S.A. Popov for film deposition, G.E. Ozur and K.V. Karlik for the irradiation of samples.

with a surface cracking due to high thermal stresses. To avoid cracking, the subsequent pulsed deposition (70 nm) and pulsed e-beam melting alloys. Increasing a number of cycles of the Al film were used for characterization of Ti–Al surface Al film. SEM/EDX, GIXRD and nanoindentation phase mixing of Ti substrate with pre-deposited (10–20 keV, 3 µs, 3.5 J/cm²) from 10 to 40 results in the increase in the Al content from ∼40 to ∼70 at. % in the ~3-µm thick surface layer. If the Al content reaches ∼55 at. %, the Ti3Al/TiAl based surface alloy was formed. Phase formation is accompanied with a surface cracking due to high thermal stresses. To avoid cracking, the subsequent pulsed melting by 3 µs e-beam at 700°C, as well as by 100 µs e-beam at RT was used. The mechanical properties of the surface alloys in dependence on synthesis mode were evaluated.

1. Introduction

The Ti3Al/TiAl based alloys have several advantages over conventional Ti alloys, such as higher elastic modulus, lower density, better mechanical properties at elevated temperature, and higher oxidation resistance [1]. These properties of Ti–Al intermetallics can be used to produce protective coatings on structural alloys. Several techniques to fabricate Ti–Al coatings have developed in the last decades, including thin film deposition [2, 3], ion implantation [4] and laser melting deposition [5].

In [6, 7] it has been shown, that liquid-phase mixing of film-substrate systems with low-energy (~20 keV), high-current electron beam (LEHCEB) of microsecond duration is an efficient method for formation of surface alloys without impairing mechanical bulk properties. This work aims to examine the possibility to produce a Ti3Al/TiAl based surface alloys by pulsed liquid-phase mixing of pre-deposited Al film with Ti substrate. The influence of thin-film synthesis conditions on the composition and crystal structure, as well as mechanical properties of the surface alloys is also considered.

2. Experimental

The Ti–Al surface alloys were produced in a single vacuum cycle using hybrid setup, that integrates a LEHCEB’s source [6] with a high-current vacuum-arc evaporator [8], joined together to a vacuum chamber, evacuated by turbopump. Using handle manipulator, a sample was located alternately opposite the evaporator’s (for Al film deposition), or the LEHCEB’s cathode (for surface melting).

The evaporator’s cathode made of pure Al (99.95 wt.% Al) was a disc of 24 mm in diameter and 4-mm thick. The rate deposition of Al film was 0.6 nm per pulse. The pulse frequency of evaporator and LEHCEB’s source were 1 and 0.1 Hz, respectively. The residual gas pressure in the chamber during the film deposition and pulsed melting was ~10⁻⁶ and 2.10⁻⁶ (Ar) torr, respectively.

The samples 18×18×1 mm made of cp Ti (99.7 wt.% Ti) were used as substrates. The substrates were mechanically polished using diamond paste. Prior to deposition, the Ti substrates were irradiated with LEHCEB (pulse duration τ = 3 µs, energy density Eₚ = 5 J/cm², pulse number n = 10) in order to avoid a local delamination of thin film at pulsed melting because of the surface cratering [6].

The thickness of deposited Al film in each synthesis cycle was 70 nm. After each film deposition the coated sample was subjected to 3-pulse melting with LEHCEB (3 µs, 3.5 J/cm²). The pulse number n = 3 was chosen to achieve the uniform liquid-phase mixing of film-substrate system. A number of cycles N of the Al film deposition and pulsed melting was varied from 10 to 40, i.e., the total thickness of deposited Al coating was varied from 0.7 to 2.8 µm.

Selected surface-alloyed samples were annealed (~700°C, 1 h) in the oil-free vacuum (~10⁻⁶ torr) in order to decrease the residual stresses induced by pulsed heating [6].

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Another part of samples was subjected to subsequent pulsed melting by LEHCEB (3 μs, 3÷5 J/cm²) at ~700 °C, as well as by submillisecond e-beam (15 keV, 100 μs, 10÷15 J/cm²) at RT to form more uniform microstructure.

The surface topography was examined with a scanning electron microscope Philips-SEM 515. The chemical composition of the surface layers was determined from EDX spectra (detector EDAX ECON IV) recorded in the same SEM. Point analysis (area ~1 μm²), as well as mapping over an area ~100×100 μm² were performed. Evaluated thickness of the analyzed layer for Ti was ~1 and ~3 μm at an accelerating voltage of 15 and 30 kV, respectively. The phase composition of the surface layers was examined by grazing incident X-ray diffraction (GIXRD) analysis at an incident angle ω = 5° with a diffractometer Shimadzu XRD 6000 using CuKα-radiation. The thickness of an analysed layer for Ti target was ~2 μm. The mechanical properties of surface layers were studied using a nanoindenter NanoTest 600 with diamond Berkovich indenter at peak load 5, 10, 20, 50, 100, 200, and 500 mN.

3. Results and discussion

3.1. Pulsed melting characteristics

To ensure a uniform liquid-phase mixing of film-substrate system it is necessary to meet two main conditions: (1) the diffusion length of Al atoms in a liquid Ti, which depends on a melt lifetime, must be much more than a thickness of the solid film; (2) the e-beam energy density should not exceed the threshold of film evaporation. The fitting of optimal modes of thin-film synthesis was carried out by comparison of results of numerical simulation with the experimental data.

Calculations showed that the thresholds of the surface melting of Ti and Al targets, irradiated with LEHCEB (τ = 3 μs), are achieved at ~2.5 and ~3 J/cm², respectively, that agrees with experiments. At $E_s = 3.5$ J/cm² the thickness of the melted layer of Ti substrate is ~2 μm; herewith the lifetime of the melt is ~3 μs, and the maximum crystallization front velocity and cooling rate at the melt-solid interface are ~5 m/s and ~10⁹ K/s, respectively.

The experiments shown that the threshold of the surface melting of Ti and Al targets, irradiated with e-beam of pulse duration τ = 100 μs, is achieved at 10 J/cm². At $E_s = 13$ J/cm² the evaluated melt lifetime of Ti substrate is ~5 μm; herewith the lifetime of the melt is ~10⁻⁴ s, and maximum cooling rate after resolidification is ~10⁶ K/s, respectively.

The experiments shown that the threshold of the surface melting of Ti substrate, irradiated with e-beam of pulse duration τ = 100 μs, is achieved at 10 J/cm². At $E_s = 13$ J/cm² the evaluated melt lifetime of Ti substrate is ~5 μm; herewith the lifetime of the melt is ~10⁻⁴ s, and maximum cooling rate after resolidification is ~10⁶ K/s, respectively.

3.2. SEM/EDX observations

The SEM pictures of the surface of the samples, subjected to thin-film synthesis in the different modes are shown in Fig. 1.

At number of cycles of synthesis $N = 10$, the network of microcracks is observed at the smoothed surface. According to the EDX map analysis (30 kV) the surface alloy of average composition Ti–43 at.% Al is formed. If $N = 15$, the Al content in the surface layer increases to ~55 at.% (30 kV) and to ~64 at.% (15 kV), herewith the microcracks are also appeared (Fig. 1, a).

The EDX point analysis shown, that dark precipitations, pointed by arrows in Fig. 1, a (supposedly, TiAl₃), have Al content a few at.% more than average value. The enrichment of the near-surface layers with Al is observed in all modes of synthesis, that agrees with the Ti–Al equilibrium phase diagram [9]. The partition coefficient of an alloying element (Al) for this system is $K_0 < 1$. It means that Al during solidification will be
Modification of Material Properties

pushed out from a growing crystal and will be accumulated at the surface, as it is observed in experiment.

A further increase in the cycle number up to \(N = 40\) leads to an increase in the average Al content in the surface layer up to \(\sim 70\) at.\% (30 kV). It should be noted that the thickness of the analyzed layer is not constant, it increases with increasing Al content, i.e., with increasing a number of cycles of synthesis. Besides, with increasing number \(N\), the surface topography becomes more inhomogeneous.

The surface cracking is associated with a low ductility of Ti–Al intermetallics at room and elevated temperatures [1] and with tensile thermal stresses, induced in the surface layers during cooling in solid [6]. Selected samples, subjected to thin-film syntheses at \(N = 40\) (average composition Ti–70 at.% Al) were irradiated, in addition, to avoid cracking, using two melting modes: (1) \(\tau = 3\ \mu\text{s}, E_r = 3.5\ \text{J/cm}^2\), pulse number \(n = 3\), initial temperature \(T_0 = 680^\circ\text{C}\); (2) \(\tau = 100\ \mu\text{s}, E_r = 12.14\ \text{J/cm}^2\), \(n = 3.9\), RT. For both treatment modes, the thermal stresses in the surface layers are much less than that of induced during the synthesis process.

Experiments have shown that the surface is fully crack-free, if due to additional pulsed melting, the Al content in the surface layer does not exceed \(\sim 35\) at.\% (30 kV). But if Al content is \(\geq 35\) at.\%, the micro-cracks are formed, though its total length is much less than that of the as-synthesized state (see Figs. 1, \(a\) and \(b\)). Decreasing the Al content to avoid surface cracking is achieved by increasing the e-beam energy density and/or the number of pulses (see Fig. 1, \(c\)).

3.3. XRD examination

Figure 2 shows the XRD patterns of the Ti–Al surface alloys, synthesized in the different modes. XRD patterns contain reflections of \(\alpha\)-Ti solid solution and intermetallics Ti$_3$Al, TiAl, and TiAl$_3$.

If the number of synthesis cycles \(N = 10\), the Ti–43 at.% Al surface alloy is formed according to SEM/EDX. From the XRD pattern (Fig. 2, \(a\)), it follows that the main phase, in agreement with phase diagram, is a hexagonal Ti$_3$Al (\(\sim 85\) vol.\%). Evaluated lattice constants of Ti$_3$Al are \(a = 0.5729, c = 0.4574\ \text{nm}\); lattice strain and average coherent scattering domain (SCD) size are \(\sim 8 \cdot 10^{-3}\) and \(\sim 10\ \text{nm}\), respectively. The second phase is \(\alpha\)-Ti (\(\sim 13\) vol.\%). Besides, a weak reflection at \(20 \sim 45^\circ\), which does not overlap with other reflections, is observed. No formation of TiAl$_3$ has been observed in this synthesis mode.

In case of \(N = 15\), the Ti–55 at.% Al surface alloy is formed. Increasing Al content leads to a significant increase in the peak intensity at \(20 \sim 45^\circ\) (Fig. 2, \(b\)). This peak corresponds to the TiAl phase, and its content is \(\sim 40\) vol.\%. However, in contrast to the equilibrium ordered tetragonal TiAl phase, the tetragonal distortion ratio \((c/a)\) is close to 1.

The subsequent vacuum annealing (700°C, 1 h) leads to an increase in TiAl content (up to \(\sim 50\) vol.\%), but no significant splitting of the reflection, belonging to TiAl, has been detected (Fig. 2, \(c\)). Evaluated lattice constants of TiAl phase after annealing are \(a = 0.3984\) and \(c = 0.4011\ \text{nm}\).

In [2], the high-dose ion implantation of Al into Ti (\(\sim 10^{19}\ \text{Al cm}^{-2}\)) was used for formation of Ti$_3$Al and TiAl phases. No splitting of peak at \(20 \sim 45^\circ\), which corresponds to disordered TiAl (fcc), has been observed in the as-implanted state. The subsequent vacuum annealing (700°C) led to the transformation of metastable fcc structure to ordered tetragonal TiAl phase.

Low tetragonality of TiAl phase, formed by a thin-film synthesis followed by vacuum annealing (Fig. 2, \(c\)), can be associated with a deviation from stoichiometry or an insufficient resolution in the XRD geometry used.

The increase in the number of cycles of synthesis \((N \geq 20)\) leads to an increase in Al content in the surface alloy \(\geq 65\) at.\%. This is, in according with phase...
diagram, leads to increase in TiAl$_3$ content ($\geq 50$ vol.%) and significant decreasing of content of Ti$_3$Al and TiAl.

Figures 2, e and f show XRD patterns of the crack-free Ti–Al surface alloys, formed at the number of cycles $N = 40$ ($\sim 70$ at.% Al) followed by microsecond (at 700°C) and submillisecond (at RT) pulsed melting. As mentioned above, no microcracks has been observed at $\leq 35$ at.% Al. In both crack-free modes the Ti$_3$Al is matrix phase (76 and 96 vol.%, respectively), that agrees with the phase diagram. Despite of the lowered thermal stresses, the Ti$_3$Al phase is characterized by high lattice strain ($\sim 10^{-2}$) and small SCD size (15±20 nm).

3.4. Nanoindentation

Figure 3 shows the nanohardness depth profiles of Ti–Al surface alloys. A significant increase in hardness compared to that of Ti-substrate is observed.

If a number of synthesis cycles $N = 10$ and $N = 15$, the evaluated thickness of Ti$_3$Al/TiAl based surface layer does not exceed 1.5±2 μm. The monotonous decrease in hardness at the depth $\leq 0.5$ μm is associated with the influence of soft Ti substrate. The subsequent vacuum annealing (700°C) of the surface alloy, synthesized at $N = 15$, leads, first, to more uniform distribution of Al in the depth due to diffusion, and secondly, to decreasing the tensile stresses, induced during thin-film synthesis. As a result, the hardness increases and the hardness depth profile becomes more monotonous.

The maximum increase in the hardness (by a factor of $\sim 2.5$) and the thickness of hardened layer (up to $\sim 2$ μm) takes place in two crack-free modes, when the surface alloy of average composition of Ti–70 at.% Al, synthesized at $N = 40$, was subjected to subsequent pulsed melting by microsecond e-beam at $T_0 = 680$°C, and by submillisecond e-beam, respectively. In both modes, as follows from the data of SEM/EDX and XRD, the Ti$_3$Al based surface alloys of average composition of Ti–33 vol.% Al were formed. The evaluated Yung’s modulus of the $\sim 1$-μm-thick crack-free surface layers is 130±150 GPa, that agrees with that of Ti$_3$Al [1].

The hardness depth profile of the crack-free surface alloy, fabricated due to additional submillisecond melting, has the $\sim 1$ μm thick plateau. This is an evidence of more uniform microstructure in depth compared to as-synthesized surface alloy. The thickness correlates with the evaluated diffusion length of Al atoms into the liquid Ti.

In conclusion, using a multiple pulsed liquid-phase mixing of pre-deposited Al film with Ti substrate by LEHCEB, the surface alloy of single phase TiAl could not be synthesized, while the Ti$_3$Al based surface alloy was found to be successfully synthesized using subsequent pulsed e-beam melting, which leads to decreasing average Al content and thermal stresses. This approach can be used for fabrication the Ti$_3$Al based surface layers of $\geq 1$ μm in thickness to improve surface-sensitive properties of Ti and Ti alloys.

References