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Vasyl Trush [1], Viktor Fedirko [2], Aleksander Luk'yanenko [3], Petro Stoev [4], Mykhail Tikhonovsky [5], Kostiantyn Kovtun [6]

1. Department of material science fundamentals of surface engineering, Karpenko Physico-Mechanical institute of the National Academy of Sciences of Ukraine, Ukraine, Lviv, Naukova street 5, E-mail: trushvasyl@gmail.com, ORCID 0000-0002-2264-3918
2. Department of material science fundamentals of surface engineering, Karpenko Physico-Mechanical institute of the National Academy of Sciences of Ukraine, Ukraine, Lviv, Naukova street 5, E-mail: fedirko@ipm.lviv.ua, ORCID 0000-0002-4337-1691
3. Department of material science fundamentals of surface engineering, Karpenko Physico-Mechanical institute of the National Academy of Sciences of Ukraine, Ukraine, Lviv, Naukova street 5, E-mail: AGNSLukyanenko@I.UA, ORCID 0000-0001-6642-2300
4. Department of pure metals, physics of metals and technology of new materials, Institute of Solid State Physics Materials and Technologies, National Science Center «Kharkov Institute of Physics and Technology» of the National Academy of Sciences of Ukraine, Ukraine, Kharkov, Akademichna Street 1, E-mail: stoev@kipt.kharkov.ua, ORCID 0000-0001-7942-5850
5. Department of pure metals, physics of metals and technology of new materials, Institute of Solid State Physics Materials and Technologies, National Science Center «Kharkov Institute of Physics and Technology» of the National Academy of Sciences of Ukraine, Ukraine, Kharkov, Akademichna Street 1, E-mail: tikhonovsky@kipt.kharkov.ua, ORCID 0000-0001-5889-0366
6. Department of pure metals, physics of metals and technology of new materials, Institute of Solid State Physics Materials and Technologies, National Science Center «Kharkov Institute of Physics and Technology» of the National Academy of Sciences of Ukraine, Ukraine, Kharkov, Akademichna Street 1, E-mail: kkovtun@kipt.kharkov.ua, ORCID 0000-0002-0524-5053

DIFFERENCES OF THE EFFECT OF THERMAL TREATMENT IN AN OXYGEN-CONTAINING GAS MEDIUM ON PROPERTIES OF THE SURFACE LAYER Ti, Zr, Hf

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Abstract. The paper presents the characteristics of the surface layer of d-elements of the IV group (titanium, zirconium and hafnium) after thermal diffusion saturation from a controlled oxygen-containing gas medium. Saturation was carried out at T = 750 °C for τ = 5 hours at different pressures ($P = 1.33 \cdot 10^{-1}$ Pa, $P = 1.33 \cdot 10^{-2}$ Pa, $P = 1.33 \cdot 10^{-3}$ Pa). Experimentally revealed differences in the characteristics of the surface layer of titanium, zirconium and hafnium.

It was shown that a hardened diffuse layer is formed with a higher hardness relative to the metal core in the reverse order of their affinity for oxygen. On titanium, zirconium and hafnium, only a diffuse layer is formed without a phase film. The appearance of the surface of the samples before and after processing is given.

According to the results of the study, chemical-thermal treatment in an oxygen-containing gas medium leads to changes in the surface layer of sheet material from titanium, zirconium and hafnium. The state of the surface layers directly affects the characteristics of finished products, in particular, fatigue life. Therefore, this treatment is a good tool for controlling the state of the surface layers of the aforementioned metals, and then their properties.

Keywords: titanium, zirconium hafnium, oxygen medium, surface layer, microhardness.

Introduction

Titanium, zirconium and hafnium together form a magnificent trio of chemically active metals, whose chemical properties are very similar. Their industrial development coincides with the growth of high-tech industries such as aerospace, nuclear energy and chemical engineering. Despite the fact that their chemical properties are very similar, however, differences in physical properties provide for their fundamentally different applications. Titanium-based alloys have a low specific gravity and, combined with good mechanical properties and high corrosion resistance, make them indispensable in aerospace engineering. Zirconium and hafnium are twin metals, but their use in the reactor core is the opposite. Zirconium does not retain neutrons, and on the contrary, hafnium absorbs (Table 1). Therefore, zirconium alloys are used to make the shells of fuel elements (fuel elements), and hafnium serves as the basis for the creation of control rods and emergency protection of nuclear reactors [1]–[5].

Table 1

Main characteristics of titanium, zirconium, hafnium [4]

Characteristic	Ti	Zr	Hf
Atomic number	22	40	72
Density, g/cm^2	4.5	6.49	13.09
Atom radius, nm	0.146	0.160	0.159
Solubility of interstitial elements in the α phase, at.%:			
oxygen	33	27	18
nitrogen	23	22	29
carbon	3	3	3
Polymorphic transformation temperature (α → β), °C	882	862	1777
Thermal neutron capture cross section, barn	5.6	0.18	115
Melting point, °C	1665	1855	2225
The coefficient of thermal expansion at 20 °C, 10^{-4} K^{-1}	8.5	5.8	115
Enthalpy of formation, kcal/mol:			
oxides	–249	–262	–270
nitrides	–73	–82	–88
carbides	–54	–44	–44
Young's modulus at 20 °C, MPa	108 000	98 000	140 000

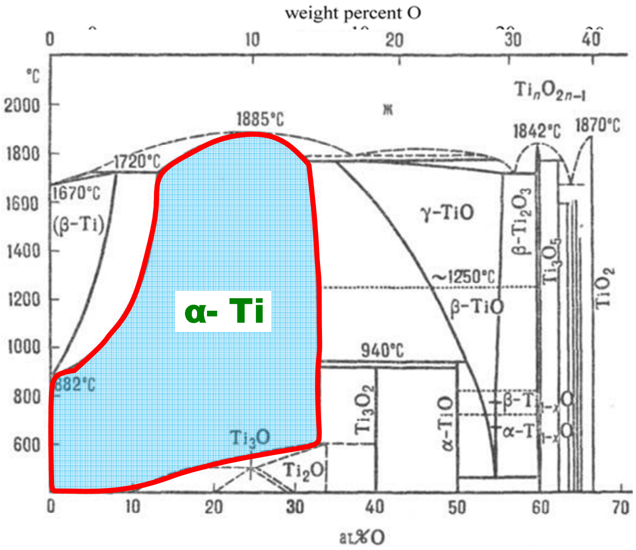
Problem formulation

Titanium, zirconium, hafnium have many similar properties: exist in two versions (low temperature – hexagonal lattice densely packed, high temperature – body centered lattice), have high affinity for the elements of the embodiment, high corrosion ability etc.

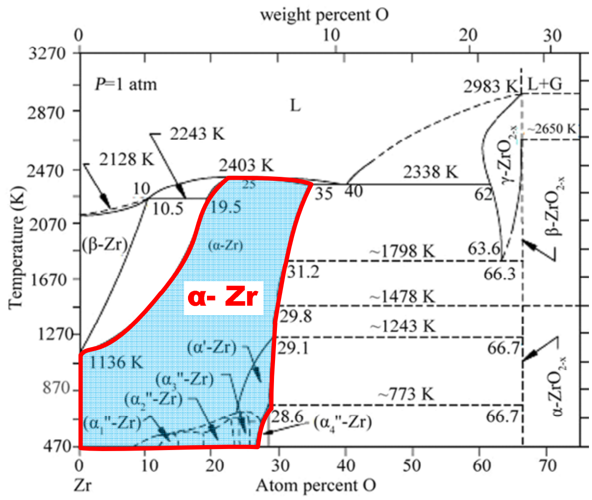
However, there are a number of factors that significantly affect the properties of the above alloys. One of these factors is the high reactivity to interstitial elements (oxygen, nitrogen, carbon). Of particular practical importance is the solubility of oxygen in titanium, zirconium and hafnium. According to the state diagram, the highest solubility of oxygen in the α-region is in titanium –33 at. %, zirconium – 27 at. % and the smallest solubility is in hafnium – 18 at. % (Fig. 1). The literature also indicates the diffusion coefficients of oxygen in titanium, zirconium and hafnium (Fig. 2).

According to the literature and technical literature, oxygen affects the physical and mechanical properties. Therefore, the high solubility of oxygen in titanium, zirconium and hafnium makes alloys of the Ti-O system Zr-O, Hf-O very promising from the point of view of the practical use of oxygen doping as a method of controlling the structure and properties of the above metals and their alloys.

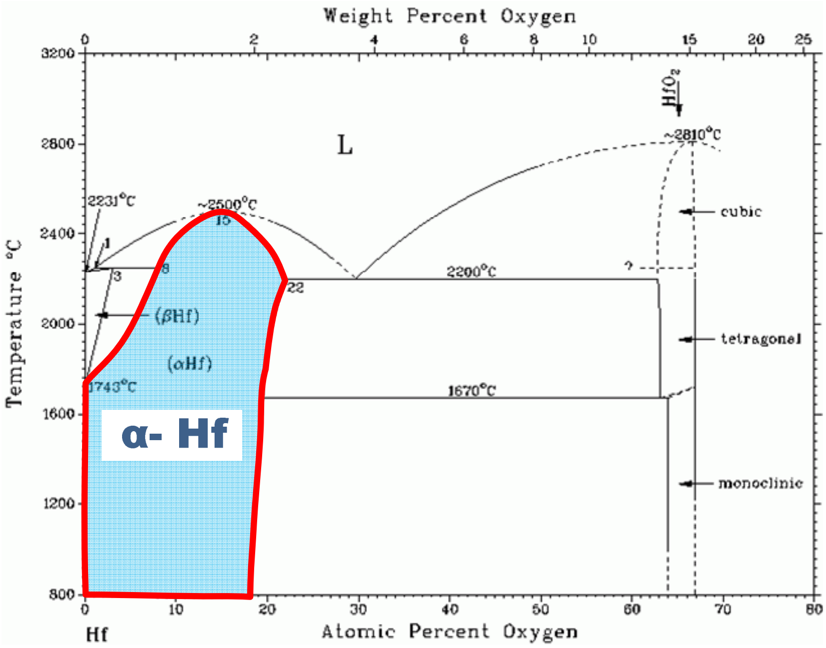
Of the elements introduced in these three metals, only oxygen is considered not only as a harmful impurity, but also as an alloying element. In addition, it should be noted that dissolved oxygen in a metal is capable of affecting the dissolution of, for example, hydrogen. That is, oxidation affects the saturation of hydrogen, for example zirconium plumbing pipes [7]–[8].



a



b



c

Fig. 1. State diagram: a – "Ti – O", b – "Zr – O", c – "Hf – O" [4]

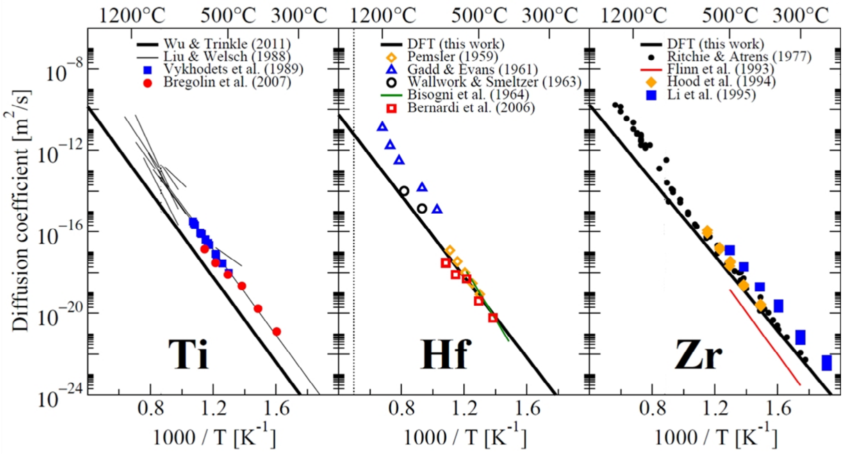
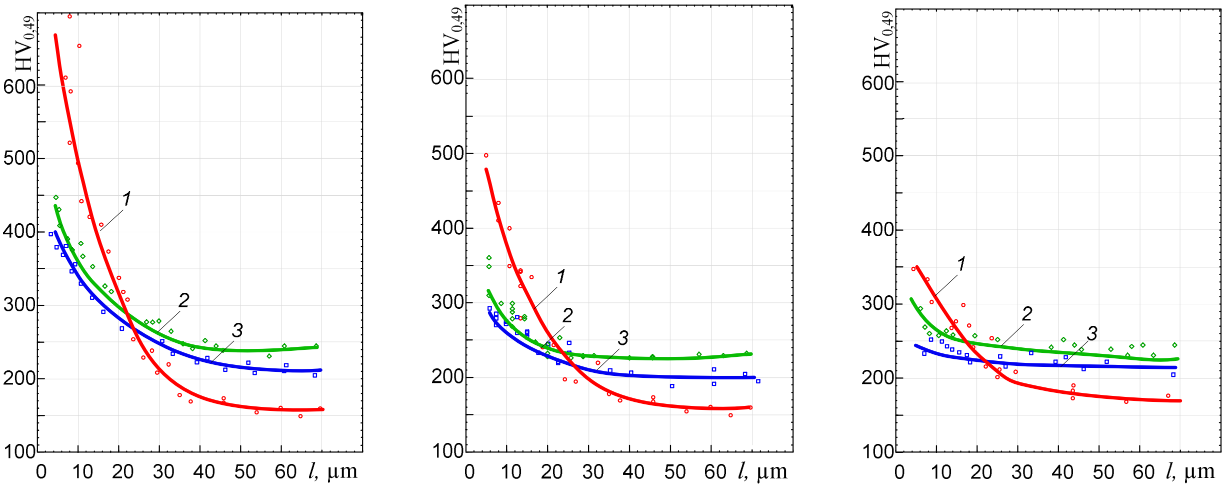


Fig. 2. Diffusion coefficients of oxygen in Ti, Zr, Hf

Main material presentation

Therefore, the aim of the work is to establish the effect of diffusion saturation in a controlled oxygen-containing gas medium by different rarefaction on the surface condition and on the size of the surface diffusion hardened metal layer of samples of thin-sheet (~ 1 mm) titanium VT1-0, zirconium Zr1%Nb and hafnium alloy HFE-1. Saturation was carried out with T = 750 °C for τ = 5 h at different pressures (mode *R1* – $P = 1.33 \cdot 10^{-1}$ Pa, mode *R2* – $P = 1.33 \cdot 10^{-2}$ Pa, mode *R3* – $P = 1.33 \cdot 10^{-3}$ Pa). The hardness of the samples was determined under the load of 0.49 N.

According to experimental research results, the degree of rarefaction affects the distribution of hardness in the surface layer on titanium, zirconium and hafnium (Fig. 3).



a b c

Fig. 3. The distribution of microhardness over the cross section of alloy samples after treatment for the modes *R1* (a), *R2* (b), *R3* (c): 1 – VT1-0; 2 – Zr1%Nb; 3 – HfE-1

Such research results are consistent with the ability of oxygen to dissolve in titanium, zirconium and hafnium. According to the results of the study, the treatment of titanium, zirconium and hafnium with the specified treatment regimes does not lead to significant changes on the metal surface (Table 2). This can be explained by a low processing temperature and a short processing time.

Table 2

The surface of the samples before and after quitting in an oxygen-containing gas medium

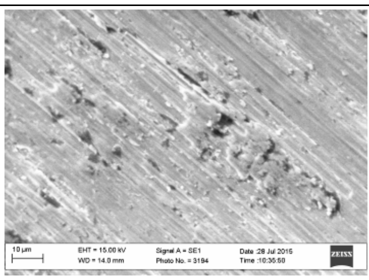
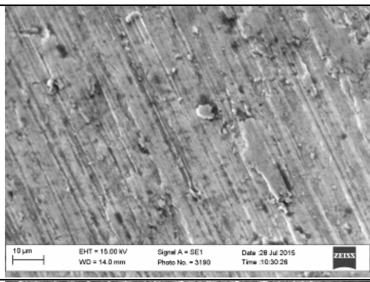
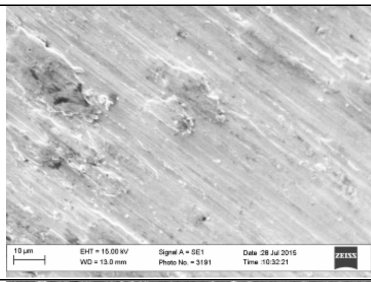
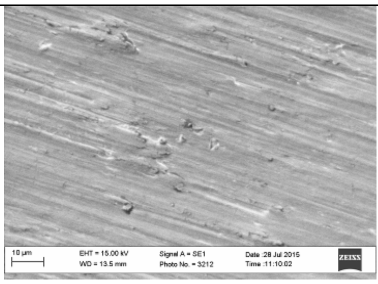
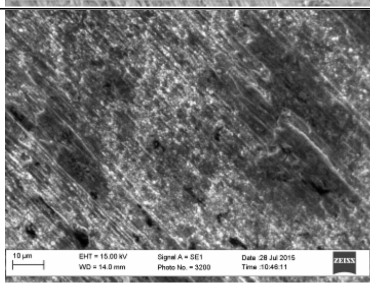
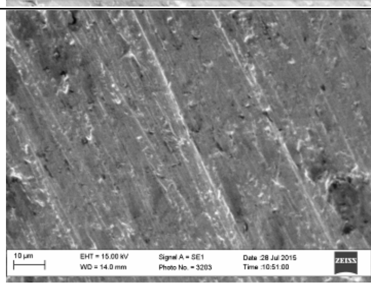
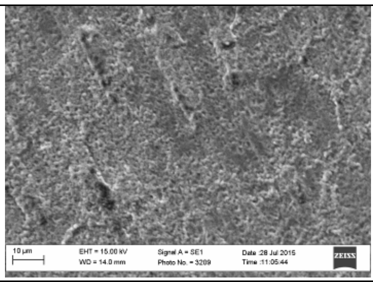
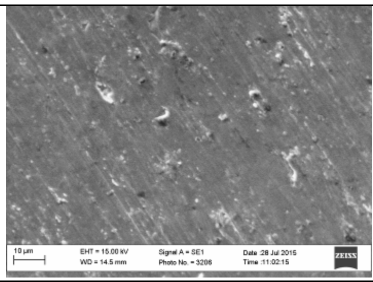
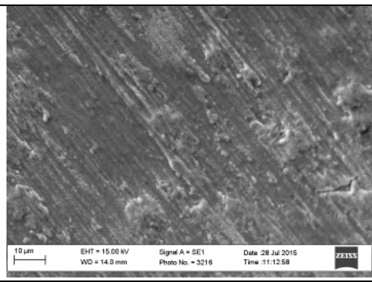
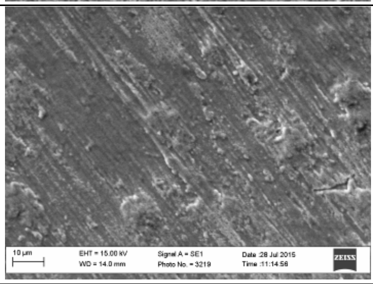
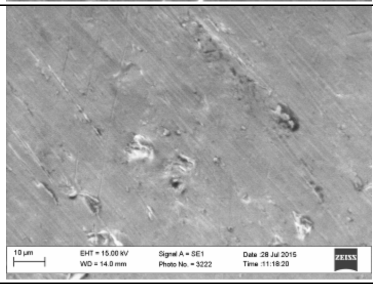
Treatment mode	Alloy		
	VT1-0	Zr1%Nb	HfE-1
before treatment			
R1			

Table 2 (Continuation)

The surface of the samples before and after quitting in an oxygen-containing gas medium

Treat-ment mode	Alloy		
	VT1-0	Zr1%Nb	HfE-1
R2			
R3			

Conclusions

Treatment in a controlled oxygen-containing gas medium at a temperature of 750 °C for 5 h in titanium, zirconium, and hafnium alloys leads to the formation of a strengthened diffusion layer with a higher hardness relative to the metal core in the reverse order of their affinity for oxygen. This may still indicate the formation of an oxide layer during the interaction on these alloys, which prevents the diffusion of oxygen into the metal in proportion to their affinity for oxygen. Treatment in such an environment does not lead to significant changes on the surface of the metal.

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