

Conference Paper

Helium Porosity Formation in Vanadium Alloys of V-Ti-Cr, V-W-Zr and V-W-Ta Systems in Comparison with Binary Alloys

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Abstract

Vanadium alloys are considered candidates for use as structural materials of fusion reactors. A large amount of helium will be accumulated in such materials. The presence of helium in the materials may result in gas swelling. This paper presents the results on helium porosity formation researches in V-Ti-Cr, V-W-Zr and V-W-Ta alloys obtained by means of TEM. Samples were irradiated by 40 keV He⁺ ions up to dose of $5 \cdot 10^{20} \text{ m}^{-2}$ at 923 K.

Alloy V-4%Ti-4%Cr has a smallest helium swelling among the ternary alloys and its swelling is significantly lower than swelling of dual V-Ti and V-Cr alloys. The swelling of the ternary V-2%W-1%Zr alloy is more than 3 times less than the swelling of vanadium, several times less than that of V-W alloys and slightly lower than the swelling of V-Zr alloys. Swelling increases by a factor of 1.5 with increasing of Zr content to 2% in the ternary V-2%W-1%Zr alloy. Similarly, gas swelling of ternary V-2%W-1%Ta alloy is significantly lower than that for binary V-W and V-Ta alloys.

Assumptions are made about the possible mechanisms of the effect of alloying elements in vanadium on helium porosity formation.

Keywords: vanadium alloys, swelling, helium, radiation resistance.

1. Introduction

The implementation of the closed nuclear fuel cycle technology along with the increase in processing capacity requires the commissioning of a new generation of nuclear power plants, primarily fast reactors (FR) with an increased fuel burn-up (from now reached $\sim 12\%$ h.a. in BN -600 to 18–22% h.a. in the future). This is impossible without the creation of new structural materials for the core, which could replace a highly swelling austenitic steel. From this point of view, vanadium is of great interest the

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Received: 21 December 2017

Accepted: 15 April 2018

Published: 6 May 2018

Publishing services provided by
Knowledge E

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Selection and Peer-review under the responsibility of the MIE-2017 Conference Committee.

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most important property of which is the low capture cross section of fast neutrons. A number of vanadium alloys show a high resistance to radiation swelling without a significant decrease in ductility under irradiation with fast neutrons as well as in simulation investigations using heavy ions [1]. Vanadium alloys have high creep resistance at temperatures up to 973–1123 K [1–4]. Vanadium is a good basis for the creation of heat resistant alloys with a rapid decline in induced activity in addition in addition [1–6]. It has a relatively high thermal conductivity and a low coefficient of thermal expansion which contribute to lower thermal stresses for a given heat flux compared to candidate structural steels of various classes. Therefore, vanadium alloys are considered promising structural materials for future fission and fusion reactors of the DEMO type [2, 3, 7].

Cores structural materials of the new generation of FR and the fusion reactors will be exposed to intense neutron fluxes up to large damaging doses. High concentrations of helium and hydrogen will be accumulated in the materials due to transmutation reactions under these conditions. Besides, helium and hydrogen isotopes can be directly introduced by radiation from the plasma in the fusion reactors. Helium affects the kinetics of vacancy porosity development and void swelling [8] and at high concentrations causes gas swelling [9–11]. As well known, pure vanadium is subject to high level of helium swelling but alloying can significantly reduce it [12, 13], but the effect of the doping on the helium porosity development can be ambiguous.

This paper presents the results of a study of the helium porosity development and gaseous swelling in ternary alloys of the V-Ti-Cr, V-W-Ta and V-W-Zr systems in comparison with binary vanadium alloys after irradiation by helium ions.

2. Materials and experimental procedure

All model alloys were melted in a vacuum-arc furnace using vanadium of 99.86 % purity. In addition, V-4% Ti-4% Cr alloys of pilot industrial smelting were investigated (Table 1). All model alloys were annealed at 1273 K for 2 h. Several types of treatments were performed for V-4%Ti-4%Cr alloys: annealing at 1273 K, 2 h; 20% cold working (CW); 20% CW + annealing at 1273 K, 2 h.

The samples were collected in special cassettes containing up to 8 samples and irradiated under identical conditions with 40 keV He⁺ ions up to a fluence of $5 \cdot 10^{20} \text{m}^{-2}$ at $T_{irr} = 923 \text{ K}$ in the ILU-3 ion accelerator of the Kurchatov Institute.

Thin foils for a transmission electron microscope (TEM) were obtained in the Tenupol-5 device by jet electro polishing. Investigation of irradiated samples

TABLE 1: The investigated materials and parameters of helium porosity in them (d_{max} and d_{av} are the maximum and average sizes correspondingly (averaged over several pictures); ρ is the bubbles density; S is swelling of irradiated layer.

Material (all is in wt. %)	d_{max} , nm	d_{av} , nm	ρ , 10^{22} m^{-3}	S, %
Model alloys				
V (99.86 %)*	11	4.4	6.6 ± 1.3	0.7 ± 0.2
V (99.98 %)	22	8.6	1.7 ± 0.4	4.5 ± 1.1
V-2%W-1%Zr	8.4	4.0	6.2 ± 1.2	0.20 ± 0.04
V-2%W-2%Zr	10.1	3.3	13.6 ± 2.7	0.30 ± 0.06
V-2%W-1%Ta*	15	9.8	1.5 ± 0.4	0.8 ± 0.2
V-4%Cr-4%Ti	2.8	2.3	16 ± 3	0.09 ± 0.02
Industrial alloys				
V-4%Ti-4%Cr (annealing)	~2	~1	360 ± 90	0.21 ± 0.04
V-4%Ti-4%Cr (20% CW)	1.5	0.8	240 ± 50	0.08 ± 0.02
V-4%Ti-4%Cr (20% CW + annealing)	1.8	0.9	180 ± 40	0.09 ± 0.03
* Refined data on swelling from work [13].				

microstructure was carried out in the LIBRA-120 TEM at an accelerating voltage of 120 kV.

3. Results and discussion

Sufficiently large bubbles (gas filled pores) of predominantly cubic form and high density are formed in vanadium at high-temperature irradiation by helium ions (Fig. 1 a). The maximum bubble size is 11 nm which determined its rather high swelling of ~ 0.7% (see Table 1). As can be seen in Fig.1 and Table 1, the purity of vanadium has a significant influence on porosity evolution and helium bubbles parameters. Fig. 1 b shows the microstructure of vanadium of higher purity irradiated under the same conditions. It can be concluded from the data in Table 1 that a more pure vanadium is prone to more gas swelling. This can be due to the fact that interstitial impurities (C, O, N) can form thermally stable complexes of $\text{He}_m\text{X}_k\text{V}_n$ type (X - is the interstitial impurity atom, V is vacancy here) [14], in which a significant part of helium can be retained, preventing the transfer of helium to the bubbles.

Fig. 2 shows microstructure of different volumes of the ternary V-2%W-1%Zr alloy. It can be seen that there is a tendency towards rounding of bubbles, and also polyhedral

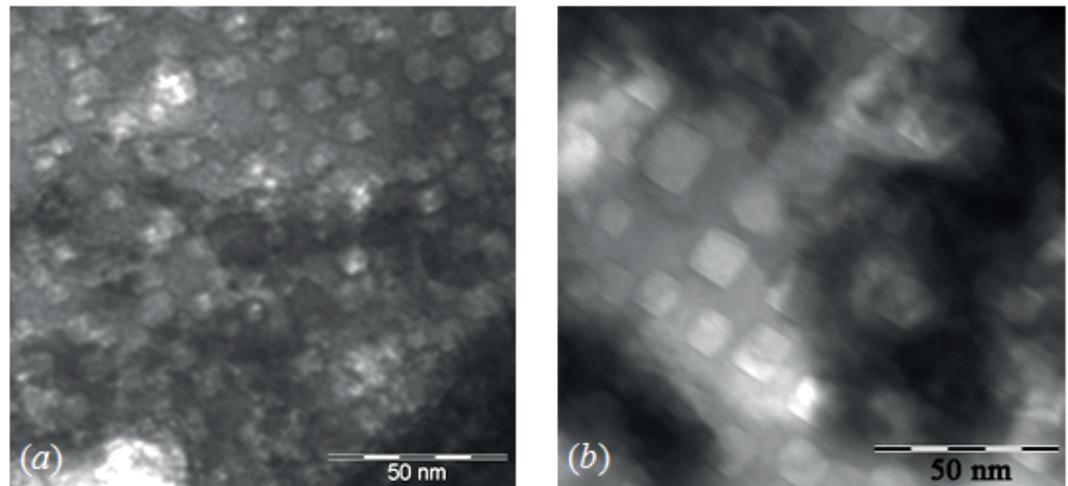


Figure 1: Microstructure of vanadium samples irradiated by He^+ ions: (a) vanadium of 99.86 % purity, (b) vanadium of 99.98 % purity.

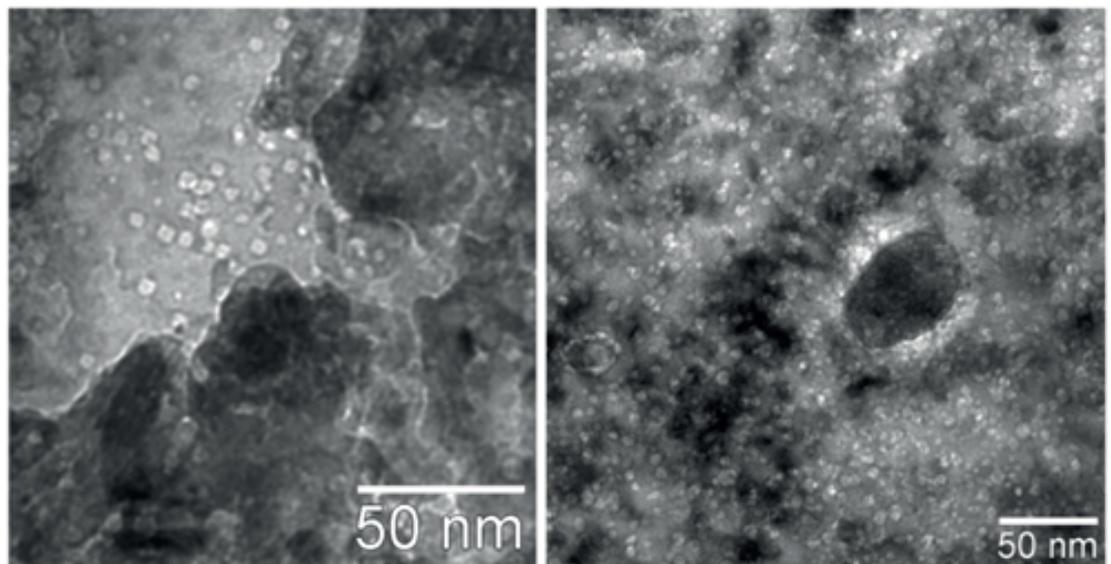


Figure 2: Microstructure of different areas of ternary V-2%W-1%Zr alloy irradiated by He^+ ions.

bubbles are observed on a par with cubic ones. With a maximum detected size of 8.4 nm, an average size of 4 nm and a bubble density of $6.2 \cdot 10^{22} \text{ m}^{-3}$, the gas swelling of this alloy was 0.2% only. Swelling of the ternary alloy is more than 3 times less than swelling of vanadium, several times smaller than for V-W alloys and slightly lower than for V-Zr alloys as shows the comparison with the porosity parameters of vanadium and binary V-W and V-Zr alloys (see Tables 1 and 2).

Photographs of different areas of the microstructure of the V-2% W-2% Zr ternary alloy are shown in Fig. 3. The proportion of large helium bubbles tends to increase and their density increases substantially as the Zr content increases from 1 to 2 wt.% (see Table 1). Despite the slightly smaller average bubble size in this alloy, an increase in the

TABLE 2: Parameters of helium porosity in binary vanadium alloys.

Material	d_{max} , nm	d_{av} , nm	ρ , 10^{22} , m^{-3}	S , %
V-1%W*	21	8.0	3.5 ± 0.7	1.0 ± 0.2
V-4%W*	29	16.5	0.9 ± 0.2	1.5 ± 0.3
V-1%Zr*	10	4.8	2.6 ± 0.5	0.4 ± 0.1
V-2%Zr*	10	3.3	9.7 ± 1.9	0.21 ± 0.04
V-2%Ta	28	12	1.6 ± 0.5	1.05 ± 0.25

* Refined data on swelling from work [13].

density of the bubbles twice and growth of their maximum size leads to a somewhat larger (1.5 times) swelling in comparison with swelling of V-2%W-1%Zr alloy. It should also be noted that the swelling of this ternary alloy is substantially lower than that of the V-W binary alloys and is approximately the same as for the V-Zr alloys (see Tables 1 and 2).

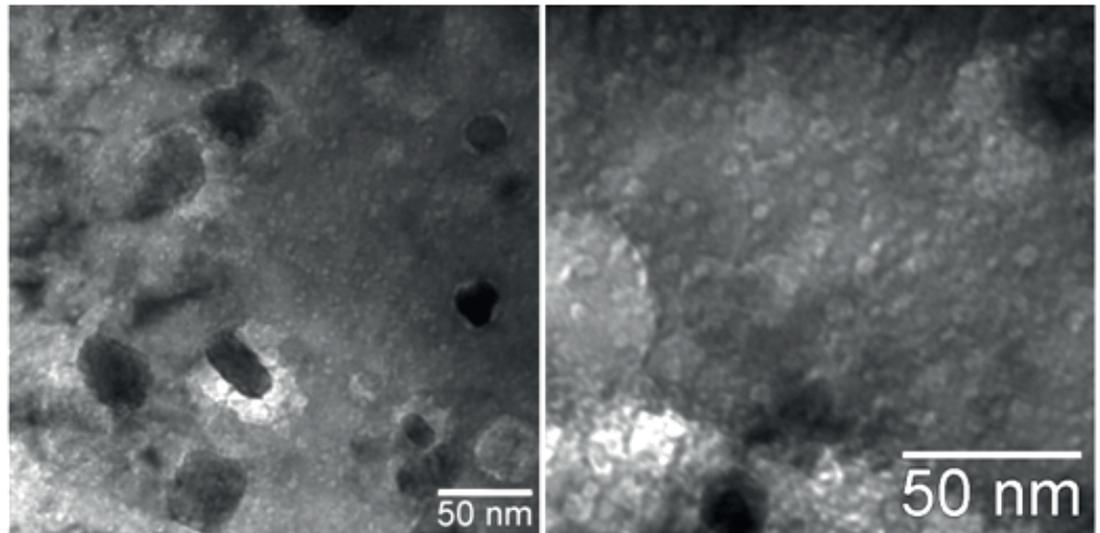


Figure 3: Microstructure of different areas of ternary V-2%W-2%Zr alloy irradiated by He⁺ ions.

Bubbles of both cubic and polyhedral forms are found in the structure of the ternary alloy V-2%W-1%Ta (Fig. 4). According to Table 1, we can conclude that the larger overall size of the bubbles and their lower density led to approximately the same swelling of this alloy as in pure vanadium. In addition, the swelling of the V-2%W-1%Ta alloy is less than that for V-W and V-Ta double alloys (see Tables 1 and 2) due to the formation of smaller bubbles.

Fig. 5 shows characteristic images of different areas of the V-4%Cr-4%Ti model alloy of laboratory melting irradiated with helium ions under conditions identical to

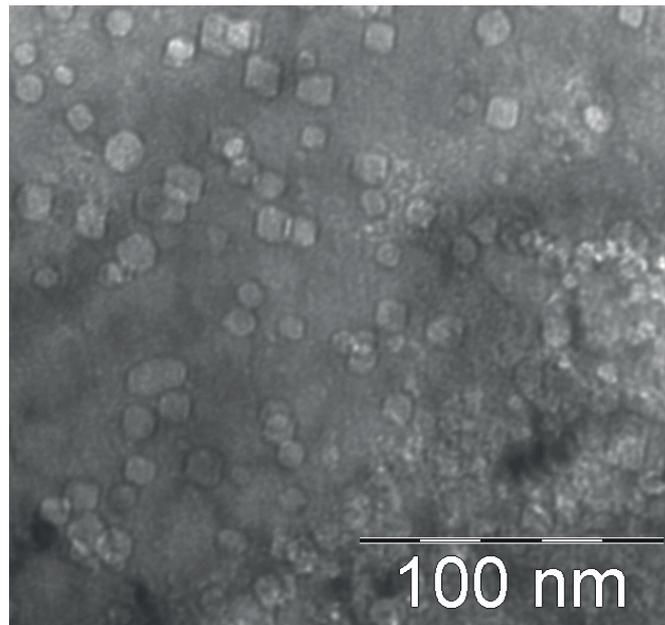


Figure 4: Microstructure of V-2%W-1%Ta ternary alloy irradiated by He⁺ ions.

irradiation of other alloys. The bubble parameters and the level of gas swelling are given in the Table 1. The smallest bubbles with dimensions of the order of 2–3 nm develop in this alloy. Such small bubble sizes despite their high density resulted in a low gas swelling value of ~ 0.1 . Chains of individual or merged bubbles along the grain boundaries were formed in the alloy V-4% Cr-4% Ti in contrast to other alloys in addition (shown by the arrows in Fig. 5). This can be a negative phenomenon since helium bubbles at the grain boundary can weaken it and lead to destruction even when low stresses.

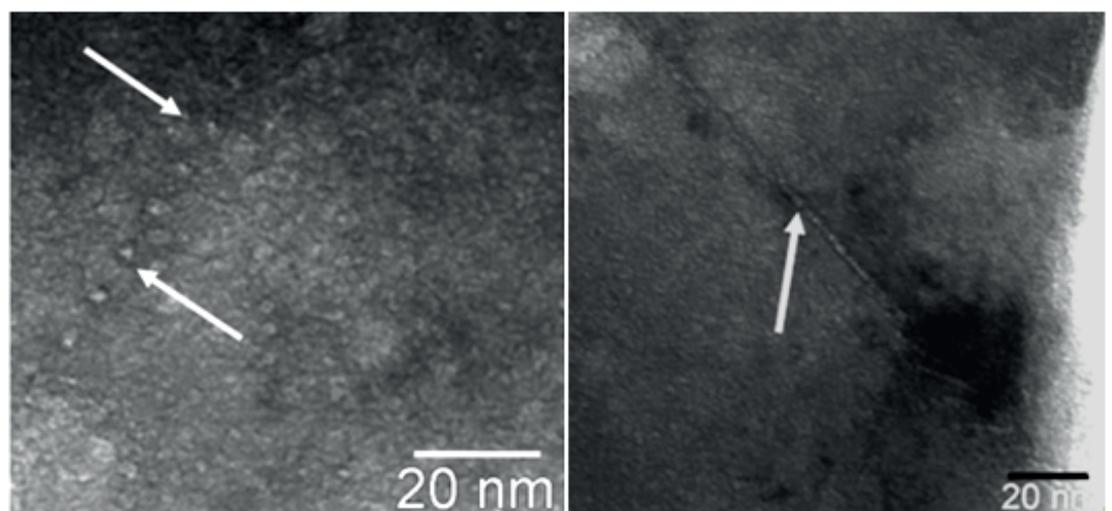


Figure 5: Microstructure of V-4%Cr-4%Ti model alloy irradiated by He⁺ ions.

Fig. 6 shows the microstructures of samples V–4%Ti–4%Cr the alloys irradiated by He⁺ ions in different initial states. Very fine high-density bubbles are formed in industrial alloys which determines very low values of helium swelling (Table 1). As seen in Fig. 6 and Table 1 the cold worked alloy has the smallest bubble sizes and swelling because of increased density of dislocations has a positive effect probably. Dislocations are sinks for point defects and nucleation centers of bubbles and an increase in the density of dislocations leads to an increase in the number of bubbles nucleations and a decrease in their size and swelling in general.

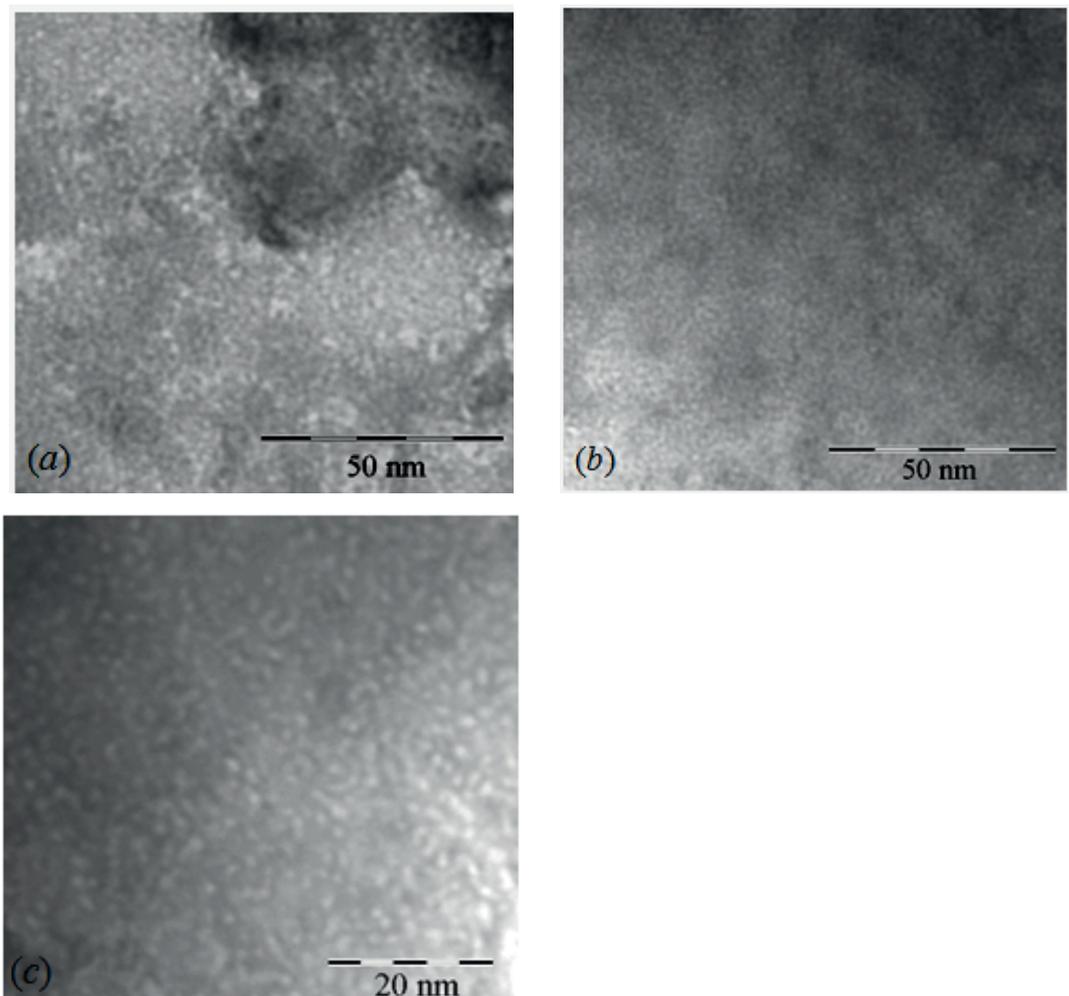


Figure 6: Microstructures of industrial alloy V–4%Cr–4%Ti irradiated by He⁺ ions after: annealing (a), CW (b) and CW + annealing (c).

Thus, analysis of the obtained microphotographs and data in Tables 1 and 2 allows us to say that, on the whole, the helium swelling of ternary alloys of V–Cr–Ti, V–W–Ta and V–W–Zr systems is lower than that of pure vanadium and V–W, V–Zr, V–Ta binary alloys. The best elements are titanium and zirconium for reduce the helium swelling both in binary and in triple vanadium alloys. Probably, this effect is realized due to

the great difference in the sizes of vanadium atoms and alloying elements in particular. Titanium and zirconium have a larger atomic sizes than vanadium. As a result, they cause compressive stresses in the vanadium lattice, which relax by the influx of vacancies. In this case, thermally stable complexes of $\text{He}_m\text{X}_k\text{V}_n$ (X is Ti or Zr) type are created [15], i.e. a significant fraction of helium and vacancies can be retained at 923 K in the lattice of vanadium alloys with "oversized" alloying elements in the form of complicative complexes. An additional effect is the creation of a larger number of bubble nucleation centers which increases bubbles density and reduces the their size [12].

The increase in gas swelling under alloying of vanadium by tungsten, the reduction in swelling during doping by zirconium, and the decrease in helium swelling in the ternary alloys of the V-W-Zr, V-W-Ta and V-Cr-Ti systems is difficult to explain from the point of view of the resulted higher models at first glance. It should be noted that the effect of alloying additives in ternary alloys is obviously more complicated. The cause of such an ambiguous influence of various alloying elements on the gas swelling can to a large extent be determined by the electronic structure of the alloying element atoms, in particular, the swelling is related to the number of electrons n_e participating in the interatomic bond in the alloy [16, 17]. Swelling is maximal at $n_e = 2, 3$ and 5 for alloys with fcc structure under irradiation by heavy ions and neutrons. Deviation from these values leads to an increase in the stability of alloys to vacancy swelling. This pattern is preserved also for irradiation by He^+ ions of double nickel alloys with various doping elements of different concentrations [18]: the gas swelling of nickel alloys is maximal with the number of electrons participating in the interatomic bond close to three. Swelling decreases with a larger and smaller number of electrons.

It should be noted that the irradiation swelling of steels and alloys with a fcc structure has been studied to the greatest degree. For bcc steels and alloys there are similar dependencies probably, but there are no data on the number of coupling electrons for maximum swelling of bcc materials in the literature.

4. Conclusions

1. Ternary V-W-Zr alloys as well as binary V-Zr alloys have significantly lower helium swelling than pure vanadium and binary V-W alloys.
2. Ternary alloy V-2%W-1% has slightly higher swelling than vanadium but its swelling is lower than that for V-W and V-Ta double alloys.

3. Alloys V–4%Ti–4%Cr have the lowest swelling irrespective of the used heat treatment and whether they are manufactured by laboratory or experimental-industrial melting.
4. Primary cold working reduces the size of the forming bubbles and gas swelling.
5. The best alloying elements are titanium and zirconium from the point of view of suppressing helium swelling in both binary and ternary alloys.

The work was carried out within under Governmental Support of Competitive Growth Program of NRNU MEPhI (agreement No.02.a03.21.0005) and Council on grants of the President of the Russian Federation.

References

- [1] D.L. Smith, B.A. Loomis, D.R. Diercks, J. Nucl. Mater. 135 (1985) 125–139.
- [2] L.I. Ivanov, Yu.M. Platov, Radiation Physics of Metals and Its Applications, Nauka, Moscow, 2002 (in Russian).
- [3] B.A. Kalin, P.A. Platonov, Yu.V. Tuzov et al., Physical Materials Science, vol. 6: Structural Materials for Nuclear Technology, MEPhI, Moscow, 2012 (in Russian).
- [4] S.N. Nikulin, S.N. Votinov, A.B. Rozhnov, Vanadium Alloys for Nuclear Application, MISIS, Moscow, 2014 (in Russian).
- [5] G. J. Butterworth, C.B.A. Forty, J. Nucl. Mater. 212–215 (1994) 628–634.
- [6] A.V. Vatulin, VANT: Mat. Sci. New Mat. 1(62) 2004 26–41 (in Russian).
- [7] I.E. Lublinskiy, A.V. Vertkov, V.A. Evtikhin et al., VANT: Fusion 3 (2005) 70–78 (in Russian).
- [8] V.F. Zelenskiy, I.M. Nekludov, T.P. Chernyaeva, Radiation Defects and Swelling, Naukova dumka, Kiev, 1988 (in Russian).
- [9] I.I. Chernov, S.Yu. Binukova, B.A. Kalin et al., J. Nucl. Mater. 367–370 (2007) 468–472.
- [10] I.I. Chernov, B.A. Kalin, M.S. Staltsov et al., J. Nucl. Mater. 459 (2015) 259–264.
- [11] S.Yu. Binyukova, I.I. Chernov, B.A. Kalin et al., J. Nucl. Mater. 367–370 (2007) 500–504.
- [12] M.S. Staltsov, I.I. Chernov, B.A. Kalin et al., J. Nucl. Mater. 461 (2015) 56–60.
- [13] M.S. Stal'tsov, I.I. Chernov, A.K. Zaw et al., Atomic Energy. 116(1) (2014) 35–41.
- [14] G.J. Van der Kolk, A. Van Veen, L.M. Caspers, Delft. Progr. Rept. Ser.: Phys. and Phys. Eng. 4(1) (1979) 19–28.
- [15] I.I. Chernov, B.A. Kalin, A.N. Kalashnikov, V.M. Ananin, J. Nucl. Mater. 271&272 (1999) 333–339.

- [16] R. Jones, D. Atteridge, *J. Nucl. Mater.* 66 (1977) 329–332.
- [17] R. Pinizzotto, L. Chen, A. Ardell, *Met. Trans.* 9A(12) (1978) 1715–1727.
- [18] S.Yu. Binyukova, I.I. Chernov, B.A. Kalin et al., *Atomic Energy* 93(1) (2002) 569–577.