ISSN 2075-1133, Inorganic Materials: Applied Research, 2015, Vol. 6, No. 2, pp. 138–142. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © Aung Kyaw Zaw, I.I. Chernov, M.S. Staltsov, B.A. Kalin, V.S. Efimov, 2014, published in Perspektivnye Materialy, 2014, No. 7, pp. 30–36.

MATERIALS OF POWER ENGINEERING AND RADIATION-RESISTANT MATERIALS

Hydrogen Retention by Vanadium–Titanium Alloys

Aung Kyaw Zaw, I. I. Chernov, M. S. Staltsov, B. A. Kalin, and V. S. Efimov

Moscow Engineering Physics Institute, National Research Nuclear University, Moscow, 115409 Russia

e-mail: mephist.aung@gmail.com, i_chernov@mail.ru, m.staltsov@gmail.com, BAkalin@mephi.ru

Received March 18, 2014

Abstract—Hydrogen retention in vanadium and its binary alloys with titanium are investigated by means of hydrogen thermal desorption spectrometry. The samples are saturated with hydrogen for 2000 h at a temperature of 620 K in an autoclave, where hydrogen is fed at a pressure of 16.8 MPa. It is shown that in V–Ti alloys there are two main types of traps for hydrogen and from which the hydrogen release occurs in the temperature range of 780–790 (peak I) and 870–880 K (peak II) The position of peak I on the temperature scale does not depend on the alloy composition, and the intensity and position of peak II on the temperature scale are determined by the alloy composition. Titanium nonmonotonically affects the amount of hydrogen retained: an addition of 0.5% Ti decreases, 1 and 5% Ti increases, and 10% Ti again decreases the amount of hydrogen in the alloy. A physical explanation of the appearance of two peaks of hydrogen thermal desorption and nonmonotonic influence of titanium on the amount of hydrogen in vanadium is proposed.

Keywords: vanadium, vanadium alloys, hydrogen, hydrogen retention, hydrogen thermal desorption

DOI: 10.1134/S2075113315020045

INTRODUCTION

Vanadium alloys with the rapid reduction of the induced activity of a V–Ti–Cr system are considered to be promising structural materials for application in future fusion reactors (FRs) of a DEMO type [1–3]. There is an interesting idea to use vanadium alloys as a fuel element cladding in fast neutron reactors (FNRs) with sodium cooling, where the required high-temperature strength is provided by a vanadium alloy and required corrosion resistance is provided by clad layers made from ferritic steel [4]. Embrittlement of vanadium alloys during operation can occur in contact with hydrogen isotopes [5–9]. For example, in [7], it is shown that a reduction in the relative elongation of V–Ti–Cr alloys in a hydrogen atmosphere (P ≈ 0.13 kPa) begins at a concentration of 360 wppm H_2. There are a number of sources where hydrogen penetrates into structural material in FRs and FNRs: the main one is transmutation reactions of type (n, p), (n, d), (n, t), and (n, n^1p), which have a threshold (energy) character. It should be noted that the amount of hydrogen accumulated in vanadium in FRs significantly exceeds that in FNRs. For example, it was calculated that ~20 appm is accumulated in vanadium after 560 days of irradiation in the BN-600, whereas ~680 appm H is accumulated in the DEMO RF [10].

Hydrogen can be specifically introduced into a liquid metal coolant to eliminate oxide deposits. Another source of hydrogen input to the structural materials of the first FR wall is plasma radiation.

Vanadium alloys which contain titanium, a strong hydride-forming element, are currently considered as structural materials for nuclear reactors [3, 11, 12]. The most promising alloy for application in FR is the ternary alloy V–4% Ti–4% Cr. This work was aimed at finding the regularities of the retention of hydrogen depending on the titanium content in the V–Ti alloys saturated with hydrogen.

EXPERIMENTAL

The first stage was to produce the samples of V–Ti alloys, namely, to prepare a master alloy (alloy with a maximum titanium content V–10 wt % Ti) by alloying vanadium with titanium in a MIFI-9 vacuum arc furnace. Model alloys with 0.5, 1, 5, and 10% Ti additions were prepared by alloying the master alloy with vanadium. The content of titanium was determined using a Camebax SX-50 microanalyzer. Pure vanadium served as a reference. The deviation of alloy composition from the calculated one was not more than 5%.

After repeated rolling with intermediate homogenizing annealing at 1080 K to a final thickness of ~0.25 mm, the samples with dimensions of $25 \times 7 \times 0.25$ mm^3 were annealed in a vacuum of 10 MPa at 1273 K for 2 h and then cooled together with a furnace. Before hydrogen saturation, the samples were electropolished to a mirror finish in a solution of H_2SO_4 (concentrate) + 5% ethanol.

The content of hydrogen in the initial samples, which was determined using a Leco RH-402 gas analyzer, was at the level of 0.0006 ± 0.0003%. The samples were saturated with hydrogen for 2000 h at a temperature of 620 K in an autoclave, where hydrogen was fed at a pressure of 16.8 MPa. All samples were weighed on AND GR-202 scales with an accuracy of ±0.01 mg for the subsequent determination of the amount of hydrogen captured. Prior to the study, we registered a hydrogen signal from a container for storage of samples by thermal desorption spectrometry (TDS). It was found that samples with hydrogen give a signal that is more than two orders of magnitude higher, so the signal from the container was neglected. The study of gas release was carried out at a rate of uniform heating of 2 K/s.

A highly sensitive Leco RHEN-602 gas analyzer was used to measure the absolute amount of hydrogen captured by the materials by the reductive melting method with the induction heating of samples in a furnace in a nitrogen stream (two series of experiments).

RESULTS AND DISCUSSION

Figure 1 shows hydrogen thermal desorption spectra of vanadium alloy samples. Two main gas release peaks are observed: low-temperature and high-temperature. All the spectra exhibit low-temperature peak I in the temperature range of 780–790 K, the height of which depends on the alloy composition in contrast to its position on the temperature scale, and high-temperature peak II at 870–880 K, the height and position of which on the temperature scale depend on the alloy composition. As Fig. 1 suggests, an increase in the titanium content in vanadium results in the change in the intensities of peaks I and II: at 0.5 wt % Ti, the ratio between the heights of these peaks hardly changes; at 1 wt % Ti, the height of peak I increases and the intensity of peak II decreases; and vice versa, at 5 and 10 wt % Ti, the height of peak I decreases and the intensity of peak II increases, this effect being more pronounced in the range from 5 to 10 wt % Ti. TDS spectra (Fig. 1) show a nonmonotonic titanium effect on the intensities of TDS peaks and the position of peak II.

It is seen from the dependence of the amount of hydrogen retained on the titanium content, which was determined by the TDS method (Fig. 2), that 0.5 wt % Ti reduces the hydrogen concentration by nearly a factor of 3 as compared with that captured by vanadium; at 1 wt % Ti, the amount of hydrogen retained returns to the initial level; the maximum hydrogen concentration is observed in the V–5% Ti alloy and it is ~5.5 × 10^{20} at H/g (ratio of the number of hydrogen atoms to the number of atoms of the alloy at H/at V is ~4.5%). The amount of hydrogen retained decreases to ~4.5 × 10^{20} at H/g (at H/at V ~ 3.8%) as the titanium content increases to 10%. In such a way, the effect of the Ti concentration in V on the amount of hydrogen retained is as nonmonotonic as its effect on the position of peak II in the TDS spectrum (Fig. 1).

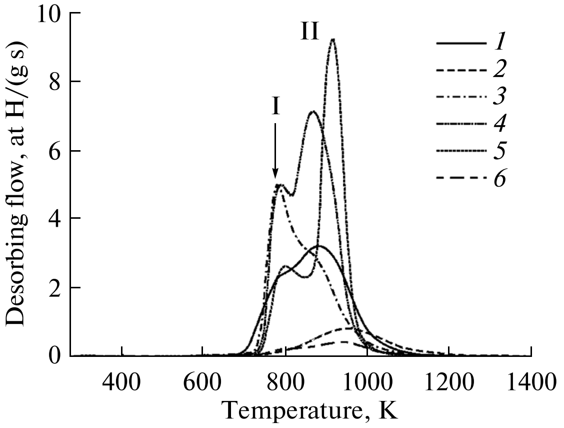

Fig. 1. Spectra of hydrogen thermal desorption from vanadium alloy: (*1*) V; (*2*) V + 0.5% Ti; (*3*) V + 1% Ti; (*4*) V + 5% Ti; (*5*) V + 10% Ti; (*6*) V + 5% Fe at a uniform heating rate of 2 K/s.

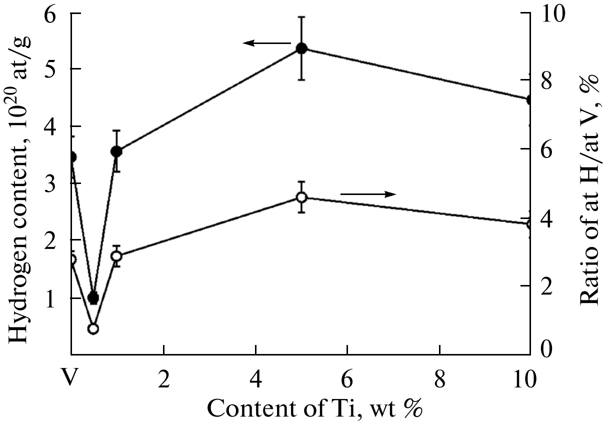

Fig. 2. Amount of hydrogen retained vs. titanium content in vanadium calculated from TDS studies.

Figure 3 shows the results of the study of the absolute amount of hydrogen retained in V–Ti, which was determined in the RHEN-602 gas analyzer. The dependence of the amount of hydrogen retained on the titanium content (Fig. 3) is similar to that obtained by the TDS method (Fig. 2).

The regularities of the capture, retention, and release of hydrogen and the effect of alloying elements, in particular, Ti in V, on these processes are largely determined by the state in which hydrogen occurs in metals. It is widely believed [12–14] that hydrogen in materials can exist in one of the following states: atomic (H^0), ionic (H^+ and H^-), molecular (H_2), in compounds with metals (hydrides M_mH_n), and in compounds with impurities (e.g., CH_4, H_2S). In addition, hydrogen can form complexes with point defects, for example, with vacancies H_mV_n (V means a vacancy; m and n are the number of hydrogen atoms and vacancies in the complex, respectively) and with

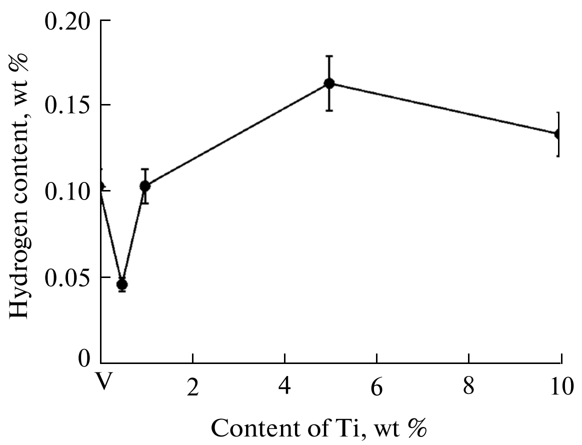

Fig. 3. Absolute amount of hydrogen trapped vs. titanium content in vanadium (RHEN-602 gas analyzer).

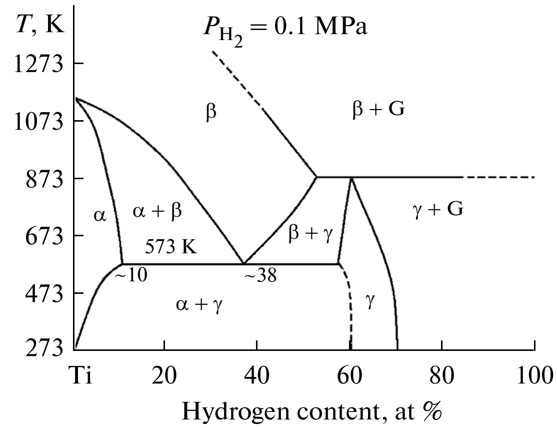

Fig. 4. Ti–H phase diagram: α and β solid solutions of hydrogen in α- and β-Ti; γ-TiH_2 [17].

vacancies and impurities $H_mX_nV_k$ (X means an interstitial impurity), and other complexes [15].

The presence of two gas release peaks in the TDS spectra indicates the existence of two main types of traps for hydrogen in vanadium and its alloys. Hydrogen was introduced into the samples in the autoclave without causing radiation damage to their structure. Since the position of low-temperature peak I on the temperature scale is independent of the chemical composition of the material (Fig. 1), we have assumed that traps for hydrogen in the temperature range of 780–790 K are such defects, whose energy of binding with hydrogen and hydrogen capacity are not affected by the presence of atoms of the alloying elements in solid solution. Since vanadium hydrides are thermally unstable, namely, they dissolve already at temperatures from 270 K [16, 17], such traps can be thermal vacancies [15], dislocations, grain boundaries, twins, discontinuities, and other hereditary defects, which in combination with hydrogen atoms have a positive binding energy. For example, in α-Fe, the binding energy is 0.45–0.53 eV for H–V, 0.71–0.90 eV for H–V_m ($m > 4$), 0.24–0.62 eV for H-dislocation, 0.78 eV for H-pore, 0.75–0.70 eV for H-helium bubble, and 0.29 eV for H–TiC [12]. It is shown by calculation [15] that in vanadium one vacancy can hold twelve hydrogen atoms when they are introduced simultaneously and six hydrogen atoms when they are introduced sequentially. It is shown in [6] that in vanadium alloys the chemical composition of the alloy is responsible for the amount of hydrogen trapped. The fact that the intensity (height) of peak I depends on the Ti content may indicate, for example, that titanium atoms change the concentration of this type of traps and/or the binding energy between them and hydrogen atoms.

Traps of the second type, from which hydrogen escaping upon heating results in the appearance of peak II, are more effective for trapping the hydrogen. In this case, both the intensity of peak II and its position on the temperature scale are determined by the titanium concentration (Fig. 1), whose influence on them and the amount of hydrogen retained are nonmonotonic (Figs. 2, 3). It can be assumed that, in addition to hydrogen captured by the traps of the first type, it is trapped by titanium hydrides, or complex hydrides like $Ti_{1-x}V_xH_y$, or γ titanium hydrides like TiH_2 (Fig. 4), since the standard enthalpy of formation of titanium hydride is less (–144.4 kJ/mol [18]) than that of vanadium hydrides (–39.9 kJ/mol [19]).

It was shown in [20] that initial V included 0.08 ± 0.01% O_2 and 0.0090 ± 0.0003% N_2, and the initial V–5% Ti alloy contained 0.32 ± 0.01% O_2 and 0.0064 ± 0.0003% N_2. It is established in the same paper using internal friction measuring methods and X-ray phase analysis that titanium at low concentrations participates in the formation of various complexes such as Ti–O, Ti–O–V, $VTiO_x$, and others, and nitrides. This occurs because the enthalpy of their formation is significantly less than that of titanium hydride (table), i.e., titanium in an amount of 0.5 wt % (0.53 at %) is

Standard enthalpy and entropy of the formation of hydride, oxides, and titanium nitride [21]

Compound	TiH_2	Ti_2O_3	Ti_3O_5	TiO_2	TiN
$-\Delta H^0_{298}$, kJ/mol	122–147	1525 ± 8	2465 ± 18	937–949	281–340
S^0_{298}, kJ/mol	30	79.0 ± 0.8	130 ± 1	~50	30.0 ± 0.4

not involved in the formation of hydrides, but is consumed for binding oxygen and nitrogen, the total concentrations of which in vanadium amounts to 0.58 at % [20]. It seems that this should not lead to a decrease in the amount of hydrogen retained in the V–0.5% Ti alloy compared with that in vanadium. This reduction in the amount of hydrogen is possible in the case where oxygen and nitrogen in a vanadium solid solution promote retention of hydrogen; for example, they greatly distort the crystal lattice as interstitial impurities. Such interstitial places play the role of vacancy sinks and, hence, they trap hydrogen atoms. The titanium-induced escape of oxygen and nitrogen from the solid solution reduces the number of such traps and leads to a reduction in the hydrogen concentration in the V–0.5% Ti alloy (Figs. 2 and 3).

The amount of hydrogen retained again increases with increasing Ti content to 1 and 5 wt %, since only a fraction of titanium is involved in the formation of oxides and nitrides, while the rest forms hydrides with a decomposition temperature of 870 K and above, which becomes clear from comparing the temperature of peak II (Fig. 1) and the temperature at which γ titanium hydride decomposes (Fig. 4).

It is shown in [22] that, at a content of ~10% Ti, vanadium begins to take up part of the electron density from titanium. Therefore, a decrease in the electron density of titanium atoms reduces the number of hydrides formed and, correspondingly, reduces the amount of hydrogen retained in the V–10% Ti alloy as compared with that in the V–5% Ti alloy (Figs. 2 and 3).

Thus, the effect of titanium content on the capture and retention of hydrogen by vanadium alloys is nonmonotonic. In this case, the specific behavior of hydrogen in V–Ti alloys is observed in the same concentration ranges (tenths of a percent and more than 5% Ti) as the nonmonotonic Ti content dependence of mechanical and high-temperature properties [3, 23], internal friction [20], the laws of the capture and release of helium [24], and the parameters of helium gas porosity and swelling [25].

CONCLUSIONS

(1) It was established that all the spectra of the V–Ti alloys saturated with hydrogen in the autoclave exhibit two peaks: low-temperature peak in the temperature range of 780–790 K, the height of which depends on the alloy composition in contrast to its position on the temperature scale, and high-temperature peak at 870–880 K, the height and position of which on the temperature scale depend on the alloy composition.

(2) As compared with the hydrogen trapped in vanadium, titanium was shown to nonmonotonically affect the amount of hydrogen retained: an addition of 0.5% Ti decreases, 1 and 5% Ti increases, and 10% Ti again decreases the amount of hydrogen in the alloy.

(3) A physical explanation of the appearance of the two peaks of hydrogen thermal desorption and nonmonotonic influence of titanium on the amount of hydrogen in vanadium was proposed.

ACKNOWLEDGMENTS

We thank A.A. Pisarev and Yu.M. Gasparyan, Plasma Physics Department of the National Research Nuclear University "Moscow Engineering Physics Institute," for the assistance and performance of thermal desorption studies.

This work was performed at the Center of Nuclear Systems and Materials and was supported by the Ministry of Education and Science of the Russian Federation (contract no. 02.a03.21.0005, August 27, 2013).

REFERENCES

1. Smith, D.L., Loomis, B.A., and Diercks, D.R., Vanadium-base alloys for fusion reactor applications - a review, *J. Nucl. Mater.*, 1985, vol. 135, pp. 125–139.
2. Votinov, S.N. and Dedyurin, A.I., Vanadium based alloys—prospective low-activation structural materials for thermonuclear reactors, *Vopr. At. Nauki Tekhn. Ser. Materialoved. Nov. Mater.*, 1995, iss. 1 (52), pp. 66–73.
3. Kalin, B.A., Staltsov, M.S., and Chernov, I.I., Low-activation vanadium alloys for nuclear and thermonuclear energy: Principles of alloying, radiation resistance, problem of helium and hydrogen, *Nucl. Phys. Engin.,* 2011, vol. 2, no. 4, pp. 320–344.
4. Alekseev, O.A., Votinov, S.N., Gubkin, I.N., Karasev, Yu.V., Kolotushkin, V.P., Nikulin, S.A., Potanina, L.V., Sergeev, S.G., and Sokolovskii, D.V., Vanadium alloy cladding by ferritic stainless steel as material for fast reactors, *Perspekt. Mater.*, 2009, no. 4, pp. 34–42.
5. Buxbaum, R.E., Subramanian, R., Park, J.H., and Smith, D.L., Hydrogen transport and embrittlement for palladium coated vanadium-chromium-titanium alloys. *J. Nucl. Mater.*, 1996, vol. 233–237, pp. 510–512.
6. Natesan, K. and Soppet, W.K., Performance of V–Cr–Ti alloys in a hydrogen environment, *J. Nucl. Mater.*, 2000, vol. 283–287, pp. 1316–1321.
7. Aoyagi, K., Torres, E.P., Suda, T., and Ohnuki, S., Effect of hydrogen accumulation on mechanical property and microstructure of V–Cr–Ti alloys, *J. Nucl. Mater.*, 2000, vol. 283–287, pp. 876–879.
8. Chen, J., Xu, Z., and Yang, L., The influence of hydrogen on tensile properties of V-base alloys developed in China, *J. Nucl. Mater.*, 2002, vol. 307–311, pp. 566–570.
9. Torres, P., Aoyagi, K., Suda, T., Watanabe, S., and Ohnuki, S., Hydride formation and fracture of vanadium alloys. *J. Nucl. Mater.*, 2002, vol. 307–311, pp. 625–629.
10. Blokhin, D.A. and Chernov, V.M., Nucleation of hydrogen and helium in structural materials of fusion and fission reactors, *Vopr. At. Nauki Tekhn. Ser. Materialoved. Nov. Mater.*, 2008, no. 2(71), pp. 112–122.

11. Petrov, V.S., Bondarenko, G.G., Vasilyevsky, V.V., and Loginov, B.A., Investigation of Ti and Nb interactions with hydrogen by thermogravimetric analysis and scanning probe microscopy methods, *Perspekt. Mater.*, 2005, no. 6, pp. 26–29.
12. Kalin, B.A., Kalashnikov, A.N., Chernov, I.I., and Shmakov, A.A., Hydrogen problems in reactor materials, *Proc. 7th Int. School of Young Scientists and Specialists (IHISM'11) "Interaction of hydrogen isotopes with structural materials,"* Zvenigorod, 2011, pp. 10–54.
13. *Fizicheskoe materialovedenie. Tom 6. Konstruktsionnye materially yadernoi tekhniki* (Physical Material Science. Vol. 6. Structural Materials of Nuclear Technique), Kalin, B.A., Ed., Moscow: NRNU MEPhI, 2012.
14. Vaynman, A.B., Melekhov, R.K., and Smiyan, O.D., *Vodorodnoye okhrupchivaniye elementov kotlov vysokogo davleniya* (Hydrogen Brittleness of High-Pressure Boilers), Kiev: Naukova Dumka, 1991.
15. Gui, Li-Jiang, Liu, Yue-Lin, Wang, Wei-Tian, Li-Jiang Gui, Yue-Lin Liu, Wei-Tian Wang, Jin, Shuo, Zhang, Ying, Lu, Guang-Hong, and Yao, Jun-En, First principles investigation on vacancy trapping behaviors of hydrogen in vanadium, *J. Nucl. Mater.*, 2013, vol. 442, Suppl. 1, pp. 688–693.
16. Muzgin, V.N., Khamzina, L.B., and Zolotavin, V.L., *Analiticheskaya khimiya vanadiya* (Analytical Chemistry of Vanadium), Moscow: Nauka, 1981.
17. Barabash, O.M. and Koval, Yu.N., *Struktura i svoystva metallov i splavov: Kristallicheskaya struktura metallov i splavov* (Structure and Properties of Metals and Alloys: Crystal Structure of Metals and Alloys), Kiev: Naukova Dumka, 1986.
18. Barin, I., *Thermochemical Data of Pure Substances. Part I–III*, Weineheim: VCH Verlags, 1995.
19. Golubkov A.N., Yukhimchuk A.A.. Equilibrium pressure of protium and deuterium over vanadium dihydrate phase, *Proc. NATO Adv. Res. Workshop on Hydrogen Materials Science and Chemistry of Materials,* 1999, Katsiveli, Yalta, Ukraine, pp. 255–264.
20. Anan'in, V.M., Kalin, B.A., Korchagin, O.N., Staltsov, M.S., and Chernov, I.I., Investigation of oxygen–titanium interaction in vanadium by internal friction method, *Inorganic Mater.: Appl. Res.*, 2012, vol. 3, pp. 243–247.
21. Ruzinov, L.P. and Gulyanitsky, B.S., *Ravnovesnye prevrashcheniya metallurgicheskikh reaktsii* (Equilibrium Transformations of Metallurgical Reactions), Moscow: Metallurgiya, 1975.
22. Votinov, S.N., Kolotushkin, V.P., and Parfenov, A.A., http://bus.znate.ru/docs/index-27154.html?page=3).
23. Yefimov, Yu.V., Baron, V.V., and Savitsky, Ye.M., *Vanadiy i ego splavy* (Vanadium and Its Alloys), Moscow: Nauka, 1969.
24. Chernov, I.I., Staltsov, M.S., Kalin, B.A., Kyi, Zin Oo, Aung, Kyaw Zaw, Statsenko, V.I., Korchagin, O.N., and Staltsova, O.S., An investigation of He thermodesorption behavior in V–Ti alloys irradiated with He+ ions at room temperature, *Fiz. Khim. Obrab. Mater.*, 2012, no. 3, pp. 22–29.
25. Chernov, I.I., Staltsov, M.S., Kalin, B.A., Mezina, O.S., Oo, K.Z., and Chernov, V.M., Mechanisms of helium porosity formation in vanadium alloys as a function of the chemical composition, *At. Energy,* 2011, vol. 109, pp. 176–183.

Translated by T. Gapontseva