

Abnormalities of physics and mechanical properties, behavior of helium and hydrogen in the V-Ti alloys (Overview)

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Abstract. The paper presents the results of studies of physical and mechanical properties, helium and hydrogen behavior in vanadium-titanium alloys depending on titanium content. In particular, the results of helium swelling research, thermal desorption studies of helium and hydrogen behavior, results of internal friction measurements, measuring amount of hydrogen retained introduced by various methods. It was shown that the addition of titanium to vanadium have nonmonotonic influence on the behavior of implanted helium and hydrogen, as well as on the physical and mechanical and radiation properties known in literature. It is expected that such an abnormal influence of titanium on various properties of vanadium-titanium alloys occurs because of the interaction of vanadium and titanium atoms with atoms of interstitial impurities.

1. Introduction

The properties of vanadium alloys are of considerable interest to researchers because vanadium considered a promising material for use as a structural material in fast and fusion reactors. Vanadium and its alloys exceed a number of other candidate materials on complex of some properties such as specific strength, drop of induced activity and etc. Of greatest interest are alloys on the base of system vanadium-titanium. A number of investigators has been observed that alloying by titanium nonmonotonically influences some alloys properties [1–9]. It is shown [10] the data the system of V-Ti alloys is abnormal on change of physical-mechanical, radiation and other properties depending on content of alloying element, especially at low concentration area from a few tenths to a few percents of titanium. It is also noted that the mechanical properties, creep, radiation swelling of vanadium alloys significantly depend on the presence and concentration of interstitial impurities (O, N, C etc.).

2. Experimental results

2.1. Internal friction

Measuring temperature dependences of logarithmic decrement damping of oscillations (abbreviation IF for later use to denote of internal friction) is one of the methods for investigation allowing to explain the processes occurring in the interaction of alloy atoms with interstitial impurities. Vanadium and its alloys with 0.3, 0.5, 0.7, 1, 5 and 10 wt.% Ti have been investigated by IF [11]. Measurements were carried out at temperature range from room temperature up to 1123–1173 K. Table 1 shows the contents of oxygen and nitrogen in the initial samples and after measurement of IF. It is seen that in the alloy V-5 wt.% Ti (as well as in other alloys with titanium) the concentration of oxygen is significantly higher than in the initial vanadium. Oxygen and nitrogen content increases during heating at IF measurements.



Table 1. The contents of oxygen and nitrogen in initial V (1), alloy V-5 wt.% Ti (3) and in V after measurement of IF (2) [11].

No	The sample	O ₂ (%)	Standart deviation	N ₂ (%)	Standart deviation
1	V	0.081	0.0098	0.009	0.0003
2	V	0.098	0.0088	0.012	0.0024
3	V-5% Ti	0.321	0.012	0.0064	0.0003

Investigations of alloys with 0.3, 0.5, 0.7, 1 and 10 wt.% Ti shown that only single peak is at temperature of 498–500 K in IF spectra of vanadium, and it is the oxygen maximum [11]. In alloys with titanium there appear two additional peaks. The peak intensities of IF increase with increasing of Ti concentration up to 0,5 wt.%, decrease with increasing of Ti contents up to 5 wt.% and increase again with increasing Ti concentrations to 10%. All three peaks disappear substantially at a high content of titanium. A small peak is in the region of the maximum II only, but there is a maximum IV at 748 K. That is, titanium nonmonotonically affects the internal friction of alloys. Microhardness and mechanical properties of alloys change at the same regularity depending on titanium concentration in vanadium (Table 2).

Table 2. Mechanical properties at room temperature of several alloys of vanadium [3].

Alloy	σ_b , MPa	δ (%)	ψ (%)	HV (Mpa)
V-1% Ti	688	~ 0	~ 0	2863
V-2.5% Ti	618	12.5	23.7	1873
V-5% Ti	525	26.5	77.9	1687
V-10% Ti	628	27.4	66.5	1900

A number of assumptions were made in the analysis of experimental results [11]. Oxygen contained in the sample can interact only with the vanadium atoms. In so doing each oxygen atom interacts with its closest atom disposed in the center of the BCC lattice of vanadium. The height of maximum I is proportional to number of interacting pairs of O-V, i.e. to oxygen content.

Titanium captures part of available oxygen in solution at presence Ti in vanadium due to a greater affinity for oxygen than that of vanadium (enthalpies of formation of oxides TiO, Ti₂O₃, VO and V₂O₅ are 524.17, 1516.50, 426.38 and 1254.00 kJ/mole, respectively [12]). Whereby the oxygen peak height decreases. Apparently, part of titanium atoms forms a bond with vanadium atoms also creating a pair of Ti-V and a maximum III in the IF spectrum [11]. The reason for maximum III increase in the alloy with 0.5 wt.% Ti compared to 0.3 wt.% Ti is obvious, since a part of oxygen atoms are already occupied, and increase the titanium content leads to an increase in the number of pairs Ti-V.

However, peaks II and III are reduced with further increasing of titanium content, i.e. number double bond reduced. It can be explained reducing of number of pair interactions with increasing titanium content if it is granted that titanium connects the connection of oxygen and vanadium to itself when titanium content greater than 1%, forming ternary complexes V-O-Ti with higher activation energy than binary complexes. In fact, alloy with 5 wt.% Ti gives a small maximum at 748 K. As this takes place, this maximum is increased approximately two times with doubling of titanium concentration [11]. It seems reasonable to say that this maximum created by complex of three atoms of Ti-O-V located in the nearest distances in the titanium lattice [13]. If this is so, the formation of same complexes of atoms can be viewed in different alloys, such as in our case: the same complex Ti-O-V with approximately the same activation energy, but in vanadium-based alloy.

One of the major reasons for non-monotonic dependencies of V-Ti alloys properties on titanium content can be peculiarity of interaction of V and Ti atoms with interstitial impurities. As discussed

above, number of binary complexes O-V, Ti-O and Ti-V increases with increase of Ti content and, apparently, their concentrations reach a maximum in the alloy with 0,5 wt.% Ti. A maximum strength (microhardness) of V-Ti alloys is observed approximately for the same concentration of titanium. Heights of IF peaks caused by binary complexes reduced due to formation of an increasing number of ternary complexes V-O-Ti with further increase of the Ti concentration [11]. Accordingly, the strength properties of alloys reduced also. In the alloy V-5 wt.% Ti, peaks due to double bonds are virtually absent, and almost all the complexes are ternary. There is a minimum of strength properties in this alloy (see Table 2). Based on these results, one can conclude that double complexes in V-Ti alloys are more effective detents for dislocations than triple bonds, causing hardening of alloys and decrease of their ductility. Repeated increase the strength properties of the alloy with 10 wt.% Ti caused by doubling the number of ternary complexes as compared with V-5 wt.% Ti alloy as demonstrated an increase two times the peak height of IF in the first alloy [11].

2.2. Regularities of helium behavior

Regularities of gas swelling as well as capture, retention and release of helium were investigated in vanadium-titanium alloys irradiated by helium ions up to fluence of $5 \cdot 10^{20}$ He⁺/m² at 273 and 923 K [14–16]. It was shown that a nonmonotonic influence of titanium on the helium porosity parameters and gas desorption peaks temperature as on IF and mechanical properties cited above.

In studying the effect of alloying elements on the behavior of implanted helium in vanadium alloys it was supposed [14, 16] that having a larger size titanium atoms ("oversized" atom) create local compression regions of in vanadium lattice, which are sinks for radiation vacancies during low-temperature irradiation (273 K). It was found several high temperature maxima of gas release during investigations the behavior of implanted helium by means of thermal desorption spectrometry (TDS). Their appearance was explained by that vacancies trapping the helium atoms along with simple complexes of type He_mV_n (He is atom of helium, V is vacancy, m and n are their number in the complex, respectively) in pure vanadium form thermally more stable complicated complexes in V-Ti alloys also. This leads to an increase of helium release temperature on doping titanium to vanadium as compared with pure vanadium. All these complexes have different bonding energy and dissociate upon heating to different temperatures accordingly. As shown in [17], thermal stability of complicated complexes of He_mMe_kV_n type are significantly higher in the substitutional alloys with "oversized" atoms than that of simple complexes of He_mV_n type. The results of [14] shows that the temperatures of the main peaks of TDS nonmonotonically depend on titanium content in V-Ti alloys as in the case of above-mentioned dependencies of mechanical properties and IF on concentration of titanium.

It is known [18] that complicated complexes of He_mXV_n type (X is oxygen or nitrogen) may be formed with interstitial impurities in the vanadium also, but their dissociation temperatures and binding energies significantly lower than that for He_mV_n for small values of n in a complex of He_mXV_n. However, cause of non-monotonic dependence of TDS peaks temperature and accordingly of activation energies of gas release on titanium content can be complex processes of various bonds/complexes formation of V-O(N). V-Ti, Ti-O(N) type, disappearance of the double bonds and the formation of ternary bonds of V-O(N)-Ti type only at high concentrations of titanium in V-Ti alloys [11].

It is unlikely formation of simple helium-vacancy complexes in pure vanadium at high-temperature irradiation (923 K) by He⁺ ions. However, thermally stable complex of He_mTi_kV_n type may be formed in V-Ti alloys, i.e. a significant part of helium and vacancies remains in the form of complicated complexes in vanadium alloyed by oversized titanium. As a result highest helium swelling is observed in pure vanadium and swelling is significantly reduced in V-Ti alloys (Table 3). However, the effect of titanium on bubble parameters is nonmonotonic. The bubble sizes and swelling are reduced with increasing of titanium concentrations up to 0.5 wt.%, they are increased when titanium content is 0.7 wt.% Ti and are decreased again in alloys with 1, 5 and 10 wt.% Ti, during which titanium concentration insignificantly affects on bubble density (see Table 3). Minimum size of bubbles and swelling are observed in the alloy V-10 wt.% Ti with a maximum content of titanium and in ternary alloy V-4 wt.% Ti-4 wt.% Cr. It is possible that factors mentioned above play a role here, namely the for-

mation of various double V-O(N), Ti-O(N) and ternary V-O(N)-Ti bonds purifying alloy matrix from oxygen and nitrogen resulting in redistribution of atoms and defects [11, 14].

Table 3. Parametres of helium bubbles in vanadium and its alloys (d_{\max} and d_{av} are maximal and average sizes, respectively, ρ is density, S is gas swelling) [14].

Material	d_{\max} (nm)	d_{av} (nm)	ρ , (10^{24} , m^{-3})	S (%)
V	~ 22	16	0.017 ± 0.004	4.5 ± 1.1
V-0.1% Ti	~ 3.5	1.9	0.9 ± 0.2	0.5 ± 0.2
V-0.3% Ti	~ 3	1.7	1.3 ± 0.3	1.1 ± 0.3
V-0.5% Ti	~ 2.5	1.5	1.7 ± 0.4	0.4 ± 0.1
V-0.7% Ti	~ 6.5	3.7	1.8 ± 0.5	0.7 ± 0.2
V-1% Ti	~ 3	2.0	1.5 ± 0.4	0.4 ± 0.1
V-5% Ti	~ 3.5	1.6	1.4 ± 0.3	0.5 ± 0.2
V-10% Ti	~ 2	~ 1	3.3 ± 0.8	0.32 ± 0.08
V-4%Ti-4%Cr	~ 2	~ 1	3.6 ± 0.9	0.21 ± 0.05

2.3. Capture, retention and release of hydrogen

It was found nonmonotonic influence of titanium on behavior of hydrogen in alloys V-Ti with different titanium content obtained in TDS studies [19]. The samples were saturated with hydrogen for 2000 h at a temperature of 620 K in an autoclave. 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. 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.

It is seen from the dependence of the amount of hydrogen retained on the titanium content, which was determined by the TDS method [19], 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 wt.% Ti alloy and it is $\sim 5.5 \cdot 10^{20}$ at. H/g (ratio of the number of hydrogen atoms to the number of atoms of the alloy at. H/at. V is $\sim 4.5\%$). The amount of hydrogen decreases to $\sim 4.5 \cdot 10^{20}$ at. H/g (at. H/at. V $\sim 3.8\%$) as the titanium content increases to 10 wt.%. 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.

It was shown in study of the absolute amount of hydrogen retained in V-Ti alloys determined in the RHEN-602 gas analyzer, that the dependence of the amount of hydrogen retained on the titanium content is similar absolutely to that obtained by the TDS method [19].

The regularities of the capture, retention and release of hydrogen and the effect of alloying elements, in particular, Ti to V, on these processes are largely determined by the state in which hydrogen occurs in metals. It is widely believed 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 of M_mH_n type), 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 vacancies and impurities $\text{H}_m\text{X}_n\text{V}_k$ (X means an interstitial impurity), and other complexes.

Hydrogen was introduced into the samples in the autoclave without causing radiation damage to their structure. 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. Since the position of low-temperature

peak I on the temperature scale is independent of the chemical composition of the material, we have assumed that traps for hydrogen in the temperature range of 780–790 K are such defects, whose binding energy 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, such traps can be thermal vacancies [20], 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 (V is vacancy), 0.71–0.90 eV for H– V_m ($m > 4$), 0.24–0.62 eV for H–dislocation, 0.78 eV for H–void, 0.75–0.70 eV for H–helium bubble, and 0.29 eV for H–TiC [21]. Calculations showed that in vanadium single vacancy can hold twelve hydrogen atoms when they are introduced simultaneously and six hydrogen atoms when they are introduced sequentially [20]. It is shown in [22] 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 release 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, whose influence on them and the amount of hydrogen retained are nonmonotonic [19]. It can be assumed that in addition to hydrogen captured by the traps of the first type, it is retained in titanium hydrides, or complex hydrides like $Ti_{1-x}V_xH_y$, or γ - TiH_2 titanium hydride, since the standard enthalpy of formation of titanium hydride is less (–144.4 kJ/mol [23]) than that of vanadium hydrides (–39.9 kJ/mol [24]).

It was shown in Table 1, vanadium contained ~0.08% O_2 and ~0.009% N_2 , and the V–5wt.% Ti alloy contained ~0.32% O_2 and ~0.0064% N_2 . It is established using IF 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 [19], i.e., titanium in an amount of 0.5 wt.% (0.53 at.%) is 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.% [11]. 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 [19].

The amount of hydrogen retained again increases with increasing Ti content to 1 and 5 wt.%, since only a part of titanium is involved in the formation of oxides and nitrides, while the rest forms hydrides with a dissociation temperature of 870 K and above, which becomes clear from comparing the temperature of peak II and the temperature at which γ titanium hydride decomposes [19].

It is shown in [25] 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 [19].

4. Conclusion

The paper shows that the effect of titanium content on helium swelling, processes of energy dissipation in the crystal lattice (internal friction), capture, retention and release of introduced helium and hydrogen in vanadium-titanium alloys is nonmonotonic, as well as the effect of titanium on some physical, mechanical and high-temperature properties and radiation resistance of V-Ti alloys are known from literature. Analysis of experimental data obtained by different methods, leads to the con-

clusion that perhaps such an influence occurs due to the interaction of atoms of vanadium and titanium with interstitial impurities, in particular redistribution of O, C and N atoms linkages between vanadium and titanium atoms.

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