formation of diffusion zones at the interfaces is observed after annealing at 600 ºC. An increase in the heating temperature to 900 °C leads to a coalescence of the particles. **Figure 6a** shows the formation of a diffusion zone at the substrate/coating interface and the formation of fine particles along the boundaries of larger particles, which, judging from the contrast, have a higher average atomic phase number. Thus, it can be assumed that as the temperature rises, as a result of the reaction between Ti and Al_3Ti, Al_2Ti and TiAl compounds begin to form along the boundaries of Al_3Ti particles. This process leads to the development of interparticle bonds, the fusion of particles and the shrinkage of the coating.

Thus, when Ti-Al coatings are annealed in the temperature range 600 °C - 900 °C, Ti-Al intermetallide phases form on the titanium surface. Al_3Ti is the first phase that forms in the coatings as a result of the interaction of Ti and Al. The compounds Al_2Ti and TiAl are formed as a result of subsequent reactions between Ti and Al_3Ti. To accelerate the formation of Ti-Al intermetallic compounds, thermal annealing should be used as a complex treatment after coating with a mechanical alloying method.

4. CONCLUSION

It has been established that in the initial stage of formation of Ti-Al coatings, the process of conglomeration of a particle of Ti and Al powders occurs, the soft-element particles, in our case Al, envelop the Ti particles, forming a plastic matrix on the surface of the substrate. Under the action of impacts, the Ti particles are driven into the plastic matrix; as a result, a coating is formed;

The mechanism of formation of Ti-Al coatings is due to cold welding due to deformation compaction of powder particles on the surface of titanium under the impact of ball hits;

When Ti-Al coatings are annealed in the temperature range 600 °C - 900 °C, Ti-Al intermetallide phases are formed on the titanium surface. Al_3Ti is the first phase that forms in the coatings as a result of the interaction of Ti and Al. The compounds Al_2Ti and TiAl are formed as a result of subsequent reactions between Ti and Al_3Ti.

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