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Surface Oxidation and Fast ^{18}O Implant Diffusion in Nanostructured Layers of Ti-6Al-4V Alloy

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A formation of the near surface barrier composite oxide film and two-stage ^{18}O implant diffusion in modified layers of Ti-6Al-4V alloy were observed in the present work. Fast and super fast regimes occur during second stage of the diffusion. Sample modification was performed using ion implantation and subsequent thermal annealing in ultra-high vacuum (UHV) atmosphere. Parameters of ion implantation are the following: $^{18}O^+$ ion energy of 30 keV; fluence of 3×10^{17} ion/cm^2; RT. Post-implantation annealing was performed in the temperature range of 100…800 °C by a step of 100 °C. SIMS and SEM techniques were applied for the sample characterisation. Effective diffusion coefficients (EDC) of ^{18}O implant were extracted from SIMS depth profiles. An Arrhenius plot of the EDC shows that ^{18}O implant diffusion in Ti-6Al-4V proceeds by the two stage mechanism: i) athermal, radiation-enhanced diffusion in range of 100-400 °C; and ii) fast, thermally activated diffusion at 500-700 °C. A super fast regime of the diffusion occurs above 800 °C. A protective composite oxide film was formed in near surface alloy layers after annealing in the temperature range of 400-600 °C. Dissolution of this film was observed at 700-800 °C. Activation enthalpy values of ^{18}O implant diffusion were obtained too. Migration of ^{18}O implant correlates with a formation of the following dielectric inclusions of a new phase that are stable up to annealing at 800 °C: particles of average size of 30 nm; and column nanocrystals oriented perpendicularly to the sample surface. Details and possible mechanisms of ^{18}O implant migration, surface oxide film formation, dielectric nanoinclusion formation and its thermal stability were discussed.

Keywords: Ti-6Al-4V alloy, Ion implantation, Thermal annealing, Oxidation, Diffusion, Nanoparticle.

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1. INTRODUCTION

A study of the radiation-induced oxidation of metals (for example, Ti, Zr) and alloys is a subject of the interest both from point of view of the fundamental and applied researches [1-7, and references therein]. Among another things, mechanisms of the oxygen diffusion and oxide layers formation in Ti, Zr, and alloys subjected to implantation with oxygen ions in different regimes are still not clear. For example, formation of thin surface rutile (TiO_2) film without oxygen vacancies on pure Ti samples were studied in [5]. The films were formed after Plasma Immersion Ion Implantation (PIII) in different regimes at elevated temperatures. A long tail of the oxygen diffusion depth profile up to a depth of about 500 nm during 1 hour annealing at 400 °C and above was detected. Original "film-substrate" interface layer was about of 15-20 nm. In [6], pure Ti samples were implanted with O ions at higher dose and temperature values ranged from – 70 to 600 °C. In the case of implantation (180 keV, 1×10^{18} O^+/cm^2, 600 °C), original Gaussian ^{18}O implant depth profile was found converted to the almost uniform depth profile layer of about 500 nm. Possible mechanisms of the fast regime of O implant diffusion to the considerable depths in works [5, 6] were not discussed.

In our particular case, Ti-6Al-4V alloy samples as an object for the study were chosen because of its wide application spectrum in the different branches of science and engineering, for example, in biomedical applications [5, 6, 9], in TOKAMAK facilities and ITER Project [7], in airspace industry, photovoltaic, catalysis [see, for example, 1 and references therein].

The main goal of the present work is to study a migration of the ^{18}O implant at elevated temperatures and microstructure of buried composite layers in Ti-6Al-4V alloy modified with ion implantation and subsequent annealing in ultra high vacuum conditions.

2. EXPERIMENTAL RESULTS AND DISCUSSION

A series of the commercial Ti-6Al-4V alloy samples (Ti64) was used for the study as plates of $1.5 \times 3.5 \times 15$ mm. A surface of the plates was mirror-like polished. The samples were implanted with $^{18}O^+$ ions in identical experimental conditions. The implantation was performed at energy of 30 keV and fluence of about 3×10^{17} atm/cm^2 at room temperature. The samples were subjected to a post-implantation annealing in UHV conditions at temperature range of 100…800 °C by a step of 100 °C. Annealing time was about 15-30 minutes.

Masse depth profiles of electropositive isotopes (hereinafter as profiles) of O, C, Ti and Al, and some of the composites of these elements were measured using SIMS technique (mass-spectrometer CAMECA IMS 5F). Cs^+ ions were used as a primary beam at accelerating voltage of about 12.4 kV. Spectra of the secondary electropositive ions were recorded. At each analytical step, the sample surface was sputtered and analyzed from a crater of about 150×150 microns. Mass-lines of the certain isotopes were chosen from the spectra for the subsequent measurement of secondary ion yield intensity as a function of the depth. An influence of the thermal annealing upon the ^{12}C, ^{16}O, ^{18}O, $^{27}Al^{16}O$, $^{48}Ti^{16}O$ SIMS profiles was studied.

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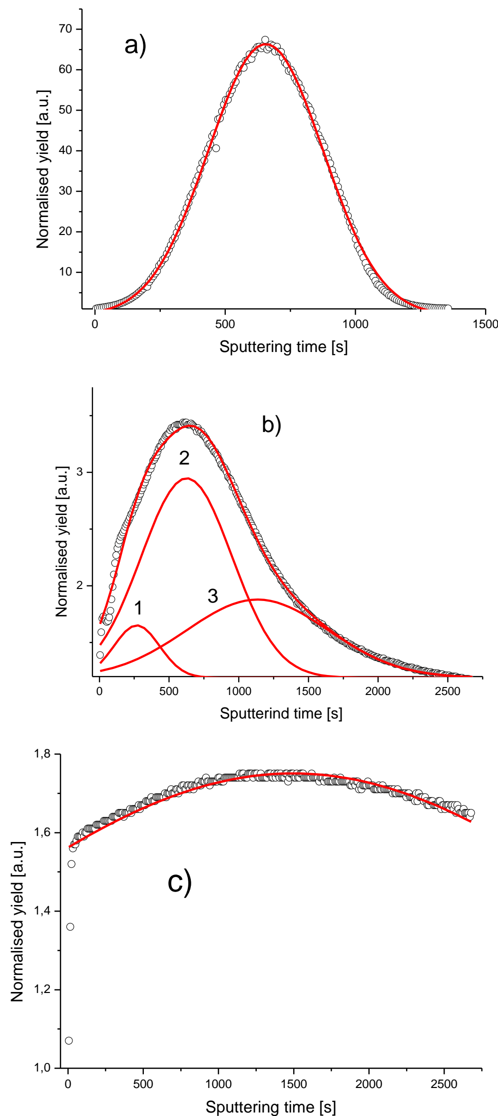

Fig. 1 – Typical SIMS depth profiles of ^{18}O implants in Ti64 alloy annealed at different elevated temperatures. Experimental distribution is dotted, fitting curves are lined

Morphology of the sample surface, crater bottoms, craters size and its depths after the SIMS analysis was analyzed using SEM technique.

Fig. 1 shows typical experimental depth profiles of secondary mass concentration of ^{18}O isotope in Ti64 alloy formed after ion implantation and post-implantation thermal annealing in vacuum at temperatures of 200 (a), 600 (b), and 800 °C (c). Normalized yield as (Y[^{16}O] – Y[^{18}O]) / Y[^{16}O] is set on the ordinate axis, Y is a secondary masses yield of $^{18}O^+$ ions; time of surface sputtering by primary ions in seconds is set on the abscises axis. Profiles of ^{18}O for temperature range up to 400 °C are fitted by one Gaussian; for the range of 500-700 °C – by superposition of three Gaussians; and for 800 °C – by a considerably broadened Gaussian function. Fig. 1a shows a typical SIMS implant depth profile measured for the sample annealed at 200 °C. Such profiles are fitted by one Gaussian and slightly differ from each other in temperature range from RT to 400 °C by a step of 100 °C. Good agreement of experimental and fitting is clearly seen. An experimental width of the distribution was normalized to the broadening parameter calculated using SRIM2008 code [9] and estimated to be ± 24 nm at projected range of Rp = 52 nm for 30 keV $^{18}O^+$ ions. Broad central distribution (Fig. 1b) with maximum concentration is attributed to the isotropic distribution of ^{18}O isotopes over the depth of implantation modified alloy layers (as well as for distribution at temperature range from RT to 400 °C by a step of 100 °C, and at 800 °C). Narrow peak at the surface is assumed to be a result of formation of fine dielectric nanoprecipitates. The peak disappears after annealing at temperature of 700 °C. The last observation, as it will be shown further, is in agreement with the results of SIMS depth analysis of $^{48}Ti^{16}O$ molecules. The partial SIMS yield of $^{48}Ti^{16}O$ forms a buried step-shaped "plateau" in SIMS depth profile. This plateau indicates a formation of the buried oxide film in the samples annealed at lower temperatures. At 700 °C, this plateau disappears. Simultaneous disappearance of the first near-surface peak (Fig. 1b) in ^{18}O depth profile and plateau of $^{48}Ti^{16}O$, $^{27}Al^{16}O$ yields in SIMS spectra may be explained by migration of isotopes of oxygen-18 into the depth and dissolution of the protective barrier surface oxide composite layer. This assumption is consistent with further evolution of the ^{18}O profile after annealing at 800 °C (see Fig. 1c). Broad deeper peak (Fig. 1b) with a tail to the sample depth could be related to the distribution of ^{18}O implant in the second type of nanoprecipitates. SEM analysis of the walls and bottom of SIMS craters demonstrates a dielectric nature of these precipitates. The inclusions have columnar form and penetrate into a considerable depth (several microns) perpendicularly to the sample surface. Charging of these nanocrystals under an analytical electron beam, its species and sizes are quite similar to those of the oxide prismatic and plated nanocrystals of micron length observed in pure Ti (VT1-00, 99.58-99.9 %) formed after Inductive Heating Oxidation at 800 °C in [8]. Such nanocrystals demonstrate an intensively grain growth from the randomly distributed point oxide structures of 30 nm in size originally formed at a 600 °C oxidation. Contrary to the results of work [8], a temperature stability of the 30 nm nanoparticles at near surface layers is the main peculiarity of our observations. Calculations of vacancy depth distribution using SRIM2008 code [9] (ions of $^{18}O^+$ with starting energy of 30 keV at normal beam incidence onto pure Ti target) predict an average depth of about 60 nm from the surface. Half-width at half-height of the distribution is substantially equal to an average size (30 nm) of dielectric nanoparticles (DNP) and thickness of the buried near-surface oxide composite film. The observed correlation indicates an enrichment DNP with ^{18}O implant. It is also proved by an effect of isotope exchange. Fig. 1b shows a considerable deviation of the experimental SIMS normalized yield (Y[^{16}O]-Y[^{18}O])/Y[^{16}O] of ^{18}O secondary ions from summary fitting curve at near-surface layers of Ti64 alloy after its sputtering with primary Cs ions. Thus, the last correlation findings demonstrate a radiation nature of the near surface nanoparticles and buried oxide composite formation.

Finally, Fig. 1c shows SIMS ^{18}O implant depth profile in Ti64 alloy after annealing in vacuum at 800 °C. Near homogeneous depth profile of oxygen, a shot time

of annealing of about 15 min and deep depth of diffusion of about 4.7 microns demonstrate super fast migration and near complete dissolution of oxygen implant over the sample depth.

Effective diffusion coefficients (EDC) of ^{18}O in a Ti64 alloy are shown on Fig. 2 as function of temperature in Arrhenius coordinates. Diffusion coefficients were extracted from the SIMS profiles of concentration distribution of oxygen-18 isotopes over the depth of the alloy modified by ion implantation. Since the SIMS profiles were fitted by the Gaussians, the diffusion coefficient was calculated in one-dimentional approximation as [10]:

$$D = \frac{\sigma_i^2 - \sigma_0^2}{2t}, \quad (2.1)$$

where σ_i is a parameter (width at half-height) of the Gaussian distribution at i-th temperature (units are in centimeters); σ_0 is a parameter of the Gaussian distribution for the as-implanted sample; t is a time of the annealing in seconds.

An Arrenious plot of diffusion coefficients (Fig. 2) inflects at a point of the annealing temperature value between 500 and 600 °C. The inflection indicates that ^{18}O implant migrates in two different ways at low-temperature and high-temperature ranges. Values of effective diffusion activation enthalpy (EDAE) were found to be 0.035 (Fig. 2.2) and 1.16 eV (Fig. 2.1) for temperature values of RT…500 °C and 600…700 °C, respectively. Athermal nature and EDAE value indicate radiation enhanced diffusion (RED) occurred at annealing temperature range of RT…500 °C. The obtained EDAE values are in a good agreement with the calculated data in [see, for example, review 11] where behaviour of vacancy-like defects was studied in amorphous metal alloys using Molecular Dynamics Simulation. For example, height of activation barriers was distributed from 0.034 to 0.08 eV in various models at medium vacancy formation energy of 0.062 eV.

A character of the diffusion coefficients dependence, and values of EDAE for 600…700 °C temperature range indicate a thermally-activated nature of the ^{18}O isotope migration. A driving force of such a migration may be a phase transition α-Ti ↔ β-Ti. The EDAE value is in a good agreement with the calculated data of [1]. Energy parameters of oxygen diffusion in α-Ti samples in various crystallographic directions are studied in this work. The value of diffusion activation enthalpy in our paper is quite close to the value of energy transition of oxygen in one of the crystallographic directions in a α-Ti cell that is 1.19 eV [1]. Referenced in this paper experimental data agree very good with the values of activation enthalpy but differ essentially from the values of diffusion coefficients.

A fast growth of the plated and prismatic oxide uniform microcrystals (at 800 °C and above) from the randomly distributed point oxide structures of 30 nm in size (formed at a 600 °C) in samples of pure Ti were observed in [8]. More enhanced growth of metal-oxide coating occurred at temperature over the phase transition of α-Ti ↔ β-Ti. Fast thermal migration of ^{18}O implant in our case may be driven by this phase transition.

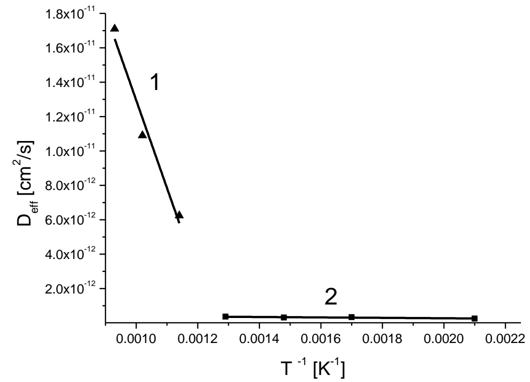

Fig. 2 – Arrhenius plot of effective diffusion coefficients of ^{18}O implants in a Ti64 alloy as a function of the post-implantation annealing temperature. Curves of different diffusion processes are numbered

O diffusion was studied in Ti (99.99 %) in [6]. Ti samples were implanted with O^+ ions at energy range 100-400 keV with fluence $1 \times 10^{17}…2.2 \times 10^{18}$ O^+/cm^2. The Gaussian distribution of oxygen was observed up to fluence 4×10^{17} O^+/cm^2. Intensive diffusion for implantation at energy of 180 keV with fluence 1×10^{18} O^+/cm^2 was observed at 400-600 °C, where oxygen completely dissolves in the explored layers at depths near 700 nm at temperature of 600 °C. Starting temperature range of fast diffusion activation is in good agreement with data of the present paper, however, temperature value of super-fast diffusion is about 200 °C less than that in our work.

In [5], the samples of pure Ti were implanted with oxygen ions by Plasma Immersion Ion Implantation (PIII) technique. Parameters of implantation are the following: pulse rate of 1 kHz; voltage of 30 kV; dose in the range of $3\text{-}24 \times 10^{17}$ cm^{-2}; temperature range of 265-550 °C. Pure rutile layer without of oxide vacancies was formed. Diffusion rate was about 0.5 micrometers per hour at temperature above 400 °C. A deep diffusion "tail" into the sample was observed at 550 °C. An activation energy value of the oxygen diffusion was found to be 0.85 eV, while that for the volume growth of rutile monocrystals (TiO_2) was to be 0.5-0.6 eV.

A temperature value (of 550 °C) when the fast diffusion of oxygen implant observed in [5] is practically the same one (of about 530 °C) of ^{18}O implant observed in our present study (see Fig. 2). In our case, the temperature value was obtained as a result of an extrapolation of the high-temperature curve of Arrhenious plot to zero point.

Two-stage diffusion of Ti implant in polycrystalline corundum (α-Al_2O_3) was also observed in our previous work [12]. Despite of quite different ion implantation regimes, ion species, matrix composition used in present work and in [12], a temperature behavior of the implant transport is quite similar. Moreover, a super-fast regime of the oxygen implant diffusion observed in present work proceeds like catastrophic oxidation of metals at elevated temperatures [see, for example, review 13].

A more detail study of the fast and super fast diffusion of oxygen in a Ti-6Al-4V alloy and other systems is required in the further works.

3. CONCLUSION

Thus, two-stage diffusion of implanted oxygen-18 isotopes in Ti-6Al-4V alloy was observed for the first time: athermal, radiation-enhanced diffusion (activation enthalpy $E_a = 0.035$ eV) at temperature range of 100-400 °C; and fast, thermally activated ($E_a = 1.16$ eV) at 500-700 °C. Thermal diffusion is characterized by fast and super-fast (at 800 °C) regimes. Atom migration proceeds simultaneously with a formation of two species of the dielectric inclusions. Fast and superfast diffusion are accompanied with ^{18}O implant migration and dissolution of a protective barrier near surface oxide composite layer. Values of the effective diffusion coefficients of ^{18}O implant, activation enthalpies are allowed to suggest a medium in which the fast and super fast migration occur. Further experiments are needed for a clarification of the fast migration mechanism and its medium, a structure and phase composition of the dielectric nano- and micro-inclusions, and growth and dissolution mechanisms of the near surface composite oxide film.

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Окисление поверхности и быстрая диффузия ^{18}O-импланта в наноструктурированных слоях сплава Ti-6Al-4V

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В настоящей работе обнаружено образование приповерхностной барьерной композитной оксидной плёнки и две стадии диффузии имплантированных изотопов ^{18}O в модифицированных слоях сплава Ti-6Al-4V. Вторая стадия диффузии протекала в быстром и сверхбыстром режимах. Модификация образцов была выполнена с использованием ионной имплантации и последующего термического отжига в сверхвысоком вакууме (СВВ). Параметры ионной имплантации: энергия ионов $^{18}O^+$ 30 кэВ; флюенс 3×10^{17} ионов/см^2; температура RT. После имплантационный отжиг был реализован при температурах в диапазоне 100…800 °C с шагом в 100 °C. Вторичная ионная масс-спектрометрия (ВИМС-SIMS) и сканирующая электронная микроскопия (СЭМ-SEM) использованы для исследования образцов. Из ВИМС-профилей была извлечена зависимость величин эффективных коэффициентов диффузии (ЭКД) импланта ^{18}O от температуры в аррениусовых координатах. Аррениусова кривая ЭКД показывает, что в сплаве Ti-6Al-4V диффузия ^{18}O-импланта протекает в две стадии: i) атермической, радиационно-стимулированной диффузии при температурах в диапазоне 100-400 °C и ii) быстрой, термически активируемой при 500-700 °C. Сверхбыстрый режим диффузии наблюдается при температуре 800 °C и выше. Защитная композитная оксидная плёнка была образована в приповерхностных слоях сплава после отжига при температурах в диапазоне 400-600 °C. Растворение этой плёнки обнаружено при 700-800 °C. Миграция ^{18}O-импланта протекает на фоне образования следующих диэлектрических включений новой фазы, стабильных вплоть до отжига при 800 °C: частиц со средним размером 30 нм; и столбчатых нанокристаллов, ориентированных перпендикулярно поверхности образцов. Обсуждаются подробности и возможный механизм миграции ^{18}O-импланта, образование поверхностной оксидной плёнки и диэлектрических нановключений, их термическая стабильность.

Ключевые слова: Сплав Ti-6Al-4V, Ионная имплантация, Термический отжиг, Окисление, Диффузия, Наночастица.

Окислення поверхні та швидка дифузія ^{18}O-імпланту в наноструктурованих шарах сплаву Ti-6Al-4V

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У даній роботі спостережено формування приповерхневої бар'єрної композитної окисної плівки та швидка дифузія імплантованих ізотопів ^{18}O в модифікованих шарах сплаву Ti-6Al-4V. Друга стадія дифузії протікає у швидкому та надшвидкому режимах. Модифікація зразків була виконана з використанням іонної імплантації та наступного термічного відпалу. Параметри іонної імплантації: енергія іонів $^{18}O^{+}$ 30 кеВ; флюенс 3×10^{17} іонів/см^2; температура RT. Після імплантаційній відпал був реалізований при температурах у діапазоні 100…800 °C з відстанню у 100 °C. Вторинна іонна масспетрометрія (ВІМС-SIMS) та скануюча електронна мікроскопія (СЕМ-SEM) виконані для дослідження зразків. З ВІМС-профілів була витягнута залежність величин ефективних коефіцієнтів дифузії (ЕКД) імпланту ^{18}O від температури у ареніусових координатах. Ареніусова крива ЕКД показує, що у сплаві Ti-6Al-4V дифузія ^{18}O-імпланту протікає у дві стадії: i) атермічної, радіаційно-прискореної дифузії при температурах у діапазоні 100-400 °C та ii) швидкої, термічно-активованої при 500-700 °C. Надшвидкий режим дифузії спостерігається при температурі 800 °C та вище. Захисна композитна окисна плівка була утворена в приповерхневих шарах сплаву після відпалу при температурах у діапазоні 400-600 °C. Розчинення цієї плівки виявлено при 700-800 °C. Міграція ^{18}O-імпланту протікає на тлі утворення наступних діелектричних включень нової фази, стабільних аж до відпалу при 800 °C: часток з середнім розміром 30 нм; і стовпчатих нанокристалів, орієнтованих перпендикулярно поверхні зразків. Обговорюються подробиці та можливий механізм міграції ^{18}O-імпланту, утворення поверхневої окисної плівки та диелектрічних нановключень, їх термічна стабільність.

Ключові слова: Сплав Ti-6Al-4V, Іонна імплантація, Термічний відпал, Окислення, Дифузія, Наночастка.

REFERENCES

1. H.H. Wu, D.R. Trinkle, *Phys. Rev. Lett.* **107**, 045504 (2011).
2. N. Bererd, N. Moncoffre, A. Chevarier, H. Jaffrezic, H. Faust, E. Balanzat, *Nucl. Instrum. Meth. B* **249**, 513 (2006).
3. D. Corse-Pomonti, N.-L. Do, N. Bererd, N. Moncoffre, G. Baldinozzi, *Mater. Res. Soc. Symp. Proc.* **1514** No 11 (2013).
4. T. Roller, W. Bolse, *Phys. Rev. B* **75**, 054107 (2007).
5. G. Thorwarth, S. Mandl, B. Rauschenbach, *Surf. Coat. Tech.* **136**, 236 (2001).
6. C. Hammerl, Y. Bohne, W. Assmann, K. Helming, B. Rauschenbach, *Nucl. Instrum. Meth. B* **206**, 1072 (2003).
7. J.W. Davis, M.A. Ulrickson, R.A. Causey, *J. Nucl. Mater.* **212-215**, 813 (1994).
8. A.A. Fomin, A.B. Steihauer, I.V. Rodionov, M.A. Fomina, A.M. Zakharevich, *Tech. Phys. Lett+* **39** No 11, 969 (2013).
9. J.F. Ziegler, J.P. Biersack, M.D. Ziegler, http://www.lulu.com/content/1524197.
10. J. Philibert, *Atom Movements. Diffusion and Mass Transport in Solids* (Paris: Les Editions de Physique. Les Ulis: 1991).
11. D.K. Belashchenko, *Phys-Usp+* **42**, 297 (1999).
12. S.M. Duvanov, A.G. Balogh, *Nucl. Instrum. Meth. B* **171**, 475 (2000).
13. V.V. Belousov, *Russ. Chem. Rev.* **67** No 7, 563 (1998).