**QUEEN'S
UNIVERSITY
BELFAST**

Fabrication of Ti-Al coatings by mechanical alloying method

Romankov, S., Sha, W., Kaloshkin, S. D., & Kaevitser, K. (2006). Fabrication of Ti-Al coatings by mechanical alloying method. *Surface and Coatings Technology*, 201(6)(6), 3235-3245.
<https://doi.org/10.1016/j.surfcoat.2006.06.044>

Published in:
Surface and Coatings Technology

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Fabrication of Ti–Al coatings by mechanical alloying method

S. Romankov ^{a,*}, W. Sha ^b, S.D. Kaloshkin ^c, K. Kaevitser ^c

^a *Institute of Physics and Technology, 050032, Almaty32, Kazakhstan*

^b *Metals Research Group, School of Planning, Architecture and Civil Engineering, The Queen's University of Belfast, Belfast BT7 1NN, UK*

^c *Moscow State Institute of Steel and Alloys, Leninsky Prosp. 4, 119049, Moscow, Russia*

Received 17 March 2006; accepted in revised form 28 June 2006

Available online 8 August 2006

Abstract

By means of the mechanical alloying (MA) method, Al and Ti+Al coatings were deposited on Ti alloy substrates. During the mechano-activation processing, the substrate surface was impacted by a large number of flying balls along with particles of powder. The repeated ball collisions with the substrate resulted in the deposition of powder on its surface. MA technique produced Ti+Al coating with a thickness of 200 μm and Al one with a thickness of 50 μm after 2 h milling at room temperature. The as-synthesized coatings showed structures with high apparent density and free of porosity. The surface morphology of the MA-coatings was very rough. Annealing treatment led to the leveling of this uneven morphology. Annealing at temperatures ranging between 600 °C and 1100 °C gave different aluminide phases on the samples. In the case of Al coating, Al₃Ti and Ti₃Al compound were observed upon heating up to 1100 °C. In the case of Ti+Al coating, Al₃Ti, Al₂Ti, TiAl and Ti₃Al were formed on the surface.

© 2006 Elsevier B.V. All rights reserved.

PACS: 68.55.Ac; 68.35.Fx; 68.55.Jk

Keywords: Coating; Mechanical alloying; Titanium alloys; Titanium aluminides; Phase transformation; Microstructure

1. Introduction

Ti and its alloys have been widely used in various applications. However, their wearing behavior and corrosion resistance can be improved in order to ensure long-term durability. The available experimental data show that aluminide phases of the Ti–Al system can be used as a protective coating for industrial titanium alloys [1–4]. Intermetallic compounds of the Ti–Al system have been considered extensively for high-temperature structural applications because they offer a combination of good oxidation resistance and useful mechanical properties at temperatures higher than those possible with conventional titanium alloys [5]. The optimum surface properties should not have conflict with other requirements such as low material cost, ease of fabrication and high strength. Therefore, there is a continuing trend in materials science to develop new surface modification methods. Recently, a surface mechanical attrition treatment technique has been developed for obtaining

nanostructured surface layers [6,7]. In these papers, the surface layer was subject to repeated ball collisions and as a result the coarse grained structure at the surface became refined into a nanometer scale. The nanostructured surface layer with thicknesses of 10–50 μm was obtained. In the present work, we introduce the mechanical alloying method for the fabrication of Ti–Al coatings. The structural formation of aluminized layer during subsequent annealing was studied.

2. Experimental procedures

The commercial Ti–4%Al–3%Mo–1%V alloy was used as substrates. This alloy consisted mainly of α -Ti and a small amount of β phase. The dimensions of the samples were 2 × 7 × 10 mm. The surface of the samples was polished before processing.

Fig. 1 shows a schematic illustration of the mechanical alloying (MA) method used in the present work. By means of the MA method, Al and Ti+Al coatings were deposited on the substrates. The samples and the powder along with the steel balls were placed into the vibration chamber vibrated by mechano-reactor with the frequency of 50 Hz and amplitude of

* Corresponding author.

E-mail address: romankovs@mail.ru (S. Romankov).

13 mm. The chamber volume was 20 cm³. This experiment used Al and Ti powders with a purity of 99.9% and particle size smaller than 50 µm. In the case of pure Al coating, the weight of Al powder was 3.4 g. In the case of Ti+Al coating, the weight of mixture of Ti and Al powders was 3.4 g = 1.7 g Ti + 1.7 g Al. No process control agent was added to the powder. The ratio of the ball mass to the powder mass was 10:1. The diameter of the balls was 5 mm. The milling process was carried out in air. The chamber was just sealed in order to prevent contamination from the atmosphere. The duration of mechanical alloying was 2 h. The temperature of the chamber walls during MA processing did not exceed 100 °C. The temperature was measured by using a chromel–alumel thermocouple. During mechano-activation processing, the sample surface was impacted by a large number of flying balls along with particles of powder. The repeated ball collisions with the sample resulted in deposition of powder on the surface (Fig. 1). After that, as-synthesized samples were annealed successively in vacuum of 10^{−5} Pa at temperatures ranging between 600 °C and 1100 °C at every 100 °C and were then cooled in the furnace. In all cases, the annealing time was 2 h. The resulting structure was studied by X-ray diffraction (XRD) analysis (CuK_α) and scanning electron microscopy (SEM). The composition was analyzed by energy dispersive X-ray spectroscopy (EDS) using Link System (Oxford Instruments, Oxfordshire, England) light element detector. The surface morphology was observed with the Solver PRO scanning probe microscope using atomic force microscopy (AFM).

3. Experimental results and discussion

3.1. As-synthesized samples

Fig. 2a and b shows the cross-section microstructure and concentration profile of Ti+Al coating produced by MA method. The thickness of Ti+Al coating was about 200 µm. The MA-coating showed a structure with high apparent density, free of porosity and cracks. The coating consisted of Ti particles in the Al matrix. The Ti particles were non-uniform in their sizes. The maximum Fe content in Ti+Al coating was about 0.3 at.% near the coating/substrate interface. It decreased in the

direction of the coating surface. The reason for such low contents of Fe is that the balls and the chamber inner walls were being coated by Ti+Al layer in the early stages of MA processing, preventing the release of Fe into the coating. There were no traces of nitrogen and oxygen to be found in Ti+Al coating by using EDS. The magnitude of contamination during MA depends on the time and intensity of milling, nature of the powder, ball-to-powder weight ratio, seal integrity, and others (see, for example, Ref. [8]). If the container is not properly sealed, the atmosphere surrounding the container leaks into the container and contaminates the powder. Thus, when reactive metals like titanium are milled in improperly sealed containers, the powders are contaminated with nitrogen and oxygen. By careful control and improvements of the seal quality, the interstitial contaminants in the titanium alloy could be reduced to as low as 100 ppm of oxygen and 15 ppm of nitrogen [8]. In our case, the intensity of milling was not high and the duration of milling was short. The chamber volume was small. Therefore, if the chamber was properly sealed the oxygen and nitrogen contents might be below the sensitivity of the light element detector of the Link System.

Fig. 2c shows the surface microstructure of the sample with Ti+Al coating. The microstructure was rough. No clear grain structure was observed on the coating surface. Fig. 2d presents a typical surface morphology of Ti+Al coating obtained by AFM. This morphology appears similar to a ductile fractured surface. The nodules in the image could show flow of material at fracture. Furthermore, the dimple structure in some areas of Ti+Al coating at high magnification might provide a clear evidence of the ductile behavior of the material during MA processing (Fig. 2e).

Fig. 3a and b shows the cross-section microstructure and concentration profile of the sample with Al coating produced by MA method. The thickness of the coating was about 50 µm. There was no clear interface between substrate and Al layer. The coating was continuous and very dense (Fig. 3c). The surface of Al coating was flatter and more homogenous than the one of Ti+Al coating (Fig. 2). The morphology was again similar to a fracture surface (Fig. 3d). The dimple structure and microcracks in some areas of Al coating at high magnification were observed (Fig. 3e). In the X-ray diffraction pattern of the sample with Al coating the peaks of α-Ti, β-Ti and Al were detected (Fig. 4a). The lines of β-Ti from substrate were not observed in the X-ray diffraction pattern of the sample with Ti+Al coating (Fig. 4b). It was related with the thickness of the Ti+Al coating. The thickness of Al one was a quarter of the thickness of Ti+Al coating. The weight of Al powder in Ti+Al mixture before the deposition was half of the Al powder weight used for the deposition of pure Al layer. However, by examining the intensity of the diffraction lines, the absolute amount of Al in Ti+Al coating was more than that in Al coating.

Thus, during MA processing Al was better deposited on the surface in the presence of Ti particles. The microstructure of the coating surface provides evidence of ductile behavior of material during MA (Figs. 2 and 3). This behavior would indicate that the local temperature under the ball impacts was higher than the temperature of the chamber walls. The stress

Fig. 1. Schematic illustrations of MA method.

generated during MA might be rather high as well [8]. The Ti particles were in the Al matrix (Fig. 2a). Consequently, it can be assumed that Ti served as a supportive material and Al served as a bonding one. Cold welding between particles and substrate under repeated ball collisions led to the formation of a composite coating. Al flowed into the pores between Ti particles under the impact of balls. As a result a dense Ti+Al coating grew. Cold welding occurred non-uniformly on the sample. Therefore a very rough surface of Ti+Al coating was formed (Figs. 1 and 2c). In the case of using the powder of pure Al, Al layer with some thickness was coated on the sample but addi-

tional cold welding between Al particles and Al layer could not happen. Cold welding might occur in the early stages of MA, when the Al particles were soft, and their tendency to weld was high. Under deformation the particles and Al layer became harder and more brittle [8]. This is confirmed by the microcrack observation in Fig. 3d. With increase of MA-time, cold welding was restrained. Under the ball collisions, Al coating started flaking and became smoother in comparison with Ti+Al one (Figs. 1, 2c and 3c). In the case of Ti+Al coating, alloying might occur rapidly in the presence of Ti particles. There was no time for the coating to become brittle. It has been found in

Fig. 2. Structure of as-synthesized Ti+Al coating produced by MA method: (a) cross-section microstructure; (b) concentration profile; (c) surface microstructure; (d) morphology of Ti+Al coating; (e) dimple structure.

further investigation that Ti+Al coating could be formed after 30 min trial.

3.2. Annealing treatment of Al coating

Fig. 4a shows the X-ray diffraction patterns of sample with Al coating after annealing at temperatures ranging between 600 °C and 1100 °C. Table 1 summarizes the phase composition of the coating as a function of annealing temperature. The phases of the substrate, α -Ti and β -Ti, are not listed in Table 1. During annealing, on the surface of the sample different aluminide phases were formed as the result of interdiffusion and

reaction between Ti and Al. Al reacted with Ti on heating up to 600 °C formed an Al_3Ti compound. No diffraction peaks of pure Al were detected in the X-ray diffraction pattern (Fig. 4a). Al completely reacted on the formation of Al_3Ti .

Fig. 5a shows a cross-section microstructure of Al coating after annealing at 600 °C. The contrast difference observed in Fig. 5a, a back-scattered electron image, reflects different compositions. On heating up to 600 °C, Al diffused into substrate. The gray dark layer from the side of the substrate was enriched by Al (Fig. 5b). The thickness of the diffusion layer was about 80 μm . The coating itself became porous after annealing treatment at 600 °C. The microcracks between substrate and

Fig. 3. Structure of as-synthesized Al coating produced by MA method: (a) cross-section microstructure; (b) concentration profile; (c) surface microstructure; (d) morphology of Al coating; (e) dimple structure.

coating were observed (Fig. 5a). The coating surface was porous and rough as well. Upon heating up to 600 °C, the pits were formed on the surface (Fig. 5c).

After annealing treatment at 600 °C, the sample was annealed at 700 °C. The second anneal led to the formation of a

Ti₃Al compound on the surface (Table 1, Fig. 4a). In addition, new diffraction lines with $d=2.48$ and 2.15 Å were observed in the X-ray diffraction pattern (Fig. 4a). In Table 1 and Fig. 4, this phase is denoted as X-phase. These lines could not be definitely attributed to the known titanium aluminide phases according to

Fig. 4. X-ray diffraction patterns (CuK α) of MA-coatings: (a) Al coating; (b) Ti+Al coating.

Table 1
Phase composition of the coatings as a function of annealing temperature

°C	Phase composition	
	Al coating	Ti + Al coating
600	Al ₃ Ti	Al ₃ Ti, α -Ti
700	Ti ₃ Al, X-phase	Al ₃ Ti, Al ₂ Ti, TiAl, Ti ₃ Al, α -Ti
800	Ti ₃ Al, X-phase	Al ₃ Ti, Al ₂ Ti, TiAl, Ti ₃ Al
900	Ti ₃ Al, X-phase	Al ₃ Ti, Al ₂ Ti, TiAl, Ti ₃ Al
1000	Ti ₃ Al, X-phase	Al ₂ Ti, TiAl, Ti ₃ Al, α -Ti, X-phase
1100	Ti ₃ Al (trace), X-phase	TiAl, Ti ₃ Al, α -Ti, X-phase

the Powder Diffraction Standards [9]. After subsequent increase of annealing temperature from 700 °C to 1000 °C, the intensity of the X-phase diffraction lines increased while the intensity of the Ti₃Al ones decreased. It indicates that increase of annealing temperature increased the volume fraction of X-phase at the expense of Ti₃Al. After annealing treatment at 1100 °C, only slight asymmetry of the α -Ti diffraction peaks at the high-angle side might indicate the presence of the Ti₃Al phase (Fig. 4a). The intensity of the X-phase lines with $d=2.48$ and $d=2.15$ Å considerably decreased after annealing at 1100 °C in comparison with treatment at 1000 °C, while the other strong peaks with $d=2.40$ and $d=2.08$ Å appeared in the X-ray diffraction pattern (Fig. 4a).

The lines with $d=2.48$ and $d=2.15$ Å could be attributed to TiC, and the ones with $d=2.40$ and $d=2.08$ Å could be attributed to Ti₃AlC. The above sequence of peak appearing means that Ti₃AlC could be formed from TiC (see, for example, Ref. [10]). Formation of carbide phases during annealing treatments could be due to carbon contamination of the coating during MA. It was difficult to determine the accurate carbon content in the coating because of the presence of residual carbon in the microscope chamber from the diffusion pump. However, as it has been shown in Ref. [11], formation of X-phase on the Ti surface coated by Al film during annealing treatments was not related to a fixed temperature. The diffraction lines of the X-phase were detected only along with the Ti₃Al ones. The X-phase completely disappeared after the elimination of aluminized layer. If carbide phases form after annealing treatment at 900 °C, it is unlikely for them to disappear completely after treatment at 1000 °C [11]. It means that the X-phase could be also some metastable phases. The formation of the X-phase deserves further studying.

Moreover, in Ref. [11] case, formation of Al₂Ti and TiAl compounds on the Ti surface coated by Al film preceded formation of Ti₃Al. In the case of sample with Al coating produced by MA, Al₂Ti and TiAl phases were not observed. It could be a result of the stress and structural features of MA-coating. During MA processing, the sample surface and coating were plastically deformed. It led to the grain refinement into the nanometer scale and an extremely high density of dislocations [6]. The large amount of grain boundaries and defects might provide rapid atomic diffusion in the surface layers. As a result, diffusion transformation on the sample with Al coating produced by MA could occur very fast, and Al₂Ti and TiAl phases would not remain after 2 h annealing. It is also possible that these phases might be skipped altogether. Defect structure formed during MA

processing could have a great effect on the thermodynamics of interdiffusion growth.

Fig. 6 shows the evolution of surface microstructure of Al coating during annealing treatments. With an increase of annealing temperature, a gradual leveling of coating happened (Fig. 6a and b). Annealing at 1000 °C gave homogeneous and

Fig. 5. Structure of Al coating after annealing at 600 °C: (a) back-scattered electron image showing cross-section microstructure; (b) concentration profile; (c) surface microstructure.

even microstructure on the sample with Al coating (Fig. 6b). In the high magnification micrograph of the sample with Al coating, micropits were observed after annealing at 900 °C. The sizes of micropits increased and coating became porous as annealing temperature rose to 1000 °C (Fig. 6c and d). With subsequent increase of temperature up to 1100 °C, the coating structure coalesced (Fig. 6e), and the surface morphology became flat (Fig. 6f). Thus, annealing treatment resulted in the gradual leveling of MA-coating surface, which was very rough in the as-synthesized condition (Fig. 3d).

After annealing at 1100 °C, the MA-coating itself showed structure with high apparent density (Fig. 7a). However, there

were some pores and peeling in some areas along the coating/substrate interface (Fig. 7a and b). Fig. 7b is a back-scattered electron image of coating after treatment at 1100 °C. It shows a different composition of Al coating. The jump in Al concentration was observed at the interface (Fig. 7c). It was consistent with the clear contrast in the back-scattered electron image (Fig. 7b). The diffusion layer from the side of the substrate was formed. The substrate itself had a coarse grain lamellar structure. The concentration of Al at near surface region of the substrate was about 16 at.% after annealing at 1100 °C. It was two times the Al concentration in the substrate.

Fig. 6. Microstructural evolution of Al coating after annealing: (a) 800 °C; (b) 1000 °C; (c) 900 °C; (d) 1000 °C; (e) 1100 °C, (f) coating morphology after 1100 °C.

Fig. 7. Cross-section microstructure of Al coating after annealing at 1100 °C: (a) secondary electron image; (b) back-scattered electron image; (c) concentration profile.

Thus, significant changes in the structure of Al coating were observed after annealing at temperatures above 800 °C. At about 880 °C, α -Ti (hcp) to β -Ti (bcc) transformation in the substrate started. At 900 °C, diffusion coefficients for the Ti–Al compounds changed and mobility of atoms increased dramatically [12]. The intense interdiffusion between substrate and coating led to the recrystallization of coating structure. Moreover, at the temperatures exceeding 900 °C, the nucleation and

growth of β -grains in the substrate occurred. Al increased the temperature of α -Ti to β -Ti transformation and stabilized α -Ti. The concentration of Al at the near-interface region increased significantly upon heating. As a result α -Ti to β -Ti transformation in the substrate and near-surface region of the substrate did not occur simultaneously. Annealing at temperatures above 900 °C led to the recrystallization of the near-surface region and stabilizing α -Ti at the interface. Then, the lines of β -phase were

Fig. 8. Structure of Ti+Al coating after annealing at 600 °C: (a) back-scattered electron image showing cross-section microstructure; (b) concentration profile; (c) surface microstructure.

not observed in the X-ray diffraction patterns of the sample with Al coating after annealing treatment above 900 °C (Fig. 4a).

3.3. Annealing treatment of Ti+Al coating

Annealing of Ti+Al coating at 600 °C resulted in the formation of the Al_3Ti compound (Table 1, Fig. 4b). Al completely reacted on the formation of Al_3Ti . The peaks of $\alpha\text{-Ti}$ were observed in the X-ray diffraction pattern after annealing treatment at 600 °C (Fig. 4b). It means that the particles of pure Ti were present in the coating. Fig. 8a shows the cross-section microstructure of Ti+Al coating after annealing treatment at

600 °C. The coating was porous. It consisted of non-uniform particles. A layer with the thickness of about 12 μm from the side of the substrate was enriched by Al (Fig. 8b). However, in comparison with the sample of Al coating the diffusion layer was substantially thinner (Fig. 5a and b). After annealing at 600 °C, the surface microstructure of the sample with Ti+Al coating was porous and rough. Annealing led to the formation of very fine particles on the surface (Fig. 8c). Comparison between the two types of coatings might indicate that in the case of the sample with Al coating, formation of Al_3Ti compound resulted from interdiffusion between Ti substrate and Al layer. In the case of sample with Ti+Al coating Al_3Ti was mainly

Fig. 9. Microstructural evolution of Ti+Al coating after annealing: (a) 800 °C; (b) 1000 °C; (c) 1100 °C; (d) 900 °C; (e) 1100 °C, (f) coating morphology after 1100 °C.

formed as a result of reaction between Ti particles and Al matrix in the coating. Formation of Al_3Ti particles led to the porosity of Ti+Al coating.

Annealing sample with Ti+Al coating at 700 °C resulted in the decrease of intensity of Al_3Ti and $\alpha\text{-Ti}$ diffraction peaks in the X-ray diffraction pattern (Fig. 4b). Ti_3Al lines along with the wide asymmetric peaks of the Al_2Ti phase were detected. The Al_2Ti and TiAl compounds have close lattice plane spacing. The wide asymmetric peaks of Al_2Ti in the X-ray diffraction pattern were overlapping diffraction lines from Al_2Ti and TiAl. That observation means that Al_2Ti , TiAl and Ti_3Al were formed as a result of reaction between Al_3Ti and Ti particles on heating up to 700 °C. By comparing the intensity of the diffraction lines after subsequent increase of annealing temperature from 700 °C to 900 °C, the volume fraction of Al_3Ti gradually decreased while the volume fraction of Ti_3Al , Al_2Ti and TiAl increased. Ti in Ti+Al coating completely reacted on the formation of these compounds after treatment at 800 °C (Fig. 4b). Al_3Ti only decomposed on heating up to 1000 °C. Annealing at 1000 °C gave Al_2Ti , TiAl and Ti_3Al on the sample with Ti+Al coating (Table 1, Fig. 4b). In addition, the peaks of the X-phase were observed in the X-ray diffraction pattern after treatment at 1000 °C. What is important that the diffraction peaks of $\alpha\text{-Ti}$ were again detected after annealing at 1000 °C (Fig. 4b). Then, with an increase of annealing temperature to 1100 °C, the intensity of $\alpha\text{-Ti}$ peaks increased dramatically while the

intensity of the Ti_3Al lines decreased. It could be related with the rapid releasing of Al into substrate when the mobility of atoms increased. The TiAl compound on the sample with Ti+Al coating did not decompose completely after annealing at 1100 °C (Table 1, Fig. 4b).

Fig. 9 shows the evolution of the surface microstructure of Ti+Al coating during annealing treatments. With an increase of temperature from 800 °C to 1000 °C, the microstructure of the coating became very inhomogeneous (Fig. 9a and b). Annealing gave very rough and irregular hillock like structure. Large microcracks appeared on the smooth areas (Fig. 9b). With subsequent increase of annealing temperature from 1000 °C to 1100 °C, the microstructure of Ti+Al coating started leveling (Fig. 9c). In the high magnification micrograph of the sample with Ti+Al coating, micropits were observed after annealing at 900 °C. The surface was porous (Fig. 9d). The coating structure coalesced as annealing temperature rose from 1000 °C to 1100 °C. The microcracks started healing (Fig. 9e). During the annealing treatment, the surface morphology of Ti+Al coating became less rough compared to the as-synthesized MA-coating (Figs. 2d and 9f).

Fig. 10a shows the cross-section microstructure of Ti+Al coating after annealing at 1100 °C. No peeling, microcracks or pores were observed. The coating was very dense. It had a good apparent adherence to the substrate after treatment at 1100 °C. Back-scattered electron imaging showed a multilayered

Fig. 10. Cross-section microstructure of Ti+Al coating after annealing at 1100 °C: (a) secondary electron image; (b) back-scattered electron image; (c) concentration profile (d) back-scattered electron image of the substrate at interface.

structure of coating (Fig. 10b). The layers had a different thickness (Fig. 10b and c). Instead of the expected smooth change in concentration from α -Ti to TiAl compound, the jumps in the concentration were observed. The discontinuity was consistent with the clear contrast difference seen in the back-scattered electron image (Fig. 10b and c). Fig. 10d shows a diffusion layer from the side of the substrate. The substrate itself had a coarse grain lamellar structure. Such structure might be formed from the coarse grains of β -Ti upon cooling [13]. The columnar structure was formed at the near interface region. The concentration of Al in that area was about 50 at.% after annealing at 1100 °C. There was a layer with fine lamellar structure between the columnar and coarse lamellar grains.

Thus, recrystallization of Ti+Al coating also started at temperatures above 880 °C, as α -Ti $\rightarrow$ β -Ti transformation in the substrate happened (Fig. 9). Formation of microcracks on heating up to 1000 °C could be a result of a strong stress being developed because of crystallographic differences between multilayered coating and substrate. Recrystallization of the near surface region of the substrate, caused by change in Al concentration, could lead to partial stress relaxation. Increase of atom mobility with an increase of annealing temperature resulted in healing microcracks.

Distinction between Al and Ti+Al coatings produced by MA was that the aluminide phases in Ti+Al coating were formed successively during annealing treatment, similar to the Ti samples coated by Al film [11] (Table 1). However, in Ref. [11] case, Ti_3Al compound started decomposing only after the decomposition of TiAl one. In the case of Ti+Al coating here, the volume fraction of Ti_3Al decreased dramatically while TiAl compound did not decompose completely (Fig. 4b). The differences in structural formation and its transformation between Al and Ti+Al coatings during annealing treatments might be related with the thickness of the coatings. Thicker coating required more time for its diffusion transformation and recrystallization [11]. On the other hand, the presence of Ti particles in the as-synthesized Ti+Al coating might have some effect on the thermodynamics of the reactions. The powders of pure Ti and Al were mixed in the proportion for TiAl compound. Upon heating, Al mainly reacted with Ti in Ti+Al coating forming aluminide phases. As a result, releasing Al and its diffusion into the substrate might be restrained. TiAl compound was stabilized up to 1100 °C. Interdiffusion growth of aluminide phases could dominate at the substrate/coating interface. Interdiffusion gave a good apparent adherence to the substrate on heating up to 1100 °C (Fig. 10). However, the dynamics of interdiffusion growth might slow down in the direction of the coating surface. Also, it is necessary to note that after treatment at 1100 °C, adherence to the substrate was better for Ti+Al coating than for Al one (Figs. 5 and 10). It could be related with the thickness and structures of the coatings.

4. Summary

By means of the MA method, Al and Ti+Al coatings were deposited on the Ti alloy substrates. During mechano-activation

processing, the sample surface was impacted by a large number of flying balls along with the particles of the powder. The repeated ball collisions with the sample resulted in deposition of powder on the surface. During MA processing, Al was better deposited on the surface in the presence of Ti particles. The MA technique produced Ti+Al coating with a thickness of 200 μm and Al one with a thickness of 50 μm after 2 h milling at room temperature. The Ti+Al coating consisted of Ti particles in the Al matrix. As-synthesized coatings showed structures with high apparent density and free of porosity. However, the surface morphology of the MA-coatings was very rough. Annealing treatment led to the leveling of surface microstructure. Recrystallization of coatings started at temperatures above 880 °C, as α -Ti $\rightarrow$ β -Ti transformation in the substrate happened. Annealing at temperatures ranging between 600 °C and 1100 °C gave different aluminide phases on the samples. In the case of Al coating, Al_3Ti and Ti_3Al compound were observed upon heating up to 1100 °C. In the case of Ti+Al coating, Al_3Ti , Al_2Ti , TiAl and Ti_3Al were formed on the surface. After heating at 1100 °C, Ti+Al coating showed multilayered structure with high apparent density, free of porosity, which had a good adherence to the substrate.

Thus, the MA method allows to produce very thick Ti–Al coatings after a short time at room temperature. No special milling atmosphere is required. Ti–Al intermetallic coatings can be produced by subsequent annealing treatment. MA method is likely to be used for fabrication of other diffusion coating as well. However, to achieve the optimum treatment regime, the process of MA-deposition deserves further studying.

Acknowledgement

This research was partially supported by RFBR Foundation Grant 06-03-32220.

References

- [1] C. Leyens, M. Peters, W.A. Kaysser, *Surf. Coat. Technol.* 94–95 (1997) 34.
- [2] T. Matsubara, T. Shibutani, K. Uenishi, K.F. Kobayashi, *Intermetallics* 8 (2000) 815.
- [3] M.S. Chu, S.K. Wu, *Surf. Coat. Technol.* 179 (2004) 257.
- [4] Z. Liu, G. Wang, *Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process.* 397 (2005) 50.
- [5] D.M. Dimiduk, in: Y.-W. Kim, R. Wagner, M. Yamaguchi (Eds.), *Gamma Titanium Aluminides*, TMS, Warrendale, PA, 1995, p. 3.
- [6] Z.B. Wang, N.R. Tao, W.P. Tong, J. Lu, K. Lu, *Acta Mater.* 51 (2003) 4319.
- [7] N. Tao, H. Zhang, J. Lu, K. Lu, *Mater. Trans.* 44 (2003) 1919.
- [8] C. Suryanarayana, *Prog. Mater. Sci.* 46 (2001) 1.
- [9] Powder Diffraction File 2. 2001.
- [10] A. Zhou, C. Wang, Y. Huang, *Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process.* 352 (2003) 333.
- [11] S. Romankov, W. Sha, E. Ermakov, A. Mamaeva, *J. Alloys Compd.* 420 (2006) 63.
- [12] Y. Mishin, Chr. Herzig, *Acta Mater.* 48 (2000) 589.
- [13] W. Sha, Z. Guo, *J. Alloys Compd.* 290 (1999) L3.