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V.V. Larionov, E.N. Stepanova Thermoelectric power properties of hydrogenated alloy Ti-6Al-4V subjected to mechanical impact and electron irradiation

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Received December 16, 2023

Revised March 10, 2024

Accepted March 15, 2024

The thermoelectric power properties of the Ti-6Al-4V alloy hydrogenated with hydrogen (hydrogen content 0.002 wt.% and 0.23 mass.%), subjected to mechanical rupture (up to 25 to 450 MPa) and irradiation with a pulsed electron flow with an energy of 18 keV to 25 J/cm² and duration 15 μs. The role of individual Al and V components in relation to changes in the thermoelectric properties of the alloy is noted. Of interest is not only the stabilization of phases, but also the transformation of the alloy under study into a layered medium due to hydrogenation and fixation of hydrogen in traps. The change in the Seebeck coefficient *S* varies for different conditions in the range (from 0.0011 to 0.0030 mV/K. Due to its stability and strength properties, this kind of alloy can be suitable for use in systems for monitoring the properties of implants and non-traditional energy.

Keywords: thermoelectric power, Ti, Al, V, Seebeck coefficient, pulsed electrons, hydrogen.

DOI: 10.61011/TP.2024.05.58520.311-23

Introduction

Alloy Ti-6Al-4V is widely used as material for implants in the system of additive technologies, in aerospace industry and chemical industry, during manufacturing of gas turbines, armaments, and domestic electronic appliances [1,2]. Aluminium in alloy stabilizes α -phase of titanium, and vanadium stabilizes β -phase. Hydrogenation of titanium, as an element of hydrogen technologies, depends on many factors, in particular on the phase state. Hydrogen atoms easier diffuse in the lattice β -Ti, then in lattice α -Ti. In interphase state $\alpha + \beta$ the hydrogen atoms occupying tetrahedral void of β -phase, will dominate in diffusion process. For non-stoichiometric dihydride δ -TiH_{2-x} with face-centered cubic (FCC) sublattice Ti energies of hydrogen diffusion activation lie in range 0.46–0.53 eV [1–3]. Thus, hydrogen diffusion constant for α - and β -phase according to Arrhenius law for temperature, are equal respectively $D_{\alpha} = 1.8 \cdot 10^{-2} \exp\{-12380/(RT)\} \text{ cm}^2/\text{s}$, $D_{\beta} = 1.95 \cdot 10^{-3} \exp\{-6640/(RT)\} \text{ cm}^2/\text{s}$, where the exponent is given in cal/mol. For H in α -phase of titanium the diffusion constant at 313 K is $D = 2 \cdot 10^{-10} \text{ cm}^2/\text{s}$, in β -phase of titanium at 303 K $D = 2 \cdot 10^{-9} \text{ cm}^2/\text{s}$ [1–3]. The titanium saturation with hydrogen in its α -state is impossible, at the same time in β -titanium there are tetrahedral pores, which size is close to atomic radius of hydrogen, therefore β -titanium well hydrotreated. These states affect the thermoelectric properties of the studied alloy. Interest is paid not to phases stabilization, but to alloy transformation into lamellar medium for possible

use in modern systems of two-dimensional materials. Layering refers to the concentration layers of hydrogen in the alloy caused by the presence of hydrogen traps. Introduction in various structures, for example, load sensors, to monitor state of structural materials, results in increased requirements for mechanical strength of sensors. It is expected that key for many technologies is lamellar medium, when two-dimensional materials are basis of products. They can be used for painting objects of various purposes, to manufacture sensors for monitoring cracks, external defects, etc. [2,4,5]. Films made of them and intended to absorb radio waves can power supply the electronic appliances. Single-phase or composite materials are of interest, when composition or microstructure change uniformly or practically by jumps, which ensures change of local properties of materials [2,4–6]. It is known that in some cases hydrogenation results in lamellar medium [1,7]. Hydrogen in material has significant effect on the phase composition and type of defects [8,9], As results in formation of defects in materials and actively interacts with available structure defects [8–10]. Wide use of discussed materials arises the problem of dynamic strength increasing, wear decreasing, corrosion strength increasing [8,9]. The solution to this problem is the use of ion implantation of the surface, irradiation with electrons and other charged particles [11–13]. Efficiency of this methods depends, in its turn, on multiple factors, such as formation of defects in surface layer, of the additional stresses, formation of unwanted impurities, phase composition change, and, in our case, change in thermoelectric properties of the material. In surface layer during irradiation the phase

composition changes due to high temperature. The density of defects increases, which in turn creates instability of product properties caused by high temperatures. The modified surface layer and introduced hydrogen can affect the operation properties of product during deformation and result in distortion of their thermoelectric properties.

This paper objective is study of thermoelectric properties of hydrogenated alloy Ti-6Al-4V, subjected to mechanical action and irradiation with electrons.

1. Samples and study methods

The experiments were performed in two-phase ($\alpha + \beta$) titanium alloy Ti-6Al-4V containing Al 5.9 and V 3.9 mass.%. The hydrogen in initial alloy Ti-6Al-4V was in amount of about 0.002 mass.%. For comparison samples of technical titanium VT1-0 were manufactured with different hydrogen concentrations. The hydrogen concentration was measured by gas analyzer RHEN 602 with accuracy 0.0001%. The samples were prepared from blanks using the electric spark method. Sample surfaces were grounded and electrolytically polished. In study samples of alloy Ti-6Al-4V were used in form of plates $5 \times 1.5 \times 1$ mm, electrolytic vanadium grade VEL-1 (TU48-05-33-71), purity 99.9, technical aluminium grade AD(123). Oxidized vanadium was obtained by heating in chamber in purified oxygen at temperature 900°C . Hydrogen lamination was achieved by hydrogenation at different concentrations in alloy. For samples irradiation pulse accelerator of electrons SOLO of RAS SB (Russia, Tomsk) was used [11]. The irradiation chamber comprises argon at pressure 0.02 Pa. Density of energy of electrons flow was selected in range about 5 and 12 J/cm^2 . These values were selected experimentally such that surface melting will occur ($\sim 5 \text{ J/cm}^2$) and with melting ($\sim 12 \text{ J/cm}^2$), when high speed crystallization of sample surface is observed. Irradiation pulse width was $50 \mu\text{s}$, frequency – 0.3 s^{-1} . One irradiation act contains three pulses. At electron energy 18 keV and current density up to 50 A/cm^2 the irradiation power was $6 \cdot 10^4 \text{ W/cm}^2$. Part of samples before irradiation was subjected to hydrogenation to concentration 0.23 ± 0.01 mass.% H. Samples were hydrogenated at temperature 773 K and hydrogen pressure 1 atm by Sieverts method in unit Gas Reaction Controller (Advanced Materials Corporation, (LECO, USA)). Samples before and after irradiation were studied using transmission electron (JEM-2100) and optical (AXIOVERT 200MAT) microscopes. Tension tests were performed in modernized test setup PV-3012M in vacuum at residual pressure 10^{-2} Pa using flat dumbbell samples with measuring sections $5 \times 1.5 \times 1$ mm. Maximum breaking strength of samples was 450 MPa. To measure thermo-emf the modified temperature stabilization unit PKKEM (Russia) with gold electrode was used. To calibrate electrode we selected thermo-emf Cu ($1.8 \mu\text{V/K}$), Pt ($-5.3 \mu\text{V/K}$) relative to Ag

(thermo-emf $1.5 \mu\text{V/K}$) [7] with measurements accuracy about 5% for all alloys.

Hydrogen content in alloy Ti-6Al-4V before irradiation is ~ 0.002 mass.%. From Fig. 1, a it follows that the alloy has polycrystalline structure. Grains of α -titanium mixed with layers of β -titanium. Value of β -phase in alloy reaches 6 vol.% and varies depending on hydrogen content. Size of grains in α -phase is about $14 \mu\text{m}$, and size of layers varies in range $1.5\text{--}3.5 \mu\text{m}$. At that the average grain size of α -phase of alloy Ti-6Al-4V during its hydrogenation does not change until concentration 0.23 mass.%. The hydrogenation process results in increase in volume fraction of β -phase and is (14 ± 2) vol.%. X-ray diffraction analysis shows that lattice parameter of β -phase increases from 0.3224 to 0.3300 nm, i.e. amount of α -phase in layers of β -phase decreases. Accordingly vanadium content in volume of β -phase decreases [13]. Hydrogenation is accompanied by phase transformations and changes in thermo-emf. The hydride composition corresponds to phase with lower hydrogen content, i.e. phase transition takes place. Detachment of already small amount of hydrogen shall result in change in thermo-emf value, as during the hydrogenation process of alloy Ti-6Al-4V transformations are possible, which are characterized by presence of ($\alpha + \delta + \beta$) regions [14]. At low hydrogen content in the presence of vanadium at ratio hydrogen/metal 1.06 δ -phase is not observed.

2. Theoretical analysis

Values of thermo-emf are theoretically justified in papers [15–17], where formulas were derived:

$$E_S = \frac{k_B}{e} \xi k_B (T_0 T)^{1/2} \frac{\partial(\ln g(E_F))}{\partial E}, \quad (1)$$

where $g(E_F)$ — density of states at Fermi level, $\xi = 0.1$ — numerical coefficient. We also know the dependence $E(T)$ in form of law $E \propto T^{1/2}$ [15]. For thermo-emf in hopping region, which is typical for the lamellar medium, studied in the present paper, the linear asymptotics $E \propto T$ can be characteristic:

$$E_S = \frac{\pi^2 k_B}{3e} k_B T \frac{\partial(\ln \sigma(E_F))}{\partial E}, \quad (1)$$

where $\sigma(E_F)$ — conductivity at Fermi level.

Dependence of thermo-emf on $T^{1/2}$ and T was obtained in paper [15]. This formula has no theoretical justification in hopping conductivity region, natural for the lamellar medium, with variable hop length of carrier [13,15]. It is often emphasized that there is a deviation from the formula (1), when in region of Mott law action the thermo-emf does not depend on temperature $E_S(T) \sim \text{const}$. Such behavior can be result of special form of density of states in the vicinity of Fermi level [13]. In our studies we observed abruptly heterogeneous dependence of thermo-emf on T , at that in some cases with sign change. In region of

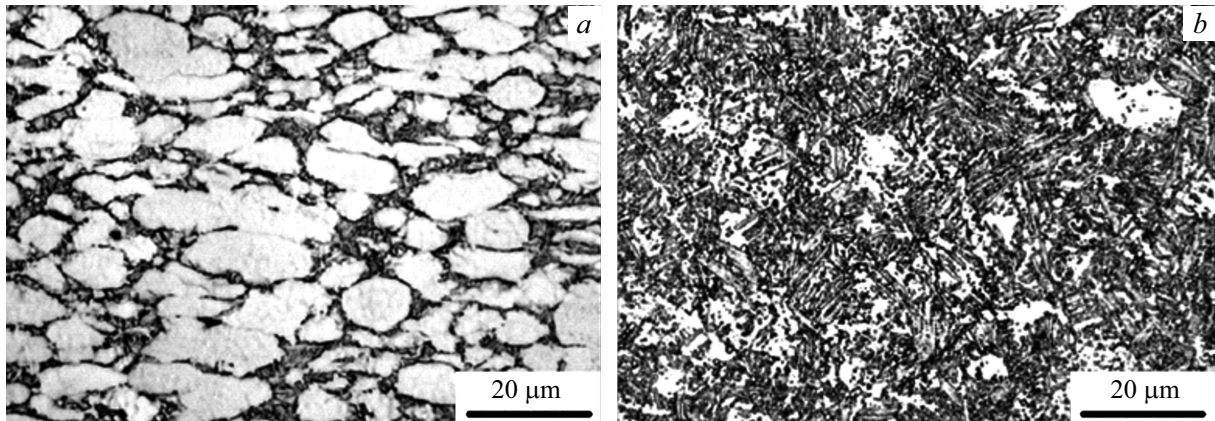


Figure 1. Structure of alloy Ti-6Al-4V before irradiation (a) and after (b) irradiation with electron beam having energy 12 J/cm^2 in mode of surface melting [13].

Mott law action for the hopping conductivity with variable hop length [16,17] characteristic for lamellar medium, the conductivity varies as per law $\sigma_h = \sigma_{ho} \exp[-(T_0/T)^{1/4}]$, ($T_0 = 17.6/g(E_F)a^3k_B$, a — density of states and radius of localization at Fermi level). We expect that thermo-emf is described by Zvyagin formula (1). This statement is confirmed by calculations. Seebeck coefficients were calculated as per standard method by formula $S = \Delta E/\Delta t$. Range of changes for various conditions is, as we see from Fig. 2–5, from 0.0011 to 0.0030 mV/K.

3. Discussion of the experiment results

Main measurement results are shown in Fig. 2–5. As it follows from Fig. 2, phases stabilization and hydrogenation of alloy Ti-6Al-4V (curve 1) result in increase by more than 2 times in values of thermo-emf at temperature $80\text{--}90^\circ\text{C}$ as compared to technical titanium (curve 3) and aluminium (curve 4), and non-hydrogenated alloy Ti-6Al-

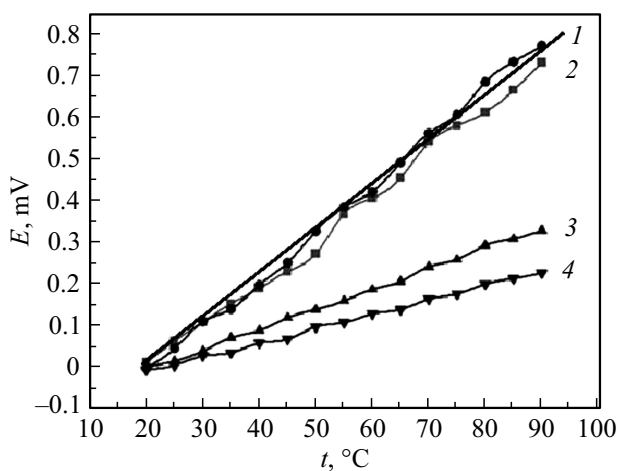


Figure 2. Thermo-emf vs. temperature: 1 — Ti-6Al-4V ($C_H = 0.23$ mass.%); 2 — Ti-6Al-4V ($C_H = 0$); 3 — BT1-0 ($C_H = 0$); 4 — technical aluminium Al AD1(123) ($C_H = 0$).

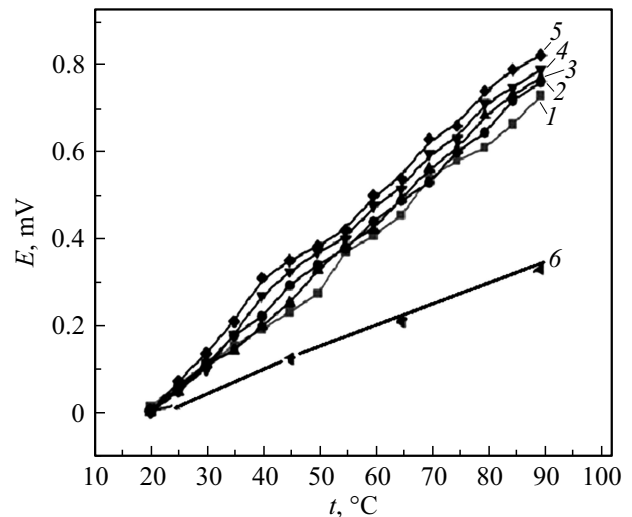


Figure 3. Thermo-emf of alloy Ti-6Al-4V vs. temperature, C_H : 1 — 0, 2 — 0.085, 3 — 0.23, 4 — 0 (irradiation 5 J/cm^2), 5 — 0.085 mass.% (irradiation 25 J/cm^2); 6 — titanium BT1-0 ($C_H = 0$).

4V (curve 2). The same is applied to values of Seebeck coefficient $S = \Delta E/\Delta t$.

Exposure to electron beam results in minor increase in thermo-emf within 10–14%, at that linear dependence (2) is kept within error of experiment. This effect of the hydrogenation can be explained by strengthening of β -phase and by hydrogen diffusion. Redistribution of hydrogen in the sample is possible under the influence of elastic stress fields [18]. In stressed regions hydrogen is accumulated as result of deformation localization [19]. This is confirmed by hydrogen concentration increasing in non-irradiated sample of alloy Ti-6Al-4V (from 0.23 to 0.28 mass.% H) under load conditions up to 450 MPa. In place of destruction the hydrogen concentration increases to 0.27 mass.%, i.e. in volume of hydrogenated alloys vacancies and hydrogen-vacancy complexes appear [9,20]. This ensures effect of

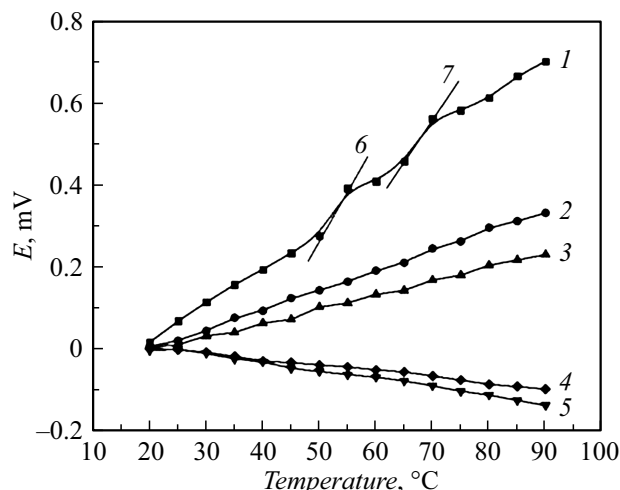


Figure 4. Thermo-emf vs. temperature: 1 — Ti-6Al-4V, 2 — VT1-0, 3 — aluminium AD1-123, 4 — oxidized vanadium, 5 — metal vanadium, 6 — Region of thermo-emf change E at temperature $t = 55\text{--}60^\circ\text{C}$, 7 — same at temperature $t = 60\text{--}65^\circ\text{C}$.

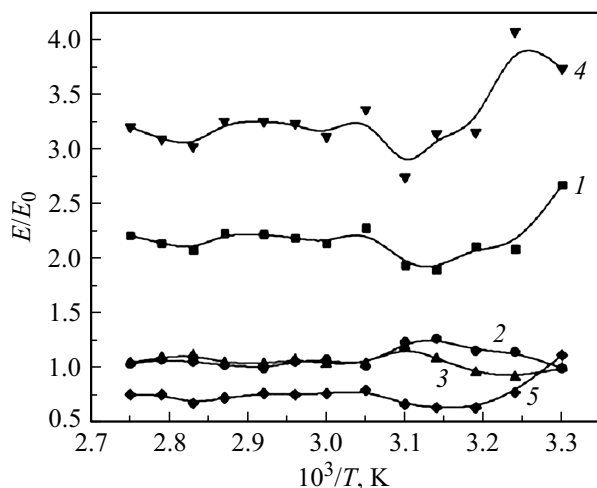


Figure 5. Ratio of thermo-emf E/E_0 vs. reverse temperature of hydrogenated for various hydrogen concentration alloy Ti-6Al-4V and elements being part of alloy composition: 1 — $\text{C}_\text{H} = 0$; 2 — 0.085, 3 — 0.023 mass.%; 4 — Al (AD); 5 — V (signal enlarged by 10 times).

separate components of the alloy during hydrogenation on behaviour of thermo-emf in the hydrogenated alloy Ti-6Al-4V. To study this effect we measured (Fig. 4) the value of thermo-emf of individual metals comprising the alloy.

Fig. 4 shows obvious effect of vanadium on values of thermo-emf. In region of temperatures $56\text{--}60^\circ\text{C}$ and $60\text{--}65^\circ\text{C}$ we observe values increasing of Seebeck coefficient S (shown by straight lines 6 and 7). In vanadium samples the inversion of sign of thermo-emf is observed (in same place, curves 4–5). It is known that in single-crystals of vanadium dioxide at a temperature $t = 67^\circ\text{C}$ (340 K) the phase transition dielectric–metal is observed. Above this temperature the material has metal conductivity [21].

Paper [22] states the ability of material based on the vanadium to absorb oxygen: „electrons concentration increases in allowed energy zone VO_2 “. This increasing occurs due to hydrogen atoms ionization in metal phase. At temperatures in range $55\text{--}60^\circ\text{C}$, apparently, concentration of free electrons increases in zone of conductivity (see dependence of thermo-emf for metal and oxidized vanadium in Fig. 4). Seebeck coefficient S in region of vanadium effect exceeds the average value of thermo-emf of alloy by 5–6 times (Fig. 4). This can be applied to study charge transfer and control the process of hydrogen migration under lamellar medium conditions. [23,24].

Fig. 5 shows ratio of values of thermo-emf E of hydrogenated alloy Ti-6Al-4V to thermo-emf of non-hydrogenated alloy E_0 . Here ratio E/E_0 for VT1-0, vanadium and aluminium are given for comparison. This value shows change in density of states at Fermi level (1) during hydrogenation. The largest contribution to the difference is made by aluminum, vanadium and VT1-0. At that change in E/E_0 during hydrogenation is observed, as, apparently, effect of hydrogen securing in traps is provided [7,24].

Conclusions

The influence of these processes on the thermoelectric properties of the alloy Ti-6Al-4V was studied by means of tensile tests, hydrogenation and irradiation with pulsed electron beam (up to surface melting). The values of thermo-emf of individual alloy components and of the alloy thermo-emf are determined. Samples deformation changes hydrogen concentration at break place from 0.23 to 0.27 mass.%, and thermo-emf changes by maximum 5%. Presence of vanadium and aluminium does not change sign of alloy thermo-emf to opposite sign, although their conductivity, as individual elements of alloy, changes according to sign of charge carriers. Seebeck coefficient in region of temperatures $55\text{--}60^\circ\text{C}$ (vanadium effect) exceeds the average value of thermo-emf of alloy by 5–6 times. Layering, in some case occurred during hydrogenation, and running of diffusion processes result in the metastable structure transformation into equilibrium one. To determine the technological parameters of alloy Ti-6Al-4V treatment (temperature, deformation, hydrogenation) it is possible to determine stability of its heterophase structures by changing the value of thermo-emf. Results can be useful in systems of properties analysis of implants.

Acknowledgments

The study was carried out using collective use means of TPU.

Funding

This study was performed as part of the Program „Priority 2030 TPU“.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] A.A. Il'in, B.A. Kolachev, V.K. Nosov, A.M. Mamonov. *Vidiridnaya tekhnologiya titanovykh splavov* (MISiS, M., 2002) (in Russian)
- [2] I.M. El-Galy, B.I. Saleh, M.H. Ahmed. *SN Appl. Sci.*, **1**, 1378 (2019). DOI: 10.1007/s42452-019-1413-4
- [3] A. Bhattacharyya, D. Maurice. *Mechan. Mater.*, **129**, 50 (2019). DOI: 10.1016/j.mechmat.2018.11.002
- [4] V. Sufiarov, A. Orlov, E. Borisov, I. Polozov, A. Popovich, M. Chukvenkova, A. Soklakov, D. Michaluk. *Tech. Phys.*, **66** (1), 23 (2021). DOI: 10.1134/S1063784221010199
- [5] P. Metalnikov, D. Eliezer, G. Ben-Hamu. *Mater. Sci. Eng.*, **811**, 141050 (2021). [DOI: 10.1016/j.msea.2021.141050]
- [6] R. Silverstein, D. Eliezer. *Mater. Characterization.*, **144**, 297 (2018). DOI: 10.1016/j.matchar.2018.07.029
- [7] S.P. Xu, V.V. Larionov, V.N. Kudiiarov, R.R. Elman, A.M. Lider. *Rus. Metallurgy (Metally)*, **11**, 1276 (2020). DOI: 10.26896/1028-6861-2020-86-8-32-37]
- [8] Y. Fukai. *The Metal-Hydrogen System* (Springer-Verlag Berlin Heidelberg, 2006)
- [9] R.S. Laptev, A.M. Lider, Yu.S. Bordulev, V. Kudiiarov, G. Garanin. *J. Alloys Compd.*, **645** (5), 193 (2015). DOI: 10.1016/j.jallcom.2014.12.257
- [10] Y.J. Liu, H.L. Wang, W.T. Hou, Y.L. Hao, R. Yang, T.B. Sercombe, L.C. Zhang. *Acta Mater.*, **113** (7), 56 (2016). DOI: 10.1016/j.actamat.2016.04.029]
- [11] N.N. Koval, Yu.F. Ivanov. *Rus. Phys. J.*, **51** (5), 505 (2008). DOI: 10.1007/s11182-008-9073-7
- [12] Yu.V. Baranov, O.A. Troitsky, Yu.S. Avraamov, A.D. Shlyapin. *Fizicheskie osnovy elektroimpul'snoj i elektroplasticheskoy obrabotki i novye materialy* (MGU, M., 2001) (in Russian)
- [13] G.P. Grabovetskaya, E.N. Stepanova, I.P. Mishin, O.V. Zabutcheko. *Rus. Phys. J.*, **63** (6), 932 (2020). DOI: 10.1007/s11182-020-02120-5
- [14] E.N. Boyangin, O.B. Perevalova, A.V. Panin, S.A. Martynov. *Phys. Metals Metallography*, **122** (2), 41 (2021). DOI: 10.1134/S0031918X21020034
- [15] I.P. Zvyagin. *Kineticheskie yavleniya v neuporyadochennykh poluprovodnikakh*. (MGU, M., 1984) (in Russian)
- [16] S.I. Demishev, M.V. Kondrin, A.A. Pirnin, N.E. Slushko, N.A. Samarin, A.G. Lyapin, D. Biskupsky. *Pis'ma v ZhETF*, **68** (11), 801 (1998) (in Russian).
- [17] N.F. Mott, E.A. Davis. *Electronic Processes in Non-Crystalline Material*, 2-nd ed. (Oxford University Press, 2012)
- [18] B. Yuan, J. Du, X. Zhang, Q. Chen, Yu. Wan, Zh. Xing, H. Zhang. *Int. J. Hydrogen Energy*, **45** (46), 25567 (2020). DOI: 10.1016/j.ijhydene.2020.06.265
- [19] B.A. Kolpachev. *Vodorodnaya khrupkost' metallov* (Metalurgiya, M., 1985) (in Russian)
- [20] X. An, H. Zhang, Te Zhu, Q. Wang, P. Zhang, Ya. Song, M. Wan, T. Yang, X. Cao. *Int. J. Hydrogen Energy*, **47** (13), 8467 (2022). DOI: 10.1016/j.ijhydene.2021.12.192
- [21] A.A. Bugaev, B.P. Zakharchenya, F.A. Chudnovsky. *Fazovy perekhod metall-poluprovodnik i ego primeneniye* (Nauka, L., 1979) (in Russian)
- [22] V.N. Andreev, V.A. Klimov. *FTT*, **49** (12), 2146 (2007). (in Russian)
- [23] R.N. Yastrebinsky, V.I. Pavlenko, A.A. Karnauhov, N.I. Cherkashina, A.V. Yastrebinskaya, A.I. Gorodov. *Sci. Technol. Nucl. Installations*, **2021**, ID 6658431, 13 (2021). DOI: 10.1155/2021/6658431
- [24] Xu. Sui, V.V. Larionov, A.M. Lider. *Tech. Phys.*, **65** (1), 93 (2020). DOI: 10.1134/S1063784220010260

Translated by I.Mazurov