ISSN 1027-5495. Functional Materials, 32, No.2 (2025), p. 232-237
doi:http://dx.doi.org/10.15407/fm32.02.232

Aluminum and silicon influence on gas saturation of titanium alloys

S.O. Polishko, A.F. Sanin, A.V. Davydiuk

Oles Honchar Dnipro National University,
72 Nauky Ave, 49045 Dnipro, Ukraine

Received January 10 , 2025

The article dials with current issues of refining titanium alloys by electron beam melting (EBM) to reduce gas saturation, which is important for improving their technological and operational characteristics. Correlations between the content of aluminium, silicon and mechanical properties of titanium alloys have been identified, which allows optimizing their composition to increase the tensile strength. It has been established that the interaction of titanium with gases, with oxygen, significantly affects the formation of the surface layer, oxide films and changes in the mechanical characteristics of alloys. An analysis of changes in the surface microhardness of titanium alloys VT1-0 and VT6S at different temperatures has been carried out. The phase composition of the surface layer after heat treatment was studied by X-ray diffraction, which confirmed the formation of oxides and intermetallic, such as TiO_2, Ti_3Al and Ti_3O_5. The results obtained contribute to further improvement of titanium alloy processing technologies and development of materials with improved characteristics for use in aircraft production and materials science.

Keywords: titanium alloys, phase composition, EPP, phase composition, chemical composition, mechanical characteristics.

Вплив алюмінію та кремнію на газонасичення титанових сплавів. *С.О. Полішко, А.Ф. Санін, А.В. Давидюк*

У статті розглянуто актуальні питання рафінування титанових сплавів методом електронно-променевої плавки (ЕПП) з метою зменшення газонасиченості, що має суттєве значення для покращення їх технологічних та експлуатаційних властивостей. Виявлено кореляційні зв'язки між вмістом алюмінію, кремнію та механічними властивостями титанових сплавів, що дозволяє оптимізувати їх склад для підвищення границі міцності. Встановлено, що взаємодія титану з газами, зокрема з киснем, значно впливає на формування поверхневого шару, утворення оксидних плівок та зміну механічних характеристик сплавів. Проведено аналіз змін мікротвердості поверхні титанових сплавів ВТ1-0 та ВТ6С при різних температурах. Методом рентгенографії досліджено фазовий склад поверхневого шару після термічної обробки, що підтвердило утворення оксидів та інтерметалідів, таких як TiO_2, Ti_3Al та Ti_3O_5. Отримані результати сприяють подальшому вдосконаленню технологій обробки титанових сплавів та розробці матеріалів із поліпшеними характеристиками для використання виробництва літальних апаратів й матеріалознавства.

1. Introduction

Since the middle of the last century, non-ferrous metals have been smelted and refined in Ukraine and abroad by the electron beam melting (EBM) method. After that, it became possible to improve the properties of metals by removing harmful impurities [1–7]. Production of commercial ingots of electron beam welded titanium has also begun. This direction is promising. As a rule, industrial ingots are produced by a duplex method: EBM + vacuum arc remelting (VAR). At the same time, the influence of gas impurities in titanium alloys remains insufficiently studied, which is of practical interest and makes this research topic relevant.

The formation of the surface layer of titanium and its alloys is greatly influenced by their interaction with gases, which results in the formation of chemical compounds and solid solutions. This causes a significant change in technological and operational properties. The most important is the interaction of titanium with oxygen in the air. Due to the high affinity of titanium for oxygen, an oxide film forms on the surface of the metal even at room temperature. All technological processes for manufacturing products from titanium alloys are associated with repeated heating and holding at high temperatures. In this case, gas absorption increases and leads to irreversible changes in properties. Up to 80% of oxygen is spent on the formation of oxide films. When developing technologies for processing titanium alloys, it is necessary to take into account the change in the surface state of semi-finished products due to gas saturation [8–12].

In this regard, it was necessary to determine the phase composition, analyze the thermodynamic characteristics, and investigate the structure of the surface layer of titanium alloys, which are most widely used in the industry of Ukraine.

2. Results and discussion

The degree of gas saturation is determined by microhardness measurements. Fig. 1 shows the change in the microhardness of the surface of the VT1-0 and VT6S alloys relative to the initial value. The microhardness of unalloyed titanium VT1-0 began to change significantly at a temperature of 650 °C (by 20%); in the VT6S alloy, these changes began at lower temperatures. The relative difference in the microhardness of the surfaces of the heat-treated and initial samples was 4% at 500 °C and 15.5% at 600 °C. With a further increase in temperature, the nature of the change in microhardness in the two alloys was different. In the temperature range from 650 to 800 °C, the microhardness of the VT1-0 alloy changed slightly, while for the VT6S alloy it gradually increased. At temperatures of 900 and 1000 °C, the microhardness of the VT1-0 alloy increased sharply - by 151 and 229%, respectively, which indicated significant gas absorption. This is due to the acceleration of diffusion processes associated with both an increase in temperature and the phase transition $\alpha \rightarrow \beta$, which occurs at 882 °C in titanium. In the VT6S alloy at 870 °C, the relative change in microhardness was only 45%, even less than at 800 °C; with further increase in temperature, it increased, but much less than in the VT1-0 alloy [13–15].

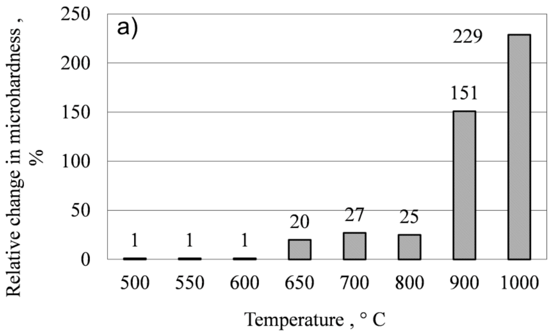
Thus, the increase in microhardness in the VT6S alloy turned out to be almost two times less than in VT1-0. This was apparently due to the action of vanadium, which slows down the gas saturation of titanium. The non-monotonic nature of the dependence of the increase in microhardness on temperature can be caused by phase transformations in the base metal, changes in the degree of alloying of the surface, the formation of oxide films and their partial peeling.

To determine the effect of the treatment temperature on the phase composition of the alloy surface, X-ray studies were carried out on samples cut from industrial sheets of one of the most common industrial alloys, VT6S, after heat treatment under various conditions. The results of X-ray phase analysis of the samples are given in Table 1.

From Table 1 it is seen that at temperatures of 500 and 600 °C only $\alpha+\beta$-phases were detected, although it is known that the oxide film is formed even at room temperature. Obviously,

Table 1 – Phase composition of VT6S alloy samples after heat treatment

Heat treatment mode	Phase composition
Initial	$\alpha+\beta$
500 °C, 20 min	$\alpha+\beta$
600 °C, 20 min	$\alpha+\beta$
700 °C, 20 min	$\alpha+\beta$, TiO_2
800 °C, 20 min	$\alpha+\beta$, TiO_2
870 °C, 20 min	$\alpha+\beta$, TiO_2, Ti_2N, Ti_3Al
870 °C, 60 min	$\alpha+\beta$, TiO_2, Ti_3O_5, TiO, Ti_3Al
970 °C, 20 min	$\alpha+\beta$, TiO_2, Ti_2N, Ti_3Al



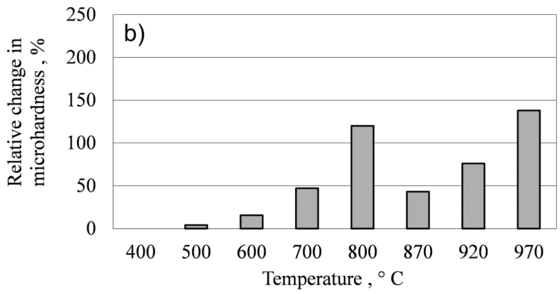


Fig. 1 Relative change in surface microhardness of titanium alloys at different temperatures: a) alloy VT1-0, b) alloy VT6S

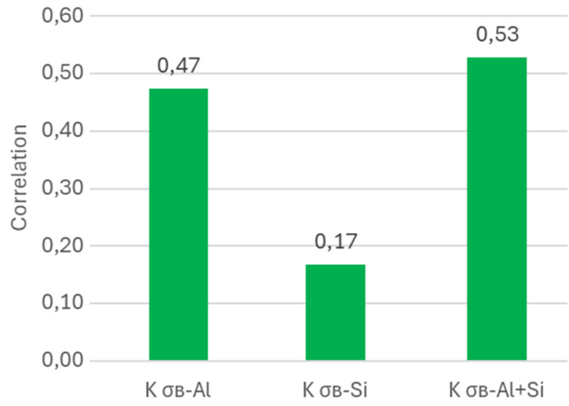


Fig. 2 Correlation coefficients showing the influence of aluminum and titanium on the ultimate strength

its thickness is too small to be determined by the X-ray method.

At temperatures of 700, 800 °C, the phase composition is represented by α+ β-phases and TiO_2 oxide in the form of rutile, which coincides with the literature data [16–18].

During holding for 20 min at 870 and 970 °C, titanium nitride Ti_2N and the intermetallic Ti_3Al additionally appear. An increase in the holding time to 60 min at 870 °C leads to the formation of oxides Ti_3O_5 and TiO along with rutile TiO_2. The appearance of the intermetallic Ti_3Al indicates the enrichment of the surface layer of the metal with aluminum up to ~ 10%. This is the concentration required to form an intermetallic compound in the temperature range from 870 to 970 °C according to the phase diagram. The VT6C alloy contains from 5.3% to 6.5% Ti_3Al. Diffusion of aluminum to the sample surface can be caused by an increase in the amount of the α-phase in the surface layer under the action of oxygen. Due to the difficulty of diffusion in the hexagonal lattice of α-titanium, enrichment with aluminum of local microvolumes of the metal is possible, in which the intermetallic is formed. The chemical composition and mechanical properties of the VT1-0 alloy are given in Table 2 [19].

Sponge titanium contains a number of impurities, most of which are not standardized, namely: Al, V, Mo, Sn, Zr, Mn, Cr, Fe, Ti, Si, Cl, Mg, Na, Ca, K, S, Ni, As, Sc, Sb, Bi, Au, Ag. Their concentrations are very low, but as a result of their interaction with titanium and with each

Table 2. Chemical composition and mechanical properties of alloy VT1-0

No.	Tensile strength σ, MPa	Chemical content, %						
		Fe	Al	V	O	N	C	H
1.	415	0.069	0.1	0.03	0.01	0.01	0.047	0.005
2.	415	0.088	0.12	0.03	0.01	0.01	0.045	0.005
3.	413	0.096	0.1	0.03	0.01	0.01	0.047	0.005
4.	415	0.086	0.13	0.03	0.01	0.01	0.046	0.005
5.	410	0.084	0.1	0.03	0.011	0.005	0.04	0.005
6.	412	0.089	0.1	0.03	0.011	0.005	0.04	0.005
7.	414	0.1	0.12	0.03	0.012	0.005	0.04	0.004
8.	415	0.1	0.1	0.03	0.012	0.005	0.045	0.005

Table 3. Characteristics of the crystal lattices of titanium and its oxides

Substance	Crystal lattice type	Crystal lattice periods, nm	Relative difference in the periods of the crystal lattice of Ti and oxides, %	
α-Ti	GPU	a-0.2951, c-0.4673	α-Ti	ß-Ti
ß-Ti	FCC	0.3302		
Ti_2O	Hexagonal	a-0.2959 s-0.4845	a$_{Ti}$/a$_{ox}$=0.2 with$_{Ti}$/with$_{ox}$=3.5	a$_{Ti}$/a$_{ox}$=10 and$_{Ti}$/s$_{ox}$=47
TiO	FCC	0.4246	a$_{Ti}$/a$_{ox}$=43.9 with$_{Ti}$/a$_{ox}$=9.2	a$_{Ti}$/a$_{ox}$=28
Ti_2O_3	Hexagonal	a-0.515 s-1,361 c/a-2.64	a$_{Ti}$/a$_{ox}$=74.5 with$_{Ti}$/with$_{ox}$=190.8	a$_{Ti}$/a$_{ox}$=56 and$_{Ti}$/s$_{ox}$=312
	Rhombic	a-0.5414	a$_{Ti}$/a$_{ox}$=83.5 with$_{Ti}$/a$_{ox}$=15.7	a$_{Ti}$/a$_{ox}$=64
Ti_3O_5	Rhombic	a-0.3754 b-0.9474 s-0.9734	a$_{Ti}$/a$_{ox}$=27 with$_{Ti}$/b$_{ox}$=222 with$_{Ti}$/ with$_{ox}$=229	a$_{Ti}$/a$_{ox}$=14 and$_{Ti}$/b$_{ox}$=187 and$_{Ti}$/ with$_{ox}$=195
	Monoclinic	a-0.9752 b-0.3802 s-0.9442	with$_{Ti}$/a$_{ox}$=230 and$_{Ti}$/b$_{ox}$=29 with$_{Ti}$/ with$_{ox}$=220	a$_{Ti}$/a$_{ox}$=195 and$_{Ti}$/b$_{ox}$=15 and$_{Ti}$/ with$_{ox}$=186
TiO_2	Tetragonal	a-0.4584 s-0.2953	and$_{Ti}$/s$_{ox}$=0.07 with$_{Ti}$/ and$_{ox}$=2	a$_{Ti}$/a$_{ox}$=39 and$_{Ti}$/ with$_{ox}$=11

other, a noticeable change in primarily plastic properties is possible. The pair and group correlation coefficients between aluminum, silicon in the ensemble with other components were determined, which are shown in Fig. 2.

From Fig. 2, it follows that *K*σv-Al = 0.47 is a moderate positive correlation between the aluminum (Al) content and the tensile strength σ in the titanium alloy VT1-0. This means that with increasing aluminum content, the tensile strength increases, but the effect is not very strong. The next coefficient *K*σv-Si = 0.17 shows a weak positive correlation between the silicon (Si) content and the tensile strength. This indicates that silicon has almost no effect on the tensile strength or the effect is minimal. The group correlation coefficient *K*σv-Al+Si = 0.53 shows that the simultaneous presence of these elements in a certain proportion can have a more significant effect on the mechanical properties of the material than each of them separately.

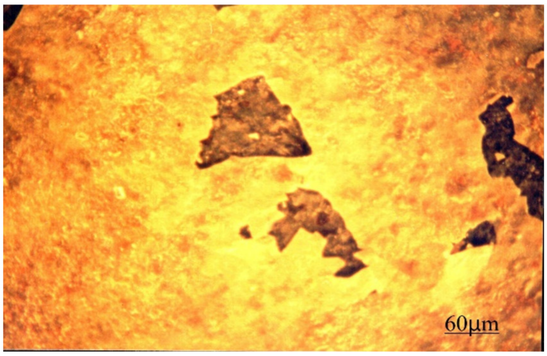
It can also be noted that *K*σv-Al = 0.47 and *K*σv-Al+Si = 0.53 are quite significant indicators, especially for real materials, where the correlation rarely reaches high values (0.7 and more). *K*σv-Si = 0.17 is quite low and, perhaps, statistically insignificant. Silicon has a limited effect on the tensile strength of titanium alloys.

Aluminum has a moderate effect on the ultimate strength of the alloy, indicating its importance in strengthening the material. This may be due to its ability to form a solid solution in the titanium matrix or to contribute to the formation of a more stable microstructure. Silicon, unlike aluminum, has little effect on the strengthening of the alloy. The combined effect of Al and Si is more significant than the effect of each element alone. This may indicate a synergistic effect at certain concentrations that improves strength.

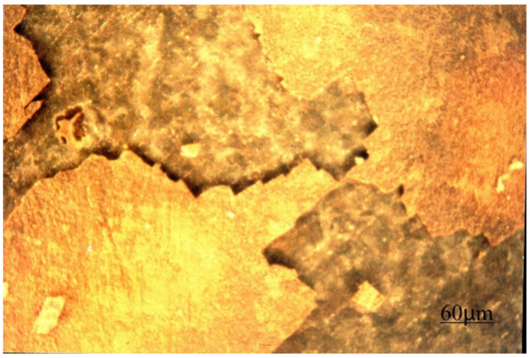
To assess the probability of the formation of a particular oxide, the thermodynamic characteristics and crystal structure of titanium oxides were analyzed. Table 3 presents data on the type and periods of the crystal lattices of titanium oxides.

The lattices of TiO_2 and Ti_2O oxides are most compatible with the lattice of α-Ti. The relative difference of the period "*a*" of α-Ti and "*c*" of rutile is only 0.07%, and the difference of "*c*" of α-titanium and "*a*" of rutile is 2%. Titanium oxide Ti_2O has a hexagonal crystal lattice, like α-titanium, the relative differences in the periods "*a*" and "*c*" of their crystal lattices are 0.2% and 3.5%, respectively, but the formation of Ti_2O was not detected radiographically.

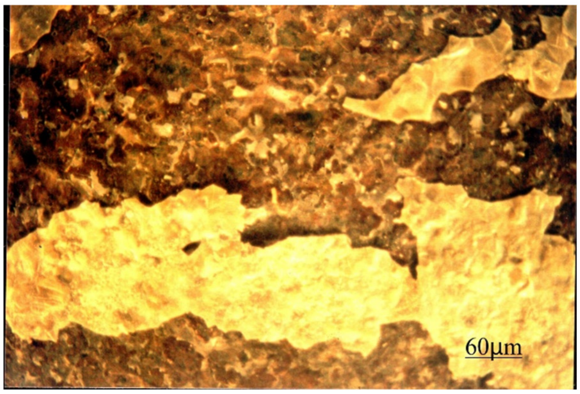
Titanium compounds with oxygen are distinguished by a variety of chemical bonds – from metallic to ionic. The most stable is tita-



a)



b)



c)

Fig. 3 Surface structure of industrial titanium alloys after holding for 4 hours at 800 °C: a) alloy VT1-0, b) alloy VT6, c) alloy VT23, x 600

nium oxide TiO_2, which uses all four valence electrons. Rutile is an *n*-type semiconductor, oxygen vacancies in which provide preferential diffusion of oxygen ions through the oxide crystal lattice compared to titanium ions. As a result, oxygen is transferred into the depth of the scale, it grows on the metal-oxide interface. At the same time, at elevated temperatures, a noticeable diffusion of titanium ions is manifested.

Fig. 3 shows the surface structure of samples of industrial alloys VT1-0, VT6, VT23 after holding for 4 h at 800 °C. As can be seen, the most continuous oxide layer was formed on the surface of samples of alloy VT1-0. With increasing alloying degree, cracking and scale delamination increased. This could be facilitated by the uncontrolled formation of complex oxides of alloying elements, intermetallic phases, for example, Ti_3Al (Table 1), with different physical characteristics. The disruption of the oxide film density facilitated the penetration of oxygen deep into the metal. These results correlate with the data obtained by us earlier on the gas absorption of alloys VT6S and VT3-1 [20].

The formation of continuous thin oxide films on the surface of titanium alloys, especially technical titanium VT1-0 and alloys doped with vanadium (VT6, VT6S), by controlled oxidation is a promising direction for protecting titanium semi-finished products from gas absorption during technological processes associated with heating and holding at high temperatures.

3. Conclusions

The study examines the importance of electron beam melting (EBM). Its implementation in the production of titanium alloys has significantly reduced the level of harmful impurities and improved the properties of the metal, which is a relevant direction in metallurgy.

It is shown that the interaction of titanium with oxygen and other gases leads to changes in the material structure, affecting its mechanical properties, particularly microhardness. In the VT1-0 alloy, a significant increase in microhardness begins at 650°C and rises sharply at 900–1000°C, indicating intensive gas saturation.

It has been proven that the VT6S alloy demonstrates more stable characteristics since vanadium slows down gas diffusion, reducing its impact on the material. At 500–600°C, the VT6S alloy retains its two-phase state (α+β). At 700–800°C, titanium oxide (TiO_2) appears, indicating an active oxidation process. At 870–970°C, additional phase components, including Ti_2N, Ti_3Al, and Ti_3O_5, are formed, which affect the structure and strength of the surface layer.

It was found that the aluminum content has a moderate positive effect on the ultimate strength of the VT1-0 alloy (correlation coefficient 0.47). Silicon has almost no effect on strength (correlation 0.17), but its combination with aluminum slightly improves the alloy characteristics (correlation 0.53).

The obtained results are important for improving titanium alloy heat treatment technologies to reduce gas absorption and enhance the operational characteristics of materials used in Ukrainian industry.

References

1. A.V.Ovchinnikov, Yu.M.Tkachenko, V.G.Kudin, V.F.Scull. *Construction, Materials Science, Mechanical Engineering*, **41**, 178–183(2007).
2. P.E.Markovsky, J.Janiszewski, S.V.Akhonin, V.I.Bondarchuk, V.O.Berezos, K.Cieplak, O.P.Karasevska, M.A.Skoryk. *Progress in Physics of Metals*, **3**, 438–475 (2022). https://doi.org/10.15407/ufm.23.03.438.
3. O.M.Ivasishin, D.V.Kovalchuk, P.E.Markovsky, D.G.Savvakin, O.O.Stasiuk, V.I.Bondarchuk, D.V.Oryshych, S.G.Sedov, V.A.Golub. *Progress in Physics of Metals*, **1**, 75–105 (2023).
4. M.Koike, K.Martinez, L.Guo, G.Chahine, R.Kovacevic, T.Okabe. *Journal of Materials Processing Technology,* **211**, 1400–1408 (2011).
5. V.A.Dekhtyarenko, T.V.Pryadko, O.I.Boshko, V.V.Kirilchuk, H.Yu.Mykhailova, V.I.Bondarchuk. *Progress in Physics of Metals*, **2,** 276–293 (2024).
6. J.M.Windajanti, M.S.Rajapadni, D.J.D.H. Santjojo, M.A.Pamungkas, A.Abdurrouf, T.Aizawa. *Progress in Physics of Metals*, **1**, p. 90–107 (2022).
7. K.Vutova, V.Vassileva, V.Stefanova, D.Amalnerkar, T.Tanaka. *Metals,* **9**(6), 683 (2019). https://doi.org/10.3390/met9060683.
8. A.Powell, U.Pal, J.van den Avyle, B.Damkroger, J.Szekely. *Metallurgical and Materials Transactions*, **28**, 1227–1239 (1997).
9. O.E.Kozhevnikov, M.M.Pylypenko, A.P.Shcherban, O.A.Datsenko, V.M.Pelykh, V.D.Virych. *Problems of Atomic Science and Technology*, **1**, 6–12 (2022). https://doi.org/10.46813/2022-137-006.
10. O.V.Shapovalov, I.A.Markova, T.I.Ivchenko. *Vesnik Academies Mint Services Ukraine*, **3**, 53–57 (2005).
11. O.M.Shapovalova, A.V.Shapovalov, E.V.Zolotko. Phase transformations in complex alloyed titanium alloys VT3-1 and VT23. Phase Equilibria, Phase Stability and Metastable States in Metallic Systems, K.: IPM Publishing House, 1993, p. 168–183.
12. S.V.Akhonin, A.Yu.Severin, V.O.Berezos, O.M.Pikulin, V.A.Kryzhanovskyi, O.G.Yerokhin. *The Paton Welding Journal*, **3**, 49–53 (2022). https://doi.org/10.37434/sem2021.04.03.
13. O.M.Shapovalova, I.A.Markova, T.I.Ivchenko. *Bulletin of Engine Engineering*, **1**, 125–128 (2009).
14. S.Polishko. *Problems of Atomic Science and Technology*, **5**, 137–142 (2023). https://doi.org/10.46813/2023-147-137.
15. S.Polishko. *Visnik Dnipropetrovsk National University im. Olesya Gonchar. Series "Rocket and Space Technology"*, **4**(29), 124–132 (2021). https://doi.org/10.15421/452113.
16. O.M.Shapovalova, O.V.Shapovalov. Titanium alloys: Patent 71465 Ua 71465 C 22C14/00 (2004.11). Soviet Department of Intellectual Power, 1, No. 11:7, 2004 [in Ukrainian].
17. O.M.Shapovalova, O.V.Shapovalov, T.I.Ivchenko. Titanium alloy: Patent 71466 Ua 71466 C 22C14/00 (2004.11). Soviet Department of Intellectual Power, 1, No. 11:7, 2004 [in Ukrainian].
18. S.A.Rysenko, T.V.Nosova, S.I.Mamchur, S.A.Polishko. Modification of titanium alloys used for the manufacture of ball cylinders. *XXI International Youth Scientific and Practical Conference "People and Space",* D.: DNU, 2021, p. 176.
19. S.Polishko, D.Shypovalova. Studies on increasing the plasticity of titanium alloy VT1-0 melted by the electron beam method. Proceedings of the 9th International Scientific and Practical Conference, BoScience Publisher, Chicago, USA, 2022, p. 118–122. URL: https://sci-conf.com.ua/ix-mezhdunarodnaya-nauchno-prakticheskaya-konferentsiya-modern-directions-of-scientific-research-development-23-25-fevralya-2022-goda-chikago-ssha-arhiv/.
20. S.Polishko, Methods development for increasing mechanical characteristics during deformation of titanium alloys with energy costs minimization, in: Sbornik nauchnykh trudov "System Design and Analysis of Aerospace Equipment", Vol. 35, No. 2, Dnipro (2024), pp. 79–85.