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Regularities of Formation of the Ordered Structures in Refractory Metals at Ion Implantation

**Riza B. Abylkalykova
Ludmila I. Kveglis* and Khamza R. Kazdaev**
*Siberian Federal University
79 Svobodny, Krasnoyarsk, 660041 Russia¹*

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Is shown, that the character of structural – phase transformations in tungsten and tantalum at ion implantation by the elements of the interstitial phase is defined, in the main, by the size factor, i.e. by the ratio of the atomic sizes of implanted elements and atoms of metal. The researches are carried out on tungsten and tantalum monocrystals at implantation by ions of, N, O, P.

Keywords: Ion implantation, structural – phase transformations, refractory metals, the size factor, the Hagg's rule, close-packed structures, Subsequent annealing, concentration profiles.

The purpose of the research is to study the mechanisms of structural and phase transformations in superficial layers of transitive metals at ion implantation and further heat treatment. As base methods of the structure research of irradiated and non-irradiated materials have been used the approved methods of X-ray-structure analysis with the use of narrow sliding monochromatic CuK_α -radiation and method of Rutherford backscattering (RBS). The experimental results allow to make the following conclusions: the basic laws of structural and phase transformations in the transitive metals (tungsten and tantalum) are established at their implantation by the ions of the elements which form introduction phases (nitrogen, oxygen and phosphorus); it is revealed that the mechanism of structural and phase transformations is determined, generally by the dimensional factor and slightly depends on physical and chemical properties and kinetic parameters of bombarding elements; it is revealed that the implantation of tungsten and tantalum by oxygen ions results in formation of highly packed structures which have been identified in the work as W_2O and TaO oxides.

Introduction

Theoretical and experimental researches on ion-beam alloying metals show the great possibilities of the method of irradiation treatment in modification of the surface properties of materials [1]. Of particular interest are coatings on refractory metals, obtained by ion implantation. For example,

* Corresponding author E-mail address: kveglis@list.ru

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refractory metals and their alloys, having the greatest resistance to erosion, are among the promising materials for structural components of fusion reactor (diverter plates, first wall, etc.) [2].

Tungsten has a minimum coefficient of dispersion and has the greatest strength in a wide range of temperatures. From this it follows that the materials and alloys, modified by method of implant metallurgy, may be among the first structural materials capable of working in extreme conditions.

Experimental data on ion implantation are rather contradictory. Since the method of ion implantation is thermodynamically non-equilibrium, synthesized structures can be metastable, as observed in the experiment. In other methods metastable phases are produced by quenching. Tempering is one of the ways obtaining metastable state due to rapid cooling of high-temperature phases. Ion synthesis leads to the emergence along the track of an introduced particle or at its end high-temperature regions, solidifying at high speed. As a result, can be formed metallic glasses – metastable phases with a stable structural condition. Introduced ions carry with them a high energy, leading to restructuring in localized areas [3].

For ion synthesis of compounds with certain defined stoichiometry the following conditions should be satisfied. First, it is getting respective concentrations in the ion-implanted layers, which is impeded by the processes of sputtering and swelling of the surface layers, which in this case may be limiting the method used. Secondly, this is accounting of diffusion processes, which in most cases are beyond the control and you can not save the achieved values of concentration in process of heating to temperatures of phase transformations.

Many works were carried out only on thin films, whose thickness is comparable with the depth of alloying impurities. The results obtained on films, may differ from similar data on bulk samples [4]. In this connection a natural question arises about the possibilities of ion implantation in terms of synthesis of compounds with a given stoichiometric composition and structure in the surface layers of materials.

The purpose of work is the study of solid state reactions in the surface layers of bulk samples of refractory metals by ion implantation and subsequent heat treatment.

Samples and Research Methods

For research on ion doping have been used single-crystal samples of polycrystalline tungsten and tantalum purity 99.96 %. Tungsten samples were cut on a plane (110) in the form of rectangular dimensions of $8 \times 1,5 \times 1 \text{ mm}^3$, samples of tantalum – with dimensions of $8 \times 1,5 \times 0,5 \text{ mm}^3$. In order to remove the deformed layers of samples after mechanical treatment they were subjected to electrochemical polishing. Ion implantation of nitrogen and oxygen with energies of 70 and 80 keV, respectively, was conducted in a vacuum $\sim 1,3 \times 10^{-3} \text{ Pa}$ at current densities not exceeding $1 \text{ mA} \times \text{cm}^{-2}$. Implantation doses were chosen as follows: $1,87 \times 10^{17}$, $3,74 \times 10^{17}$ and $5,6 \times 10^{17} \text{ ion/cm}^2$. The energies of ions were chosen in such a way as to ensure approximately the same calculated profiles of distribution without spraying. To bring into equilibrium the samples were thermally annealed in vacuum ($6,6 \times 10^{-3} \text{ Pa}$) through the 100°C in temperature range $500\text{-}1100^\circ\text{C}$ with exposure for 1 hour. To study the structure of irradiated and unirradiated materials methods of X-ray analysis with a narrow beam of monochromatized CuK_α -radiation were used. For the spatial distribution of the implanted impurity the method of Rutherford backscattering was used. This method is based on the ability to record the difference in energy of particles scattered from

the atoms, which are on the surface and at a certain depth. Experiments were carried out at RBS protons with energies of 500 keV on the accelerator UKP-2-1, on which the method of Rutherford backscattering of heavy elements was applied [5].

Experiment

Implantation of nitrogen ions in tungsten led to the emergence of a distinct set of tungsten X-ray reflections from textured (with traces of polycrystalline) phase of tungsten nitride W_2N with a close-packed FCC lattice. In textured state, it appears already at doses of $1.87 \times 10^{17} \text{ cm}^{-2}$ and $3.7 \times 10^{17} \text{ cm}^{-2}$ and, with increasing dose up to $5.6 \times 10^{17} \text{ cm}^{-2}$ passes in the polycrystalline state. According to the literature [6], among the known nitride single phase, having a close-packed structure is W_2N . Implantation of nitrogen leads to the formation of a phase W_2N with an FCC lattice, although use a set of large doses would be expected appearance WN phases with higher nitrogen content. Annealing after implantation of tungsten spacemen by oxygen, does not introduce specific changes in the observed pattern until 900°C . When this temperature is reached in the diffraction patterns an additional set of lines from the polycrystalline phase of WO_3 with a hexagonal lattice arises. Subsequent annealing at 1000°C leads to the decay of WO_3 phase and the appearance instead of it polycrystalline tungsten carbide $\gamma\text{-}W_2C$ with a hexagonal lattice. There is every reason to believe that new phase, formed in process of implantation of oxygen ions, is a tungsten oxide W_2O by analogy with the structure W_2N . The lattice parameter of this phase, as calculated by the weak lines of polycrystalline component amounted to 4.155 \AA . According to the literature [6] WO system is characterized by the presence of a number of oxides WO_2 , $W_{18}O_{49}$, $W_{20}O_{58}$, WO_3 and etc, among which the structure we found is not present. Annealing at 1100°C leads to the disappearance of x-ray reflections from the observed phases (see Table 1). Phase structure W_2N , having a face-centred cubic lattice that appears at implantation, during annealing continues. In process of oxygen implantation phase appears only in the textured state and remains in that form during annealing. Table 1 shows the main results on the structural-phase transformations, obtained using X-ray analysis.

Spectra RBS from surface samples of the tungsten implanted by ions of nitrogen and oxygen (Fig. 1 and 2, accordingly) showed, that concentration of nitrogen and oxygen in investigated layers reaches certain level. The spectrums of RBS for three samples: initial state, after implantation with a dose $1.87 \times 10^{17} \text{ cm}^{-2}$ and $3.74 \times 10^{17} \text{ cm}^{-2}$ are represented on Fig. 1a. Maximum of a curve of distribution at Fig. 1 shows that the introduced ions are located (in 2.6 times) more deeply in comparison with

Table 1. Phase transformations in ion-implanted tungsten (r_x/r_w – the ratio of atomic size of the implant to the atomic radius of tungsten)

Ion	E_s , keV	Phase	Structure	temperature, $^\circ\text{C}$		r_x/r_w
				formation	decay	
N	70	W_2N WO_3	fcc. monoclinic	at implantation	>1100	0,50
				900	>1100	
O	80	W_2O WO_3 $\gamma\text{-}W_2C$	fcc. hcp. hcp.	at implantation	>1100	0,43
				900	1000	
				1000	>1100	

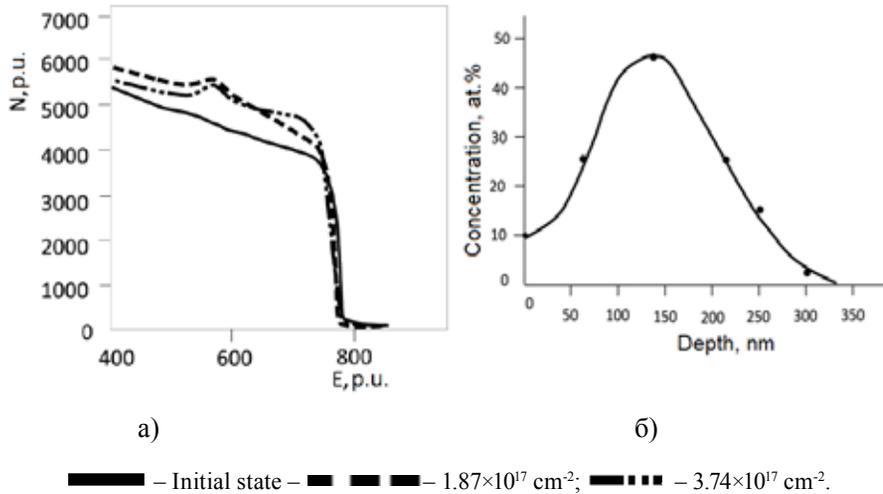


Fig. 1. a) – Spectra of a dispersion of backscattering protons from surface W, introduced by ions N^+ ; (b) – Distribution of the depth of nitrogen in tungsten with a dose $1.87 \times 10^{17} \text{ cm}^{-2}$

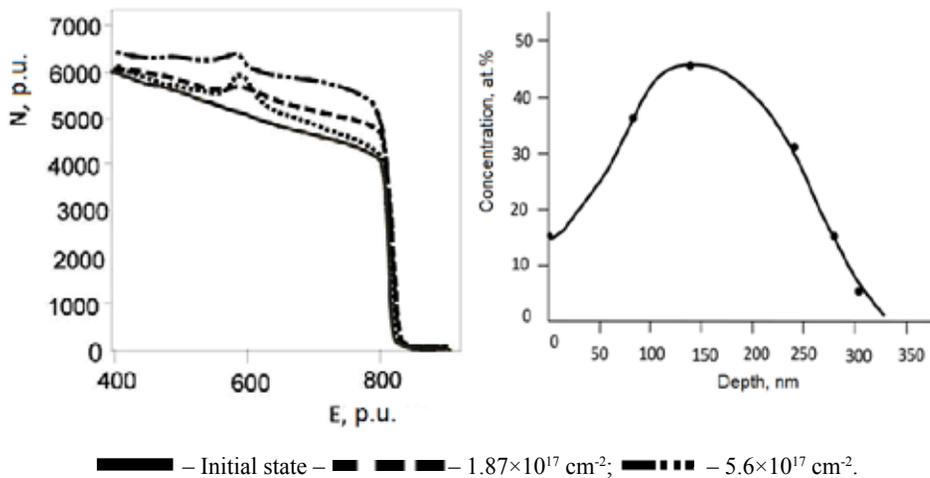


Fig. 2. a) – Spectra of a dispersion of backscattering protons from surface W, introduced by ions O^+ ; (b) – Distribution of the depth of oxygen in tungsten with a dose $3.74 \times 10^{17} \text{ cm}^{-2}$

projective value. From character of spectra RBS it is possible to make the conclusion that the reactionary diffusion occurred as a result of ionic implantation in the areas located in an interval between a surface zone and a zone, considerably removed from a surface of the sample.

After implantation of nitrogen ions in the diffraction patterns of tantalum appears polycrystalline phase – tantalum nitride TaN with a close-packed FCC lattice. Along with this phase the set of weak lines from carbide of tantalum TaC with a FCC-lattice ($a=4.4547 \text{ \AA}$) is registered, arising from the implantation of carbon from the atmosphere of the residual gas of the accelerator.

Annealing at 1000°C leads to the formation of a phase Ta_2C ($a = 3.1046 \text{ \AA}$, $a = 4.9444 \text{ \AA}$), which arises as a result of partial carbonization of sample surface in an atmosphere of residual gas furnace.

The ratio of atomic size of nitrogen to the atomic radius of tantalum $r_x/r_{Ta} = 0.48$. This is consistent with the Hagg's rule, according to which, if the ratio of non-metal atomic radius (r_{nm}) to the radius of the metal (r_m) is less than the critical size (~ 0.59), then there are simple structures that constitute the implementation phase in the lattice of metal atoms [7]. In process of implantation of nitrogen in samples of tantalum a simple connection with TaN packed with face-centred cubic lattice was obtained, although at low doses at first appearance Ta_2N phase with lower nitrogen content would be expected. Among the known nitride single phase, having a close-packed structure is the phase TaN. The maximum distribution of nitrogen in tantalum has a depth of about 190-195 nm, which is 2.7 times deeper than the calculated data. Thus, the implantation of nitrogen ions in bulk samples of tantalum has led to the synthesis of polycrystalline phases of TaN and TaC, and in addition to the formation of polycrystalline phase Ta_2C appearing as a result of tantalum surfaces carbidization in an atmosphere of residual gas furnace.

With the introduction of oxygen ions already at a dose of $\Phi_1 = 1.87 \times 10^{17} \text{cm}^{-2}$ on X-ray diffraction picture arise reflexions from a polycrystalline phase with a FCC-lattice ($a = 4.24 \text{ \AA}$). The quantity of this phase increases with increase in a dose of implantation. In addition, registered tantalum carbide TaC with the FCC lattice, are due to recoil implantation method of carbon from the atmosphere of the residual gas of the accelerator. Subsequent annealing at 800°C led to the formation of phase $\beta\text{-Ta}_2\text{S}$, which is not falling apart in the process of annealing. The ratio of atomic radius of oxygen to the atomic radius of tantalum $r_o/r_{Ta} = 0.41$. In this case, the intrusion phase is formed with a close-packed FCC lattice, similar in structure and parameters to TaN. In the case of nitrogen the formation of tantalum carbide in the first case occurs when 1000°C , whereas in the samples implanted with oxygen, this process begins at 800°C . There is every reason to suppose that the phase arising at implantation of tantalum by ions of oxygen is a tantalum oxide TaO with FCC lattice that is an analogue of phase TaN, in which the nitrogen atoms are replaced by oxygen atoms. According to published data system tantalum – oxygen is characterized by the presence of a number of oxides (Ta_2O_5 , TaO, TaO_2 , $Ta_{0.83}O_2$, TaO, $Ta_{0.97}O_2$ and TaO_x), among which the structure discovered by us is not present.

Dose dependence of Rutherford backscattering spectra for samples of tantalum implanted by nitrogen ions show that the nitrogen concentration in the implanted layers reaches a certain level, above which there is the process of ousting it in a neighbouring region with a lower concentration. Concentration profiles of the distribution of oxygen in tantalum are similar to the curves of distribution of nitrogen in tantalum. Thus, the previously unknown phase obtained by implantation of tantalum by oxygen ions in certain settings, exposure, identified as tantalum oxide TaO, which is an analogue of tantalum nitride TaN. Comparison of results on the formation of oxides in this section with the experimental results of other authors leads to conclusion that the observed phase TaO is synthesized for the first time by us. Primarily attention is drawn to the fact that the nature of the formation of compounds with the implantation of different elements depends on the type of ion being implanted. In the case of nitrogen and oxygen phases occur directly in the process of implantation. This gives rise to compounds with close-packed structures and represent a high-temperature phase, which under certain annealing temperatures disintegrate (see Table 2). The introduction of ions is usually accompanied by the formation of carbides with close-packed structures; nature of proceeding with the implantation process depends primarily on nuclear size introduced elements. In process of their increase we observe

Table 2. Phase transformations in ion-implanted tantalum (r_x / r_{Ta} – the ratio of atomic size of the implant to the atomic radius of tantalum)

Ion	E, keV	Phase	Structure	temperature, °C		r_x/r_{Ta}
				formation	decay	
N	70	TaN	fcc.	at implantation	>1100	0,48
		TaC	fcc.	at implantation	>1100	
		β -Ta ₂ C	hcp.	1000	>1100	
O	80	TaO	fcc.	at implantation	>1100	0,41
		TaC	fcc.	at implantation	>1100	
		β -Ta ₂ C	hcp.	800	>1100	

either formation of interstitial phases directly during implantation (nitrogen, oxygen), or disordered investigated layers with subsequent synthesis of the compound only when the temperature exceeds a certain threshold.

Identified patterns correlate well with the Hagg's rule, comparing the distinctive features of the formation of interstitial phases with identified in this study the regularities of structural and phase transformations during ion implantation may be noted that a decisive role in the investigated processes during the implantation process is size factor. Indeed, the implantation of carbon, nitrogen and oxygen in tungsten ($\eta_{C/W}=0.55$; $\eta_{N/W}=0.50$; $\eta_{O/W}=0.43$) and tantalum ($\eta_{C/Ta}=0.52$; $\eta_{N/Ta}=0.48$; $\eta_{O/Ta}=0.41$), simple close-packed structures are formed. In a case of phosphorus ($\eta_{P/W}=0.77$; $\eta_{P/Ta}=0.74$), conforming phosphides are formed only after additional annealing [7].

Conclusion

If the radius of the atoms of introduced non-metals satisfies the Hagg's rule, solid solutions or compounds of implantation, having simple close-packed structures are formed. Particular type of received phases in terms of stoichiometric composition will be determined largely by reached concentrations of implanted atoms and the presence of compounds in the relevant phase diagrams. However, because of the broad areas of homogeneity, the formation of these compounds should be observed in a relatively large range of doses.

1. With increasing ratio of atomic sizes of implanted elements and the matrix elements are consistently observed: the formation of superstructures, polymorphic transformation with the emergence of simple close-packed structures and, finally, the disordering of the lattice of the matrix up to the amorphization of implanted layers.

2. First synthesized phase W₂O and TaO with the FCC lattice. It means, that method of ion implantation can create a denser structure, and therefore more durable and resistant to damage of different nature.

3. Ion implantation in tungsten and tantalum is accompanied by the formation of carbides of tungsten and tantalum with close-packed structures which occur at the expense of implanting carbon residual gas accelerator.

4. The possibility of forecasting the properties of the irradiated surface due to purposeful management of solid-phase reaction.

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Закономерности образования упорядоченных структур в тугоплавких металлах при ионной имплантации

**Р.Б. Абылкалыкова,
Л.И. Квеглис, Х.Р. Каздаев**
*Сибирский федеральный университет,
Россия 660041, Красноярск, пр. Свободный, 79*

Показано, что характер структурно-фазовых превращений в вольфраме и тантале при имплантации их элементами, образующими фазы внедрения, в основном, определяется размерным фактором, который находят отношением атомных радиусов имплантированного элемента к атомному радиусу металла. Исследования проведены на монокристаллических образцах вольфрама и тантала, имплантированных ионами N, O, P.

Ключевые слова: ионная имплантация, структурно-фазовые превращения, тугоплавкие металлы, размерный фактор, правило Хэгга, плотноупакованные структуры, последующий отжиг, концентрационные профили.
