

Oxidation behavior of TiCr and TiMo alloys formed by low-energy pulsed electron beam impact

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Abstract. The titanium-based alloys with 2 – 3 at. % of chromium (TiCr) and molybdenum (TiMo) were produced on the top of titanium samples by means of the high-intense pulsed electron beam impact on the titanium with preliminary deposited Cr and Mo coatings. The TiCr and TiMo alloys were subjected to oxidation in open air atmosphere at temperature 600 °C. X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy-disperse X-ray microanalysis (EDX) were used for structure and elemental composition determination in the samples. The analysis of oxygen depth profiles showed the increase in oxygen penetration depth in the case of TiCr alloy in comparable to pure titanium. The oxygen concentration corresponding to stoichiometry of the oxide phase TiO₂ was found on the depth equaled to the thickness of the TiCr alloy that shows the enhancement of the diffusion of oxygen in the modified layer. The diffusion of oxygen at the temperature of 600 °C is enhanced by decomposition of the solid solutions based on bcc β-Ti phase with free chromium and molybdenum atoms releasing. The free molybdenum atoms take part in the stabilization of TiO₂ anatase phase while the free chromium atoms form intermetallic compound TiCr₂ preventing the sample from oxidation.

Introduction

Increase in the high-temperature oxidation resistance of different materials is an important problem in modern material science and applications [1-5]. The real practical conditions usually include the work of products in opened air atmosphere at elevated temperatures when the oxygen diffusion in the near-surface layer is enhanced by a high temperature and provides the changes in structure and phase composition of the material. It, in

turn, can result in growth of oxide film followed by flaking and cracking because of high embrittlement. The high rate of the surface oxidation influences on the mechanical properties that is usually a main reason of the products degradation and decrease in the life-time.

The high-temperature oxidation is a very crucial problem for titanium and its alloys because they are used in turbine engines which should effectively serve at elevated temperature (more than 600 °C) under a dense flow of water vapor [6-7]. There are two main ways for protection the titanium alloys from oxidation [8]: i) protective thin films and coatings deposition on the surface, and ii) alloying with additional elements that changes the structure and phase composition of titanium. Many coatings deposited by magnetron sputtering or other vacuum methods play a role of barrier which prevent the surface from the oxygen penetration. However, a lot of metal, being chosen as a protective coating, have low oxidation resistance at elevated temperatures and the boundary between the titanium substrate and the coating can possess a low adhesion strength resulting in its exfoliation. The most widespread and perspective method of the oxidation resistance improvement is to alloy with additional elements. This way allows to combine different elements and choose the optimal concentrations to save the mechanical properties and to make the structure more stable under high temperatures. Aluminum is considered as a main metal for alloying of titanium. In the presence of Al atoms, the intermetallic phases (titanium aluminides) can be grown which are reported to have a good oxidation resistance.

Another group of alloying elements for titanium contains β -stabilizing elements like Nb, Cr, Mo, W which stabilize high-temperature phase of titanium at low temperatures. Among the listed metals, Cr is more desirable element as it can form the oxide Cr_2O_3 with a high density. This oxide phase, being formed at the first stage of oxidation process, decreases the diffusion coefficient of oxygen and slows down the oxygen saturation of the surface [9-10].

Besides the alloying elements, the microstructure of the metal is assumed to play an important role in oxidation process too. For example, amorphous structure typically is reported to exhibit a higher oxidation tendency than their crystalline forms [11]. So, in the present work it was suggested to change the kinetics of titanium oxidation due to alloying with Cr or Mo atoms by means of influence of high-intensity pulsed electron beams. The pulsed electron beams treatment [12-14] as well as impact with the pulsed plasma flows [15-17] on materials is used for a long time for improving their mechanical properties because of structure and phase state changes. When applying a combined approach including the metal coating deposition and pulsed impact of the electron beams, the microstructure, phase composition and elemental composition are changed together. The technology of pulsed treatment of materials with a high energy density melts the surface layer, mixes the layers between each other's and results in fast cooling and

solidification. All mentioned processes form a disperse grain structure in the modified layer. So, the main purpose of the present work is to investigate the influence of the alloying elements (Cr and Mo) as well as microstructure dispersion after electron beam pulsed impact on the titanium behavior under the oxidation at elevated temperature.

Experimental

The plates of commercial pure titanium with a lateral size of 10×10 mm and thickness of 3 mm were used as experimental samples. Thin coatings of chromium and molybdenum were deposited on the surface of the samples by means of arc-vacuum deposition technique. The thickness of the coatings was about 1 – 2 μm.

The formed Cr/Ti and Mo/Ti systems were subjected to impact of high-intense low energy pulsed electron beams in the SOLO accelerator developed and designed at the Institute of High Current Electronics (Tomsk, Russia) [18-19]. The samples were irradiated in a vacuum chamber with pressure 10^{-2} Pa. The specimens were treated with a single pulse of low-energy electrons (20 keV), pulse duration was 100 μs. The samples were treated at the absorbed energy density 25 J/cm^2 . To reach the uniform impact of the electron beam on the surface three pulses were used for modification.

The treatment with electron beams gives the possibility to form the sub-surface alloying layers in the titanium plates saving the structure and composition in the bulk. The treated samples were oxidized in the open-air atmosphere at 600 °C during different time (up to 7 hours). The samples were placed in the chamber preheated up to the working temperature. After heat finishing, the samples were left in the furnace and they were cooling with the rate about 2 °C/min.

The elemental composition as well as phase composition and surface morphology of the titanium samples after oxidation were analyzed. The elemental composition of the treated samples was determined by means of the energy-dispersion X-ray microanalysis (EDX) in the Oxford Max^N analyser working together with the scanning-electron microscope LEO 1455 VP. The scanning electron microscopy (SEM) was also used for the surface morphology investigation. The phase composition of the oxidized layers in the titanium plates was investigated by means of the X-ray diffraction (XRD) method with Ultima IV RIGAKU diffractometer in the Bragg-Brentano geometry with parallel beams in Cu K α radiation ($\lambda=0.154178 \text{ nm}$). The range of the diffraction angles was $2\theta = 20 - 80$ degrees. The registration of the XRD patterns was made at the detector speed 2 deg/min with a step of 0.05 deg. To register narrow angular range of the diffraction and to distinguish closed reflexes the speed of the

patterns registration was decreased to 1 deg/min. The error in the lattice parameters determination with XRD method was not more than 0.1 %.

Results

Surface morphology and concentrations of elements

The influence of the high-intense pulsed electron beams with the energy density absorbed by the samples 25 J/cm^2 on the titanium with chromium and molybdenum coatings heats the surface layer above melting points of all metals. The surface of the samples melts after several tens microseconds from starting the pulse and the liquid state exists during the total pulse duration. This time is quite enough for mass transfer between the melted titanium and the melted metallic coating. Two layers of the melted metals cannot be in the equilibrium state under pulsed heating and nonuniform temperature distribution inside because of starting the hydrodynamic motions. The disturbance of the boundary between the melted layers leads to their mixing in liquid phase [20-21]. After finishing the electron beam pulse (100 μs) the two-component mixed layer begins to solidify with a high cooling rate reaching the value of $10^5 - 10^6 \text{ K/s}$. Such process provides the formation of the TiCr and TiMo alloys on the titanium surface after total cooling at room temperature. However, mixing of two metals in liquid phase during the pulse duration at the chosen regimes of the treatment is not enough for uniform distribution of Cr and Mo in the alloys. The SEM results show the presence of local areas with Cr and Mo concentrations higher in comparable with the surrounding areas. These areas with a characteristic size of 50 μm are viewed as brighter sites in the backscattering electrons detection mode (Fig. 1, 2). According to the EDX results, the average concentration of both chromium and molybdenum atoms in the formed alloys is 2 – 3 at. % and rises up to 5 – 6 at. % in the bright areas. The areas with higher metal concentration are likely to originate from capillary force arising from the difference in surface tension coefficients of titanium and chromium (or molybdenum). Indeed, the tension of the melted surface tries to pull the melted coating in small areas which are fixed after solidification of the melt. To increase the level of uniformity of mixing process we should rise the time of melted state existence that can be achieved by rising in the absorbed energy density delivering by the electron beam. But this way will provide high rate of evaporation of the melted coating and the concentration of alloying metal will significantly drop.

Heating in the air atmosphere of the samples preliminary modified under the electron beams impact results in oxidation of the surface due to diffusion activated by the elevated temperature. The EDX analysis carried out from the surface of the TiCr alloy revealed the oxygen concentration of 64 at. % in the dark areas (with lower content of Cr) and 59 at. % in the bright areas (with higher content of Cr) after 7 hours of oxidation. Taking into account a big

statistical error for light elements at EDX analysis, such as oxygen, the difference in the oxygen concentrations in the areas of the TiCr alloy seems to be quite low. The oxygen concentration on the surface of the TiMo alloy after 7 hours of oxidation is almost the same in all regions and equals to 66 – 67 at. %. The results show a weak influence of the alloying elements on the oxygen concentration.

The SEM analysis showed that the pure titanium has the same type of surface morphology after 7 hours of oxidation as before (Fig. 3a). There are no any peculiarities on the surface besides a set of chaotic oriented polishing lines. The presence of chromium and molybdenum in the titanium surface changes the morphology after oxidation. Indeed, on the surface of the TiMo alloy there is a lot of small particles with a size of 1 – 2 μm connected to new oxide phases growth (Fig. 3b). According to the EDX results, the observed particles have the same oxygen concentration as that around, but the molybdenum concentration is lower. Mo concentration in the particles is about 1.5 at. %. Taking into account the size of characteristics X-rays generation region, it can be concluded that the found concentration values almost completely characterizes the composition of the observed particles. These particles look like thin plates with tetragonal symmetry. No any such particles were found at investigation of the surface morphology of the TiCr alloy (Fig. 3c). The main change in the surface morphology of the TiCr alloy is connected to growth of a dense layer with small particles with a size less than 500 nm.

Besides the values of oxygen concentration on the surface of the oxidized titanium-based alloys, the oxygen depth distribution measured through the cross-sections by means of EDX analysis was investigated too. In the Fig. 4 the experimental oxygen depth profile in pure titanium after oxidation at temperature 600 °C during 7 hours is presented. It is clear the oxygen concentration near the surface equals 66 – 67 at. % and decreases down to zero at the depth more than 2 μm . The surface concentration of oxygen corresponds to the stoichiometric chemical composition of the titanium oxide TiO_2 . Based on the idea of solid-state diffusion under the only concentration gradient, the oxygen depth profile $C(x,t)$ is described by the well-known expression:

$$C(x,t) = C_0 \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right)$$

where C_0 is the surface concentration, D is the diffusion coefficient which is equaled to $10^{-16} \text{ m}^2/\text{s}$ for an oxygen in titanium at the temperature 600 °C [22]. The calculated oxygen depth profile for $t = 7$ hours is plotted in the Fig. 4 together with the experimental one. The presented profiles have some differences between each other. The highest calculated depth of oxygen penetration (4 μm) is more than experimental found depth (2 μm) that is a result of phase transformation from pure titanium to oxide phase occurring in the oxidized layer. The new phase

plays a role of “absorber” for oxygen atoms and prevents from their deeper penetration. According to the equilibrium titanium – oxygen state diagram, the formation of titanium oxide TiO_2 begins at the oxygen concentration exactly equals 66 at. %. So, it allows to conclude that the thickness of the oxide layer in pure titanium is not more than 1 μm after 7 hours of oxidation.

The presence of Cr and Mo atoms in the sub-surface layer of titanium in the alloys formed by electron beams impact changes the oxygen depth profile. When considering the TiCr alloy, oxygen penetration depth found by means of EDX analysis increases up to 3.5 μm . Moreover, the experimental oxygen depth profile has a great difference from the calculated one (Fig. 5). The surface concentration of oxygen saves on the constant value of 66 at. % through 2 μm inside and just after dropped down to zero value. When comparing the oxygen depth profile with the chromium distribution, it is evidently the same penetration depths. The oxygen concentration stays on the constant value through the whole depth containing the chromium atoms. Since, the chromium penetration into titanium samples occurs due to liquid phase mixing at the electron beams impact, the chromium-containing layer is a resolidified layer with dispersed grain structure [23-24]. Indeed, high cooling rate in the melted layer during the solidification results in formation a big number of crystallization nuclei and decreases in the mean size of the grains. It seems the role of grain boundary diffusion rises and becomes comparable to the ordinary inter-grain diffusion that makes the oxygen atoms move faster along the total alloyed depth.

Phase composition analysis

The titanium samples in the as-received state have the hexagonal close-packed (hcp) structure. The only low-temperature α -Ti phase with the lattice parameters $a = 0.2947$ nm and $c = 0.4684$ nm was found in the samples by the X-ray diffraction method (Fig. 6). The lattice parameters of the titanium crystal structure are close to the standard values [25].

The oxidation process at the temperature 600 °C results in changing in both structure and phase composition of the surface layer of the titanium. Heating of the titanium in a furnace at high temperatures reinforces the diffusive mobility of oxygen atoms in the solid state and provides their intensive penetration through the surface towards the bulk. After the oxidation the low-temperature hcp phase of titanium is saved without any redistribution in the intensities of diffraction reflexes from the different crystallographic planes (Fig. 6a). It indicates there is no any texture in the samples.

The XRD patterns of the titanium have some changes after oxidation. In particular, some diffraction lines have satellites, like shoulders, from the side of lower diffraction angles. It should be noted that the shoulders were found clearly only near the (002), (102) and (103)

reflexes, while the others have just small widening in the low diffraction angle side after oxidation. The observed additional diffraction reflexes can be attributed to the growth of a new phase of solid solution of oxygen atoms in the hcp titanium lattice α -Ti(O). The appearance of the shoulders near the titanium reflexes indicates the same hcp structure of the solid solution with deformed crystal lattice. The detailed registration of the diffraction lines on the patterns (Fig. 6b) shows that the relative intensity of the α -Ti(O) solid solution reflexes increases with the oxidation time.

The observed changes of the titanium structure are attributed to the oxidation process. Indeed, at the first step of the diffusion, the oxygen atoms are dissolved in the hcp crystal lattice of titanium and form a solid solution α -Ti(O) with deformed crystal lattice. The solid solution is believed to be formed as an interstitial solution where the tetrahedral pores are being occupied by the oxygen atoms. As usual, the free surface of a pure titanium is covered with a thin TiO₂ oxide layer with a thickness of several nanometers. During the oxidation process the native TiO₂ layer serves as a barrier layer and prevents the bulk part of the titanium from the oxidation. Nevertheless, at high temperature the mobility of the oxygen atoms increases and they penetrate under the TiO₂ layer and form the solid solution. When increasing in the oxidation time from 1 to 7 hours, both the oxygen concentration in the sub-surface layer and the oxygen penetration depth are increased.

The lattice parameters of the Ti and α -Ti(O) solid solution phases were calculated from the angular positions of the (110) and (103) diffraction reflexes of the diffraction patterns. The dependences of the lattice parameters (a and c) of pure titanium and the solid solution on the oxidation time are presented in Fig. 7.

The both lattice parameters a and c for pure titanium phase α -Ti weakly depend on the annealing time, remaining slightly lower than the equilibrium values. The revealed phase of pure titanium seems to be a part of the sample underneath the oxidized layer. The calculated mean oxidized depth equals to 0.8 μm after 1 hour of heating and 2.1 μm after 7 hours of heating. From the other hand, the depth of the X-rays penetration during the diffraction patterns measurement is approximately 7-8 μm . So, the obtained XRD pattern is a combination of the reflexes from both oxidized part and non-oxidized part of the titanium samples. Falling in the lattice parameters of pure titanium mentioned above is related to the concentration of point defects, vacancies, which is increased with temperature.

The highest deflection of the lattice parameter a of pure titanium from the standard values is observed in beginning of the oxidation (after 1 – 2 hours of heating). The main reason of the decrease in the lattice parameter is an excess in thermal vacancies and the residual internal stress arising during the samples preparation. After rising of the oxidation time, the vacancies

migrate towards the top oxidized layer and the residual stress disappears. So, the lattice parameter slowly grows towards the standard value. The lattice parameter c of the pure titanium leaves at the same standard value during the whole time of the oxidation.

Behavior of the lattice parameters of the α -Ti(O) solid solution has the opposite tendency. The solid solution formed after 1 – 2 hours of oxidation has the highest lattice parameter a . The oxygen atoms are occupied the pores in crystal lattice and distort it. After increasing the oxidation time there is an additional flow of vacancies from the underneath pure titanium, so, the oxygen atoms begin to occupy the vacant positions in the crystal sites. So, there two types of oxygen atoms, the first ones are located in the interstitial positions, but the least begin occupy the empty sites (vacancies) in the lattice. The latter allows to decrease in the lattice parameters of the solid solution crystal.

According to the equilibrium state diagram of Ti-O system, the low-temperature hexagonal titanium phase can dissolve oxygen with the concentration up to 30 – 35 at. % at the temperature of 600 °C. Further increase in oxygen concentration provides the phase transformation resulting in titanium oxide TiO₂ growth. Some authors indicate the presence of metastable TiO and Ti₃O₂ oxides [26] which were not found in the titanium after annealing in our experiments. These phases with a hexagonal crystal lattice can be attributed to the α -Ti(O) solid solution with different oxygen content. After 1 hour of annealing, diffraction reflections of the tetragonal rutile TiO₂ phase were found in the X-ray diffraction patterns. As annealing time increases, the intensity of these diffraction lines increases too and other lines of this phase appear. It is the result of the of the oxide layer thickness growth. It should be noted that after 7 hours of annealing, a single reflex appeared on the X-ray diffraction pattern at the diffraction angle $2\theta=25.4$ degree which was attributed to anatase modification of titanium oxide TiO₂. The small amount of the anatase TiO₂ phase can be stabilized in pure titanium by native impurities and internal stress.

The TiCr alloy was produced in the surface layer of the titanium samples by means of high-intense pulsed electron beams exposure. Before this, a thin Cr coating was deposited on the titanium surface. The parameters of the electron beams were chosen to provide the energy density enough for melting of the surface layer. The pulsed mode of the electron beam influence on a metal surface allowed to melt of the chromium coating as well as a part of titanium substrate. Then, during a pulse time, both melted metals of chromium and titanium were existing together and were mixing due to hydrodynamics motion. After finishing of the electron beam pulse, the melted layer starts to solidify. As the thickness of the melted layer is much lower than that of the bulk titanium, the crystallization occurs at high cooling rate (more than 10⁶ K/s) and high temperature gradient.

Chromium, being a beta-stabilizing element, is dissolved in the liquid phase and retains the high-temperature β -phase of titanium with a cubic bcc structure at room temperature preventing from its transition to a low-temperature hcp phase. The diffraction lines (110) at $2\theta=39.6$, (200) at $2\theta=57.9$ degree and (211) at $2\theta=72.8$ degree of β -Ti phase were found in the XRD pattern and they are shifted towards the higher diffraction angles in comparable to the standard positions [27] that indicates the formation of β -Ti(Cr) solid solution with a bcc crystal lattice (Fig. 8). The atomic radius of chromium atom is close to that of titanium atom that allows to form a substitutional solid solution based on the titanium crystal lattice with decreased lattice parameter.

During annealing at the temperature of 600 °C, redistribution of chromium atoms between the β -Ti(Cr) solid solution and low-temperature α -Ti phase takes place. After 1 and 2 hours of annealing, a shift of the diffraction lines of the β -Ti(Cr) solid solution towards larger diffraction angles is observed that shows a decrease in the lattice parameter (Fig. 9). Indeed, the lattice parameter of bcc structure in β -Ti(Cr) solid solution decreases from 0.3198 nm to 0.3182 nm being lower than that of pure β -Ti phase. In general, falling in the lattice parameter of β -Ti(Cr) solid solution in comparable to the pure β -Ti can be attributed to the formation of substitutional solid solution based on bcc crystal lattice of titanium with chromium atoms possessing lower atomic radius. The decrease in the lattice parameter after 1 – 2 hours of annealing is associated to decrease in chromium concentration in the solid solution. As the chromium concentration falls in the solid solution, it transforms into low-temperature phase that is proved by decreasing in the intensity of the corresponding diffraction lines. After 3 and more hours of annealing, there are no any diffraction reflexes of the β -Ti(Cr) solid solution on the XRD patterns. It can be a result of the solid solution decomposition with chromium atoms releasing. These chromium atoms can be distributed in the low-temperature hcp titanium phase or segregates in the grain boundaries. The concentration of the released chromium is not enough for to form a separate Cr phase observable by the XRD method. It allows to assume the decomposition of the β -Ti(Cr) solid solution with realizing of α -Ti(Cr) solid solution and intermetallic phase TiCr_2 (Laves phase). The lattice parameters of α -Ti phase, as a solid solution α -Ti(Cr), are the same as those of pure α -Ti after annealing (Fig. 9). It proves the prevailing growth of the intermetallic phase TiCr_2 . Indeed, according to the equilibrium state diagram of Cr-Ti system the chromium solubility in low-temperature titanium phase is less than 0.5 at. %. A part of the chromium atoms takes part in the intermetallic phase TiCr_2 formation. The corresponding diffraction reflexes appear in the XRD pattern after the β -Ti(Cr) solid solution decomposition after annealing during 3 hours.

The oxidation process of the sample with TiCr alloy is slightly different from the process in the pure titanium. First of all, there is no any shoulders near the α -Ti diffraction lines in the XRD spectra that were revealed during oxidation of the pure titanium. It is assumed to be a result of absence of solid solution α -Ti(O) in the sub-surface layer. The oxygen atoms diffuse through the surface layer which is a solid solution based on the bcc high-temperature phase of titanium and, due to the larger crystallographic pores, lattice deformation does not occur.

The appearance of titanium oxide TiO₂ is observed after 1 hour of annealing. However, the intensity of this diffraction line is significantly lower than that in the pure titanium. The intensity of the TiO₂ diffraction line rises with increasing the annealing time that is a result of the oxide volume fraction growth. The anatase TiO₂ phase stabilized with chromium atoms appears in the TiCr alloy after 5 hours of oxidation. The comparison of the relations between the intensities of the first reflexes of the anatase (101) and rutile (110) phases shows the larger volume fraction of anatase in the TiCr alloy in comparable to oxidized pure titanium. The formation of the oxide phase occurs in the titanium part which is resulted from β -Ti(Cr) solid solution after chromium releasing. Such process provides the motion of the chromium atoms from the lattice sites in solid solution and the sites become the vacancies which are replaced by oxygen atoms.

The influence of the pulsed electron beams on the titanium plates with the preliminary deposited Mo coating resulted in formation of TiMo alloy in the sub-surface layer. As well as chromium atoms, the molybdenum atoms are dissolved in the high-temperature β -phase of titanium and stabilize it in the form of β -Ti(Mo) solid solution with bcc structure. The molybdenum is believed to be a stronger β -stabilizing element than chromium that provide the total stabilization of high-temperature phase in the modified layer [28]. In contrast to the TiCr alloy containing both α - and β -phase of titanium, the TiMo alloy has the only β -phase that was revealed by means of XRD method (Fig. 10).

The presence of molybdenum atoms in the alloyed layer of titanium changes the structure and phase composition evolution during heating. Before the oxidation, there are only the diffraction reflexes corresponding to the β -Ti(Mo) solid solution in the XRD pattern. After 1 hour heating at the temperature 600 °C, a lot of diffraction lines corresponding to the low-temperature α -Ti phase was found in the XRD pattern. It is a result of partly decomposition of the β -Ti(Mo) solid solution with the solid solution α -Ti(Mo) formation and releasing of free molybdenum atoms. During all time of the oxidation process (up to 7 hours) the β -Ti(Mo) solid solution is saved, however, the relative intensity of its diffraction lines falls indicating the decrease in its volume fraction in the modified layer. The migration of molybdenum atoms from

the β -Ti(Mo) solid solution results in change of the lattice parameter which is weakly depends on the oxidation durations and belongs to the range 0.3201 – 0.3204 nm. The obtained values are higher than that for the β -Ti(Cr) solid solution, remaining lower than the lattice parameter for a pure β -Ti. Indeed, the atomic radius of molybdenum is higher than that of titanium and the molybdenum atoms expand the titanium crystal lattice while the chromium atoms tend to compress the lattice.

The oxidation of the TiMo alloy begins from the oxygen dissolution in the crystal lattice of the β -Ti(Mo) solid solution that provides fast rutile TiO₂ phase formation after 1 hour of heating. As well as for oxidation of the TiCr alloy, there is no any diffraction lines corresponding to the solid solution of oxygen in the crystal lattice of low-temperature titanium phase that was found before during oxidation of the pure titanium. It proved the diffusion of the oxygen atoms in the bcc β -Ti(Mo) solid solution and their interaction with α -Ti after decomposition. The main peculiarity of the TiMo alloy is the rapid growth anatase phase TiO₂ after 2 hours of the oxidation. This phase is effectively stabilized with molybdenum atoms.

Discussion

To describe the oxidation rate of titanium and the TiCr and TiMo alloys formed by the pulsed electron beams impact the relative intensities of the diffraction lines (100) of α -Ti and (110) rutile TiO₂ phases were compared. These two diffraction lines were chosen because of their close angular position in the XRD pattern that allows to make a conclusion about the relation between the volume fraction of the phases in the similar analyzed depth. The dependence of the parameter γ ($\gamma = I_{r(110)} / I_{\alpha(100)}$, where $I_{\alpha(100)}$ and $I_{r(110)}$ are the intensities of the diffraction lines (100) α -Ti and (110) rutile TiO₂ phases) on the oxidation time is presented in Fig. 11. It is viewed, the parameter γ for the oxidized pure titanium lies in the range from 0.8 to 1.0 and slowly increases with the time. It confirms the slow growth of the oxide TiO₂ (rutile) phase thickness in the analyzed layer of titanium. Alloying of titanium with chromium atoms demonstrates the drop of the parameter γ down to 0.1 – 0.4 indicating the decrease in the rate of the oxide phase formation. In contrast to chromium alloying, the formation of TiMo alloy sharply increases the oxidation rate of the surface layer where the parameter γ rises from 0.9 to 2.2 after 7 hours of annealing. The real fraction of the oxide phases in the TiMo alloy is some higher than the presented values as the anatase TiO₂ phase was not included in the calculated parameter γ . Nevertheless, the presented results show the influence of the alloying element on the oxidation resistance of titanium and demonstrate the tendency of TiMo alloy for rapid oxidizing. The Cr-contained alloy prevents the titanium from the oxidation.

It can be explained by the following way. The pulsed electron beam influences on the “Cr/Ti” and “Mo/Ti” systems and results in rapid solidification of the melted state in non-equilibrium conditions of cooling with an estimated cooling rate of $10^5 - 10^6$ K/s. In these conditions the formed solid solutions β -Ti(Cr) and β -Ti(Mo) are oversaturated with Cr and Mo atoms correspondingly where the concentrations of Cr and Mo atoms higher than that after solidification at the equilibrium conditions. The excess in the alloying elements in the titanium-based solid solutions over the equilibrium values releases from the solid solution during heating at the temperature 600 °C. It can be assumed that the Cr and Mo atoms migrate toward the grain boundaries of the bcc phase due to diffusion decreasing in the alloying elements concentration. These areas are transferred to the low-temperature α -Ti phase with hcp crystal structure. The grains of β -solid solution become surrounded with a thin layer of α -Ti phase with a thickness equaled to the mean diffusion length of chromium or molybdenum atoms in the titanium lattice. Taking into account the diffusion parameters as follows: $D_0 = 74 \cdot 10^{-4}$ cm²/s and $Q = 153$ kJ/mole (for Cr in Ti) and $D_0 = 7 \cdot 10^{-4}$ cm²/s and $Q = 155$ kJ/mole (for Mo in Ti) [29], we can calculate the mean diffusion paths for the alloying elements. Indeed, the migration distance for chromium atoms after 1-hour oxidation at temperature 600 °C equals to 1.8 μ m whereas Mo atoms migrate to the distance 0.5 μ m. Increase in the oxidation time up to 7 hours results in growth of the migration distance to 4.8 μ m (for Cr atoms) and 1.3 μ m (for Mo atoms). The results show the higher thickness of α -Ti layers in the grains in the case of chromium alloying that corresponds to the XRD data demonstrating the total decomposition of β -solid solution after 2-hours oxidation. Mo atoms obtaining the lower diffusion migration length save the β -Ti(Mo) solid solution during all time of oxidation. When segregating on the grain boundaries, chromium atoms form the intermetallic phase TiCr₂ which protect the titanium from the oxygen diffusion along the grain boundaries. The only migration path through the grains is possible. The diffusion rate in this case depends on the lattice parameters of the titanium matrix. The Mo atoms have a higher atomic radius than that of titanium and expand the crystal lattice larger than the chromium atoms. It increases the distance between the atoms and size of the interatomic pores that makes the migration of the oxygen atoms during diffusion easier. So, the TiMo alloy possesses lower oxidation resistance in comparable to the pure titanium and TiCr alloy. The oxidation of the TiCr alloy goes more slowly. The described scheme of phase transformations in TiCr alloy is presented in Fig.12.

The rutile oxide phase r -TiO₂ grows on the top of the surface where the concentration of oxygen is enough for crystal lattice transformation from α -Ti(O) solid solution to the oxide one. The lattice parameters of tetragonal rutile structure were determined according to the XRD data.

The lattice parameters (a and b) do not practically depend on the oxidation time in the investigated range. So, the parameters are $a = 0.4557$ nm and $b = 0.2960$ nm for rutile phase in pure titanium and TiMo alloy. When alloying with chromium, the rutile phase has the slightly changed parameter $b = 0.2950$ nm that can be a result of penetration of chromium atoms into the rutile crystal lattice. Indeed, having the less atomic radius, chromium atoms decrease the lattice parameters forming a structure like solid solution (Ti,Cr)O₂.

It seems that free molybdenum atoms released from the β -Ti(Mo) solid solution take part in stabilization of the anatase TiO₂ phase, while free chromium atoms released from the solid solution β -Ti(Cr) form the intermetallic compound TiCr₂. The TiCr₂ particles localized mainly on the grain boundaries decrease the rate of the grain boundary diffusion of oxygen preventing the sample from the oxidation.

Conclusion

The oxidation resistance of pure titanium, TiCr and TiMo alloys was investigated from the point of view the phase transformations. The TiCr and TiMo alloys as the alloyed top layers with a depth of 2 – 3 μ m on titanium substrate with Cr and Mo 2 – 3 at. % were synthesized by mean of high-intense pulsed electron beam impact. The oxidation process of the prepared alloys at the temperature 600 °C during a time from 1 to 7 hours showed the following:

- 1) The oxidation process of pure titanium begins from the formation of α -Ti(O) solid solution with deformed hcp crystal lattice which is transformed into rutile oxide phase TiO₂ just after 1 hour of oxidation.
- 2) The TiO₂ oxide phase in TiCr and TiMo alloys grows without formation of α -Ti(O) solid solution as the oxygen atoms migrate through the β -Ti solid solution. Mo atoms in the β -Ti(Mo) solid solution tensile the lattice increasing the rate of oxygen diffusion while Cr atoms in the β -Ti(Cr) solid solution compress the lattice prevent from the oxidation.
- 3) The released of Cr and Mo free atoms after decomposition of β -Ti(Cr) and β -Ti(Mo) solid solutions penetrate in the oxide layer and stabilize the TiO₂ anatase phase. Besides, the free chromium atoms form the intermetallic compound TiCr₂ which prevent the top layer of the TiCr alloy from the oxidation. This result shows the increase in the oxidation resistance of TiCr alloy in comparable to TiMo alloy and pure titanium.

- 4) Oxidation of TiCr and TiMo alloys based on high-temperature titanium phase and produced by high-intense electron beam impact can control the phase composition, relation between rutile and anatase phases in the top layer.

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Figure captions

Fig. 1 SEM-image of the surface of TiCr alloy after 7 hours oxidation at 600 °C (a) and the elements distribution along the line AB (b)

Fig. 2 SEM-image of the surface of TiMo alloy after 7 hours oxidation at 600 °C (a) and the elements distribution along the line AB (b)

Fig. 3. SEM-images of the surface morphology for pure titanium (a), TiMo alloy (b) and TiCr alloy (c) after 7 hours oxidation at 600 °C

Fig. 4. Oxygen depth profile in pure titanium after 7 hours oxidation at 600 °C

Fig. 5. Oxygen and chromium depth profiles in TiCr alloy after 7 hours oxidation at 600 °C

Fig. 6. XRD patterns (a) and the split diffraction reflexes of α -Ti(O) solid solution (b) for pure titanium in the as-received state (1) and after oxidation at 600 °C during 1 hour (2), 3 hours (3), 5 hours (4) and 7 hours (5)

Fig. 7. The lattice parameters of hcp structure for α -Ti and the solid solution α -Ti(O)

Fig. 8. XRD patterns (a) and the split diffraction reflexes of solid solution (b) for TiCr alloy in the as-received state (1) and after oxidation at 600 °C during 1 hour (2), 2 hours (3), 3 hours (4), 5 hours (5) and 7 hours (6)

Fig. 9. The lattice parameters of hcp structure for α -Ti in the TiCr alloy after oxidation

Fig. 10. XRD patterns (a) and the split diffraction reflexes of solid solution (b) for TiMo alloy in the as-received state (1) and after oxidation at 600 °C during 1 hour (2), 2 hours (3), 3 hours (4), 5 hours (5) and 7 hours (6)

Fig. 11. The dependence of the parameter γ ($\gamma = I_{r(110)}/I_{\alpha(100)}$) on temperature for pure titanium, TiCr and TiMo alloys

Fig. 12. The scheme of grain structure change in TiCr alloy during the oxidation

