



## Letter to the Editor

## Ways of improving the high-temperature work service of vanadium and some alloys used in reactors

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## ABSTRACT

We present new evidence for the high-temperature strength of vanadium and low-alloyed (up to 15 at.%) vanadium-based alloys under conditions of prolonged (up to 5000 h) high-temperature (973–1173 K) exposure to vacuum, helium, lithium and sodium melts, modeling reactor heat-transport media (10 Pa). The kinetics of phase transformations in alloys of the systems V–Zr–C, V–Nb–Zr–C, V–Mo–Zr–C, and V–Ti–O in the process of prolonged aging under stress is analyzed. It is established that the process of pre-decay of a solid solution has many stages and is intensified by the action of stresses. The corresponding isothermal diagrams of the decay of VTsU (V–Zr–C) alloy are constructed. We give recommendations as to the choice of alloying elements with the aim of enhancing the high-temperature strength of vanadium and vanadium alloys used for reactors. New alloys developed on the basis of the systems V–Ti–O, V–Nb–Zr, V–Ta–Hf, V–Cr–Sc, and V–Cr–Nd and a new method of strengthening thermochemical treatment of vanadium–titanium alloys with the use of oxygen from air have found application in pilot-engineering developments for high-temperature nuclear power plants.

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## 1. Introduction

The strategy of the development of power engineering consists of increasing the power of existing nuclear reactors, transferring to the use of the energy of fast-neutrons, bringing controlled thermonuclear fusion to a commercial level, and increasing the safety margin of energy production to the maximum possible extent [1–4]. The analysis of the principles of selection of materials for the operating and promising fast-neutron nuclear power plants and for fusion-type reactors shows that one of the methods of upgrading their efficiency consists of raising the operating temperatures of the processes of energy conversion and transmission up to 900–1400 K and using unconventional high-temperature media. The experience in the operation of reactors and the predictions of many scientists allow one to separate the following promising media [5–6]. For fast-fission reactors, these are heat-transport media based on sodium, helium, and, in some cases, on lithium. For fusion-type reactors, we mention lithium (blanket), eutectics (tritium-reducer), helium (heat-transport medium), and vacuum (vacuum wall). For this to be realised, the development of new materials and the improvement of the reliability and serviceability of tested high-temperature metallic materials are required. These materials should meet the requirements of not only the physics of nuclear fission and fusion, but also the physicochemical require-

ments that are imposed by their prolonged interaction with reactor media and related ones under the simultaneous action of high-temperature and loads. In this respect, according to the predictions of world-famous scientific-research centers specialising in the field of reactor materials science, the application of refractory metals, in particular, vanadium and low-alloyed vanadium alloys (up to 15 at.%), nickel-based alloys, and special steels [6,7], is gaining in importance. The advisability of using vanadium is due to the optimum complex of physicomechanical properties and its compatibility with nuclear fuel and high corrosion resistance in promising high-temperature, heat-transport media (helium, lithium, and sodium melts). To a great extent, the efficiency of using vanadium-based alloys depends on the improvement of their high-temperature strength at temperatures above 950 K. First, the principles of selection of alloying elements and formation of the heterogeneous structure and phase composition of vanadium alloys should be developed along with alternative methods of enhancing their high-temperature strength, e.g., the method of thermochemical treatment. Furthermore, the introduction of promising vanadium-based alloys as well as other reactor materials must be based on the results of high-temperature corrosion-mechanical tests of their lifetime.

Thus, the investigation of physicochemical processes occurring in vanadium alloys used in reactors as a result of the prolonged action of high-temperatures, stresses, and the corresponding media as well as the development of methods of improvement of their high-temperature strength for operation under conditions maximally

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close to those indicated above is an important scientific-technological problem. The objective of this work is to evaluate the effect of alloying elements on the structure and physicomechanical properties of vanadium under conditions of the prolonged action of vacuum and high-temperature gaseous (helium) and metallic (lithium and sodium) heat-transport media and to elaborate recommendations as to upgrading the high-temperature strength and corrosion resistance of promising vanadium-based alloys used for reactors by means of alloying and thermochemical treatment. For comparison, we present the results of analogous high-temperature tests of several other metals and alloys.

## 2. Experimental procedure

The procedure of investigations was as follows. Tests extending to 5000 h were carried out by using high-temperature equipment developed at the Physicomechanical Institute of the Ukrainian Academy of Sciences [8]. Specifically, we used multipositional units for prolonged tests of metals by static loading in vacuum and in rarefied gas flows. In some cases, the interaction of metals with melts was studied after preliminary leaching (e.g., with lithium or copper solder, which, when in the melted state, is analogous to the former in the capability of embrittling solid metals) [9,10] of their surface and after heating up to the test temperature. The high-temperature creep of metals was investigated by modeling the creep rate at the steady stage by active tension in the range 0.6–60%/h. The characteristics of strength and plasticity were evaluated by subjecting flat specimens (1 × 3 mm in cross section) to tension after recrystallizing annealing or standard heat treatment with a rate of  $5 \times 10^{-3} \text{ s}^{-1}$  in a spectroscopically pure argon atmosphere or in a medium of alkali metals in the temperature range 298–1500 K. The effect of the helium heat-transport medium on the properties of vanadium alloys was studied after dynamic bench tests, in which the chemical composition was controlled and kept constant.

Based on the familiar constitutional diagrams and temperature dependencies of solubility, we set the concentrations of impurities in melts by the temperature of the filling of ampoules. As permanent sources of oxygen and nitrogen,  $\text{Fe}_2\text{O}_3$ -type compounds and a mixture of vanadium nitrides were used (Tables 1 and 2). Corrosion tests were carried out in melts by an ampoule procedure under isothermal conditions. In order to explain the structural and phase transformations in the alloys, induced by the action of temperature and media, we performed a complex of metallophysical examinations by standard procedures. The chemical composition of gaseous constituents in metals was determined by the vacuum fusion method. The layer-by-layer fusion was followed by mass spectroscopic control and by durometric and gravimetric measurements.

Semicommercial and experimental vanadium alloys with various types of strengthening were investigated (Table 3). To obtain their comparative characteristics, we examined commercial-grade vanadium, niobium, tantalum, VNS-type steels of composition Fe-

**Table 1**  
Calculated concentration of interstitial impurities in melts.

Melt	Temperature of pouring (K)	Concentration of impurities (at.%)		
		Oxygen	Carbon	Nitrogen
Sodium 1	653	0.05	$10^{-4}$	0.5
Sodium 2	837	0.50	$10^{-3}$	1
Sodium 3	653	1.00 <sup>*</sup>	$10^{-4}$	0.5
Lithium 1	623	0.025	1.10	0.18
Lithium 2	723	0.061	2.00	0.67
Lithium 3	623	0.025	1.10	0.08 <sup>*</sup>

<sup>\*</sup> During the exposure the concentration was kept constant.

**Table 2**

Partial pressure (Pa) of gaseous impurities in helium (normal conditions) and in vacuum ( $10^{-4}$  Pa, 1173 K).

Medium	H <sub>2</sub> O	O <sub>2</sub>	CH <sub>3</sub>	CO <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	CO	Ar
Vacuum 1	1.2	0.03	–	0.2	–	0.21	0.009	–
Vacuum 2 <sup>*</sup>	3.5	3.70	–	30.0	–	10.10	56.00	–
Helium	10	1.20	25	5	125	250	250	55

<sup>\*</sup>After filling with technical-grade oxygen.

**Table 3**

Chemical composition of vanadium-based alloys<sup>\*</sup>.

System	Content of alloying elements (mass%)
<i>Alloys with solid-solution hardening</i>	
V–Nb (VN)	7.0, 9.5, 13.0, 18.0, 20.0 Nb
V–W (VW)	6.7, 14.0, 20.0 W
V–Ti (VT)	7.5, 11.0, 20.0, 30.0 Ti
V–Cr (VKh)	8.7 Cr
V–Ti–Cr (VTKh)	15.0 Ti + 8.0 Cr
V–Ta (VTa)	2.0, 12.0, 22.6 Ta
<i>Dispersion-hardened alloy</i>	
V–Zr–C (VTsU)	3.00 Zr + 0.37 C
<i>Alloys with solution–dispersion hardening</i>	
V–Nb–C (VTsUN)	0.5, 1.3, 1.5, 5.0, 6.0 Nb + (2.6–3.0)Zr + (0.3–0.4) C
V–Mo–Zr–C (VTsUN)	2.0, 3.0, 6.0 Mo + (1.5–2.6)Zr + (0.2–0.3)C
V–Ti–O (VTO)	7.5, 11.0, 20.0 Ti + 0.11, 0.14, 0.18 O

<sup>\*</sup> Nonmetallic impurities of the metals in alloys and unalloyed vanadium (VnM2), niobium (NbP), and tantalum are: 0.02–0.05 C, 0.02–0.05 O, 0.01–0.04 N, 0.001–0.002 H, and < 0.1 mass% of the rest.

(2.6, 4.0, 8.0)Ni–(13.0, 14.0, 16.4)Cr–(4.5)Mn–(1.89)Mo–(0.02, 0.03)C with 1, 4, and 12 vol.% 5-ferrite, EP202 alloy, and some other materials.

## 3. Results and discussion

An analysis of the results obtained (Fig. 1, Table 4) enabled us to establish changes in the mechanical properties of the V–A group metals, vanadium alloys, VNS-type steels, and EP alloy under the action of temperature and reactor media. An analytic estimation of the coefficients  $\beta$  and  $b$  that enter into the familiar relations  $\sigma_u = Be^{-\beta T}$  and  $\sigma_u = ae^{-b/T}$  ( $a$  and  $B$  are the factors of proportionality relating the ultimate strength of the metal  $\sigma_u$  to temperature), performed on the basis of the extrapolation of experimental data along the curves of the relations  $\sigma_u = f(T)$  and  $\sigma_u = f(1/T)$ , showed bends on them near 0.5  $T_m$  of vanadium (Fig. 1). After the bend, the intensity of the loss of strength increases (Fig. 1); however, it is much lower for vanadium, vanadium-based alloys, niobium, and tantalum than for EP and VNS (Table 4). Temperature dependencies of the strength of the V–A group metals and vanadium alloys are characterized by a single bend. The remaining alloys (EP and VNS) have two bends each (Fig. 1), the last of which coincides by temperature with the  $\alpha \leftrightarrow \gamma$  transformation. With the coefficient  $b$  taken to be related to the energy of activation ( $Q$ ) of the process of plastic deformation ( $b = Q/R$ , where  $R$  is the universal gas constant),  $Q$  increases above the temperature of bends and, according to calculations, becomes comparable to the energy of activation of self-diffusion of the base metal. Therefore, one can consider that, above 1000 K, the plastic deformation of vanadium and the alloys is controlled mainly by high-temperature mechanisms caused by the nonconservative movement of dislocations, resistance to which can be substantially increased by appropriate alloying.

Changes in the properties ( $\sigma_u$ ,  $\sigma_{0.2}$ ,  $\sigma_y$ ,  $\delta$ ,  $\sigma_{LTS}$ ,  $H_u$ ) of the metals with temperature under the action of media and soaking in them were evaluated quantitatively by the coefficient of relative influence of the medium  $K$  or  $K'$ . For instance, for the ultimate strength, they are as follows:

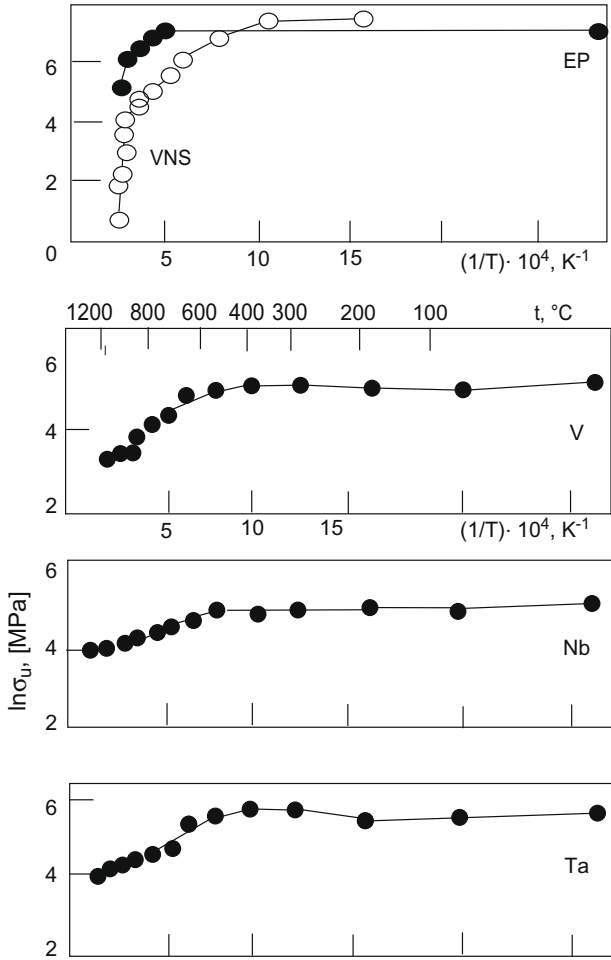


Fig. 1. Temperature dependencies of  $\sigma_u = f(1/T)$  the V-A group metals, EP alloy, and VNS steel.

Table 4  
Values of the coefficient (MPa/K), strength (MPa), and relative elongation (%) at 1000 and 1200 K.

Metal	1000 K/1200 K		$\sigma_u$	$\delta$
	$\beta$			
V	1.500/5.150		120/39	59/66
Nb	1.260/1.450		110/87	38/35
Ta	0.315/-		170/95	37/50
VNS	0.200/24.400		240/35	51/38
EP	0.032/26.000		950/39	15/37
VN13*	1.170/2.700		420/280	23/74
VKh8	2.500/3.850		300/90	25/69
VT8	1.060/2.950		310/140	29/98
VTa20	1.220/2.300		-	-
VV20	2.060/3.550		320/130	33/76
VTsU	0.780/3.650		122/60	56/90
VTsUM 3	0.500/2.400		130/62	55/80
VTsUN 10	0.330/0.600		500/380	28/70
VTsUN 15	0.069/0.400		620/400	25/68

\* The concentration of the basic alloying element.

$$K = K_{\sigma_u} = \frac{\sigma_u - {}^c\sigma'_u}{\sigma_u} \quad \text{and} \quad K' = K'_{\sigma_u} = \frac{\sigma_u - {}^c\sigma'_u}{\sigma_u}$$

where  ${}^c\sigma_u$  is the temporary ultimate strength in the medium,  ${}^c\sigma'_u$  is the ultimate strength of the metal after the action of the medium, and  $\sigma_u$  is the ultimate strength of the metal in the spectroscopically pure argon (a comparison medium) at the same test temperature. Thus,  $K_{\sigma_u}$ ,  $K_{\sigma_{0.2}}$ ,  $K_{\sigma}$ , and  $K_{H\mu}$  (see Fig. 2) are the coefficients

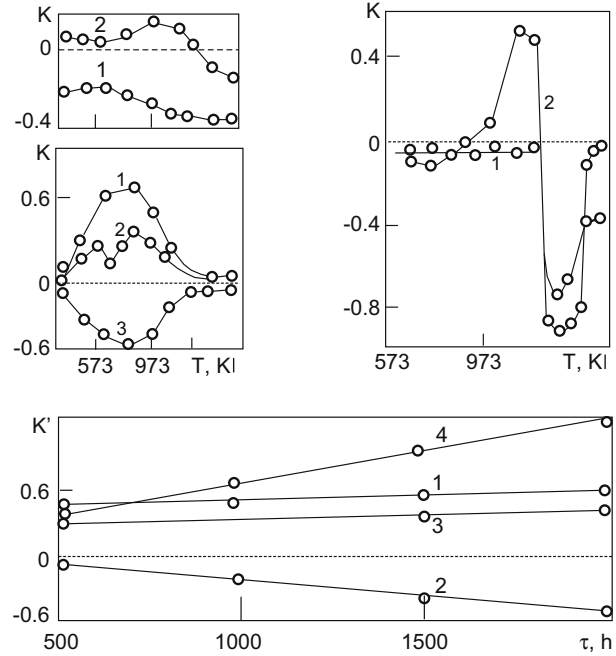


Fig. 2. Temperature (a, b, c) and time (d) dependencies of the coefficients  $K$  and  $K'$  of the effect of a medium on the mechanical properties of vanadium (a – lithium) and VNS steel (b – lead); vanadium soaked in dynamic vacuum at 1173 K for 180 h (c) and vanadium soaked in sodium at 973 K (d). (1)  $K_{\sigma_u}$ , (2)  $K_{\delta}$ , (3)  $K_{\sigma_{0.2}}$ , and (4)  $K_{H\mu}$ .

related to the effect of a medium on the corresponding properties and calculated from the results of experiments performed directly in media. Moreover, these coefficients with prime express this effect after isothermal soaking in media (for specimens-witnesses).

An analysis of values of the coefficients  $K$  and  $K'$  and their temperature dependencies (Fig. 2) for specimens tested by temporary bending in lithium and sodium melts leached with lead (for comparison) and iso-thermally soaked in these media, dynamic vacuum, and helium as a heat-transport medium [11–13] as well as for specimens-witnesses (that are in the medium but not deformed) showed that the influence of reactor media is quantitatively regulated by the test temperature, nature of the medium, duration of the interaction, and changes in the mechanical properties of the metal after isothermal soaking and in the process of

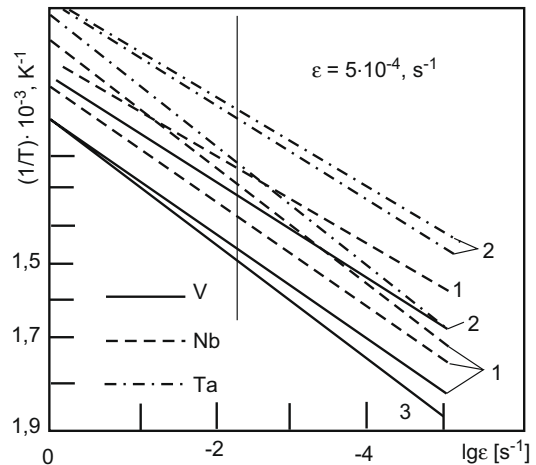
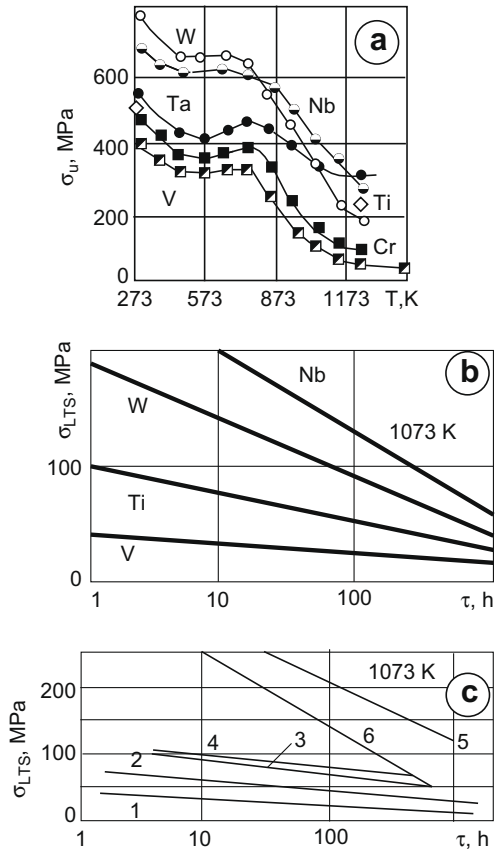


Fig. 3. Calculated curves of the dependencies of the temperature of the maximum dynamic interaction of interstitial impurities with dislocations in the V-A group metals on strain rate: (1) oxygen, (2) nitrogen, and (3) carbon.

deformation in the whole temperature range under investigation (Fig. 2a, c and d). As to the V-A group metals and alloys based on them, lithium, sodium, dynamic vacuum, and helium as a heat-transport medium exhibit a low corrosion activity caused by the redistribution of interstitial elements between the metal and the medium.

For VNS-type alloys, as an example, we established the existence of a narrow temperature range (1300–1400 K), in which

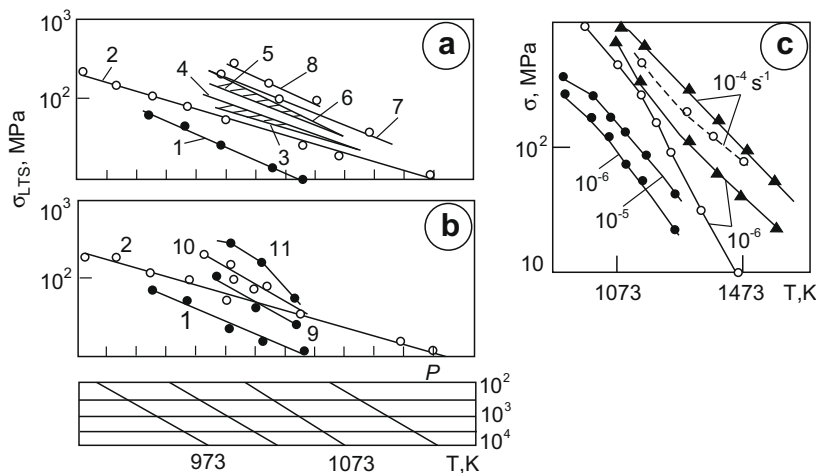


**Fig. 4.** Temperature dependencies of the strength (a) and long-term strength (b) of vanadium (1) and its alloys with a concentration of alloying elements of 7.5 at.% and of the complexly alloyed alloys (c) V-3 Zr-0.32 C (2), V-2 Mo-2.6 Zr-0.30 C (3), V-1.3 Nb-2.6 Zr-0.30 C (4), V-15 Nb-2.6 Zr-0.30 C (5), and V-20 Mb (6) mass%.

the adsorption action of a reactor medium (lead- and copper-based melts), in contrast to the corrosion action characteristic of lithium and sodium, results in an unpredictable sharp decrease in strength and plasticity due to high-temperature liquid metal embrittlement (Fig. 2b). At temperatures of the maximum manifestation of this effect, the relative elongation is close to zero and strength decreases by 80–90%. However, the mechanical properties of vanadium are scarcely affected by lead, which is mainly due to the fact that it does not wet vanadium.

The strengthening of vanadium and other refractory metals with interstitial elements (in the concentration range of the existence of solid solutions) is insignificant owing to their high diffusive mobility and small solubility as compared to substitutional elements. However, in the process of deformation by tension, in some temperature ranges we recorded anomalous deviations of the temperature dependencies of strength and of the conventional yield point from the expected ones, characteristic of refractory body-centered cubic metals containing no interstitial impurities. These deviations look like extreme on the curves  $\sigma_u$  and  $\sigma_u = f(T)$  (see Fig. 1).

The maxima of strength corresponds to the minima of the plastic properties of the material. The deformation of the metal in these temperature ranges is accompanied by a break in the stability of the plastic flow. The temperature extreme was found to satisfactorily agree with the predicted relations of the theory of dynamic strain aging of metals. These relations connect the strain rate ( $\dot{\epsilon}$ ) with the diffusion coefficient ( $D$ ) of interstitial impurities, which form retarding atmospheres on moving dislocations, by the relation  $\dot{\epsilon} = 10^9 D$ . According to our calculation (see Fig. 3), the temperature-rate ranges of retardation of dislocations in the V-A group metals depend on the nature of interstitial impurities and must be individual for every metal-interstitial impurity couple. This was substantiated experimentally. Indeed, after saturation of vanadium, niobium, and tantalum with interstitial elements, the extreme on the corresponding dependencies break down into several ones (Fig. 2c, curve 3). For strain rates of about  $5 \times 10^{-3} \text{ sec}^{-1}$ , the temperature ranges of dynamic strain aging of the V-A group metals are close and lie within 500–900 K. We established that, in the temperature range of deformation strain aging, the concentration dependencies of the maximum strengthening of vanadium containing nitrogen and oxygen can be described as follows:  $\Delta\sigma = A \cdot C_{N+O}$ , where  $C$  is the total concentration of interstitial elements (mass%) and  $A$  is the strengthening coefficient of vanadium, close to 1700 MPa/mass%.



**Fig. 5.** Resistance to long-term deformation (a, b) of unalloyed VnM2 vanadium (1) and vanadium-based alloys VTsU (2), VV (3, 4), VN (5, 6), VT11 (9), VTO (10), and VtsUN10 (11) in Larson–Miller coordinates at  $c = 20$  and isolines of the creep rate (c) as a function of temperature–stress conditions of tests: ● VnM2, ○ VN18, ▲ VTsUN10.

The capability of vanadium of forming continuous series of solid solutions with most metals whose melting points are close to or higher than that of vanadium makes it possible to form binary and somewhat more complex alloys on its basis [14]. According to the data of mechanical tests, alloying significantly increases the resistance to deformation of vanadium (Fig. 4). The long-term strength (Fig. 4b and c) and creep resistance also increase (Fig. 5a and b). By efficiency of the influence on hardening, alloying elements can be ranked in the order Zr, Cr, Ti, Ta, Nb, and W. Zirconium, titanium, and chromium harden vanadium slightly, while the rest harden it significantly.

It is well known that, in the case of the solid-solution method, strengthening with interstitial elements is determined by the strength of a matrix ( $\sigma_M$ ), by the difference in the sizes of atoms of the base and alloying element ( $\sigma_V$ ) (the dimension factor), by

**Table 5**

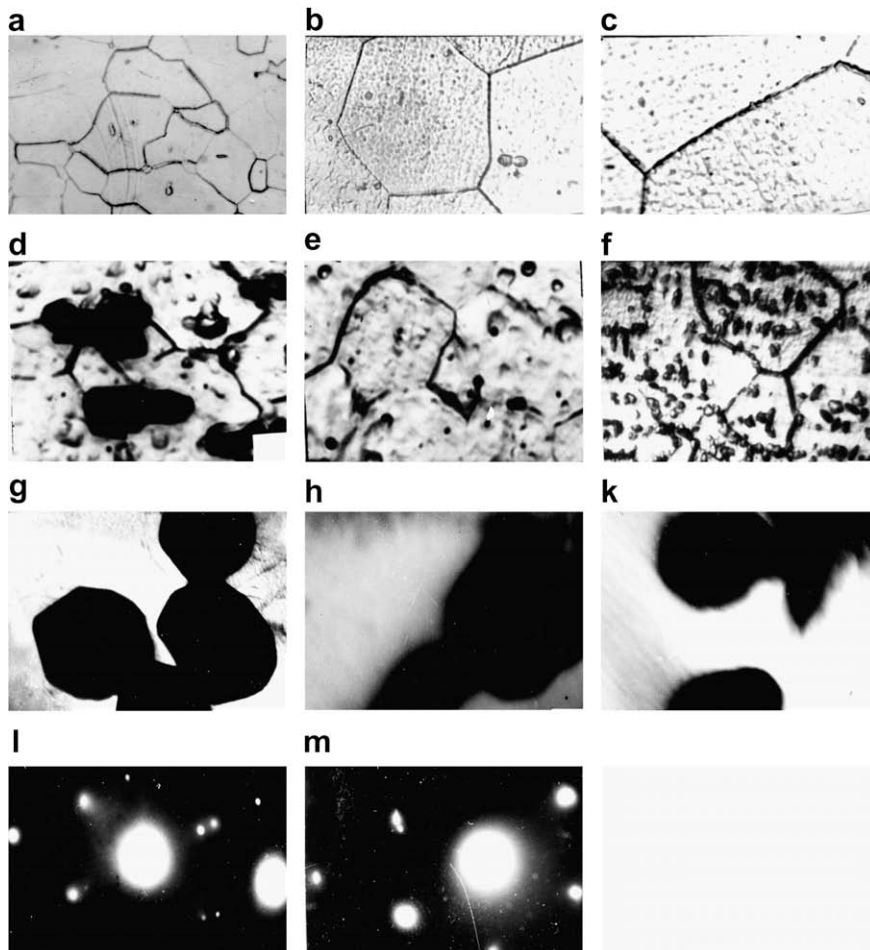
Relative contribution (%) of the differences in atomic radii ( $\sigma_V$ ) and in modulus of elasticity ( $\sigma_G$ ) to the increase in the yield limit of binary vanadium-based alloys at 293 and 1273 K.

Element	$\sigma_V$ (%)	$\sigma_G$ (%)
	293 K/1273 K	293 K/1273 K
Ti	100/100	0/0
Ta	100/70	0/30
W	15/40	85/60
Cr	100/-	0/-
Nb	54/58	48/42

the difference in their elastic properties ( $\sigma_G$ ) and by the disturbance of a short-range order ( $\sigma_{SS}$ ). An analysis of the results obtained for vanadium and the data available in the literature for niobium and tantalum alloyed with elements of groups IV, V, and VI-A of the periodic table with respect to their influence on strength and hardness showed the correlative dependence of these properties on the differences in atom radii and plastic properties between the base metal of the alloy and the alloying element. According to the quantitative assessment performed by the Harris procedure, the dimension factor plays a dominant role in the strengthening of vanadium, while the role of the difference in plastic properties is smaller. The contribution of the dimension factor was found to increase with temperature up to 1000 K and above (Table 5). The exception is tungsten alloys, since tungsten exhibits anomalously high elastic properties. We performed calculations for only one (7.5 at.%) concentration of alloying elements, which enabled us to take the component  $\delta_{SS}$  to be constant for various alloys.

Though zirconium and titanium harden vanadium slightly, they are important for the realisation of the dispersion and solution-dispersion types of strengthening due to their capability of forming thermodynamically stable and metastable compounds (e.g., MeC, MeO, V<sub>2</sub>C, etc.).

Stable compounds in the form of disperse particles in the matrix of the alloy, providing the morphology and distribution are optimum, can be efficient barriers against moving dislocations under deformation. Specifically, zirconium carbide ZrC significantly enhances the resistance to deformation and fracture of



**Fig. 6.** Structure of unalloyed VnM2 vanadium (a) and VnM2-based alloys VN7 (b), VTa20 (c), VTsU (d), VTsUN (e), VTO (f) (500), electron micrographs of typical precipitates in the matrices of VTsU (g), VTsUM (h) and VTsUN (k) alloys (100,000), and electron diffraction patterns of V<sub>2</sub>C (l) and VC (m) carbides.

vanadium under long-term loads even for 5000 h, when the efficiency of the solid-solution strengthening is low. The joint alloying of vanadium with niobium, zirconium, and carbon further enhances the hardening. The strength of alloys of the V–Nb–Zr–C system at 1273 K ranges from 100 MPa for a niobium concentration of 0.3 mass% to 350 MPa for that of 15 mass%. The values obtained exceed the established values for a binary vanadium–niobium alloy with 20 mass% Nb. At a niobium concentration of 10 mass%, the ultimate strength after testing for 1000 h (1173 K) was 120 MPa, which is five times that of VTsU alloy and eight times that of unalloyed vanadium (Fig. 4c). Alloys of the analogous system with molybdenum rank below those with niobium in high-temperature strength.

Alloying with titanium increases the limit of long-term strength of vanadium only at its low concentrations (3–8 mass%) in the alloy. However, as compared to vanadium, titanium is more active with respect to oxygen, which implies the possibility of oxide hardening. Tests for long-term strength showed that it is increased in oxygen-containing vanadium–titanium alloys. After testing at 1173 K for 5000 h, the strength of V–11Ti alloy with 0.17 mass% oxygen was almost twice that of a binary V–11Ti alloy, while the long-term strength of the former was three times that of the latter.

The results of mechanical tests and structural examinations are of great importance in determining the regularities of the influence of alloying elements and long-term, high-temperature aging under load and without it on the stability of the structure and the high-temperature strength of vanadium alloys. Electron spectroscopy and X-ray structural-phase analysis of ternary alloys containing zirconium and carbon revealed the existence of an additional phase consisting of precipitates of ZrC, V<sub>2</sub>C, and VC with different dispersity and morphology (Fig. 6). We established that the addition of niobium and molybdenum somewhat reduces them in size, resulting in changes in their shape from globules to plates. The identification of phases indicates that, as in the case of alloys of the V–Nb–Zr–C system, precipitates of zirconium carbide, close to ZrC in stoichiometry, with face-centered cubic lattice are globular in shape. Precipitates of metastable carbide V<sub>2</sub>C in the form of large lamellar particles also have a face-centered lattice. The identity of the phase composition of VTsU and other alloys, which are alloyed in a complicated way and contain zirconium and carbon, and their different high-temperature strength indicate the efficiency of the solution–dispersion type of strengthening as compared to the purely carbide or purely solid-solution types.

One of the factors determining the high-temperature strength of metallic materials is the stability of controlled properties under the prolonged action of high-temperature. According to the results of prolonged high-temperature life tests, the pre-decay of the solid solution occurs in the heterophase alloys VTsU, VTsUN, and VTsLJM in the course of time, which is confirmed by a decrease in the lattice parameter of the matrix (Fig. 7a). The phase composition of the carbide component remains constant in the process of aging. However, the amount of ZrC increases and depends in a complex manner on the stresses applied. Changes in the lattice parameters of the matrix of VTsU alloy and of the main carbide phase ZrC, in the intensity of its line  $\alpha [1\ 1\ 1]$ , and in the strength of aged specimens (Fig. 7b) testify to the fact that stresses accelerate the pre-decay of the solid solution. Up to certain (critical) stresses, this process is intensified and accompanied by the precipitation of zirconium carbide. At higher stresses, this effect is absent. We established that, at aging temperatures of 1073 and 1173 K, the critical stresses constitute 15–20% of the long-term strength limit. In X-ray diffraction measurements of the oxygen-containing alloys of the V–Ti system, finely divided titanium and vanadium monoxides as well as oxides of the (V, Ti)<sub>x</sub>

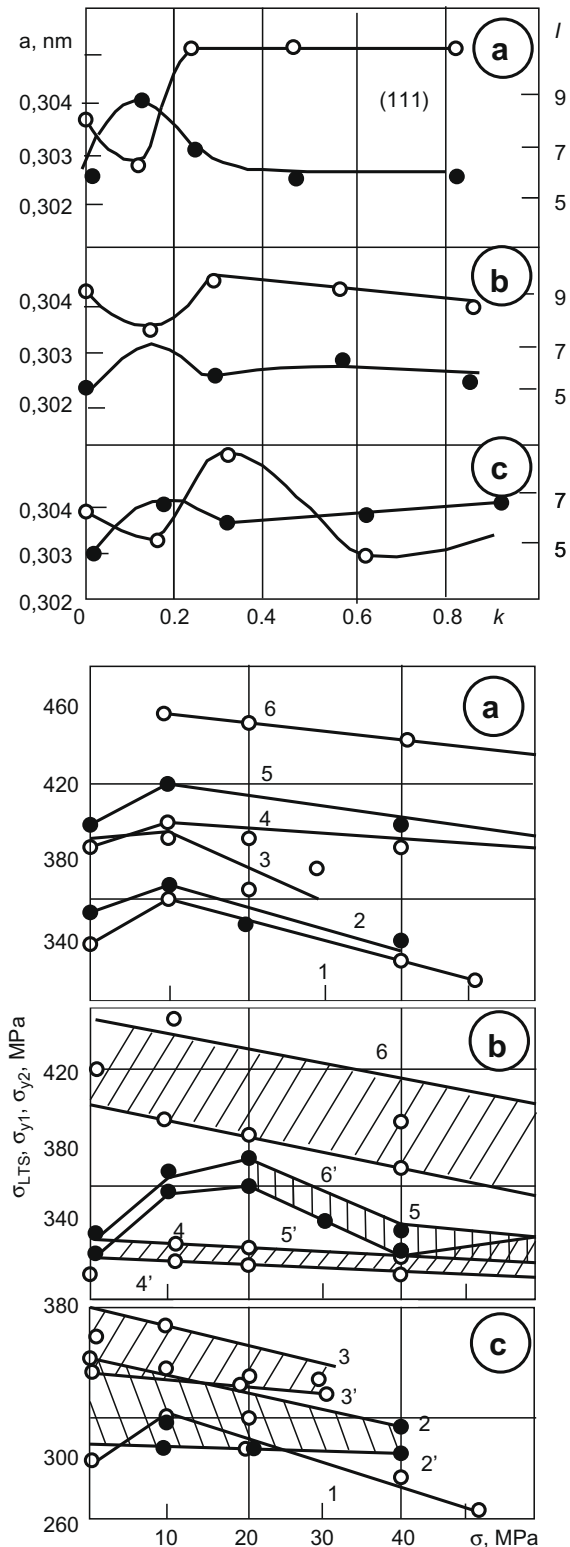


Fig. 7. Influence of the level ( $k$ ) of stresses ( $\sigma$ ) of preliminary loads and the soaking time ((a) 100 h, (b) 500 h, (c) 1000 h) on the lattice parameter of the matrix of VTsU alloy (○), the intensity of the line [1 1 1] of carbide ZrC (●)  $I(A)$ , and the mechanical properties (B) ( $k = \sigma_{y1,2}/n\sigma$ ).

type were detected. Under the prolonged action of temperature, the phase composition of these alloys varies. The formation of an oxide close to TiO<sub>2-x</sub> in stoichiometry is observed. Despite the process of pre-decay, alloys with oxide strengthening and

those with carbide strengthening retain high levels of  $\sigma_u$  and  $\sigma_{LTS}$  at elevated temperatures.

As for the influence on the high-temperature strength of vanadium alloys, uncontrollable saturation with oxygen and nitrogen in reactor media is of importance, and the formation of vanadium pentoxide  $V_2O_5$  with a low melting point (948 K) on the surface of the metal is most detrimental. According to thermodynamic calculations [12], the fusible oxide  $V_2O_5$  must be unstable at temperatures above 820 K in a helium heat-transport medium (the partial pressure of oxygen, at which  $V_2O_5$  forms, is lower than the equilibrium partial pressure of oxygen in a gaseous mixture). Under these conditions, lower vanadium oxides  $V_2O_4$ ,  $V_2O_3$ , VO and vanadium monocarbide are more stable.

In sodium (at the given oxygen concentrations),  $V_2O_5$  does not form, and lithium is known to reduce vanadium oxides to the pure metal. Durometric measurements performed after long-term soaking in vacuum and helium revealed regular changes in microhardness across the cross section of the unalloyed metal and some alloys. This fact, along with the data of chemical analysis (Table 6), confirms the fact of gas exchange in the system “structural metal-reactor medium.” We established experimentally that, in vacuum free of oil (1), the saturation with interstitial impurities is practically absent, and it is insignificant (Table 6) and uniform across the cross section in dynamic vacuum (2) at 1073 K.

X-ray analysis, gravimetric measurements, the analysis of microhardness profiles across a cross section, and the layer-by-layer chemical analysis of surface and interior layers of the metal indicate that, under the interaction of vanadium and its alloys with helium, oxides and carbides of alloying elements are formed on their surface. On unalloyed vanadium, the near-surface layer consists of oxide  $V_2O_3$  (traces) and carbide VC, exhibiting certain protective properties, due to which corrosion does not develop to the bulk of the metal in the course of time. According to the results of tensile tests, alloys with tungsten, niobium, zirconium, chromium, and molybdenum embrittle after prolonged soaking in helium (at 1023 and 1173 K), and their relative elongation decreases down to less than 1%. The relative elongation of the binary alloys with titanium ranges from 8 to 11% and that of VnM2 is 24%. As compared to the initial state, the long-term strength of vanadium and its alloys increases after soaking in helium 1 and 2 at 1073 K.

Prolonged corrosion tests in helium 1 of specimens of vanadium and VTsu alloy preliminarily soaked iso-thermally (1173 K) in vacuum under load and without it and a subsequent analysis of changes in the relative elongation revealed that the metal held under load had a lower plasticity.

It is characterized by significant residual strains and a highly defective structure. Tests for corrosion in lithium and sodium at 973 K testify to the saturation of vanadium and its alloys by nitrogen in the first case and by oxygen in the second. The saturation increases with the concentration of active gases in melts. A relatively high rate of saturation causes changes in the mechanical properties of materials already in the process of tensile tests. Specimens of group V-A technical-grade metals and alloys based on them can be separated into several types by changes in the microhardness across the cross section: I – uniform across the cross section, II – with an increase in the hardness at the edge, III – with a decrease in the hardness at the edge, IV – intermediate, and V – with extrema [15–16]. According to the data of microstructural and X-ray analyzes, the type of microhardness profiles is governed by the nature of the metal and the medium and by operating parameters.

After soaking in helium, the long-term strength increases, while it decreases after soaking in lithium (Fig. 8). This is attributable to the features of gas exchange between the liquid and solid phases [16], different diffusion mobility and directions of fluxes of its com-

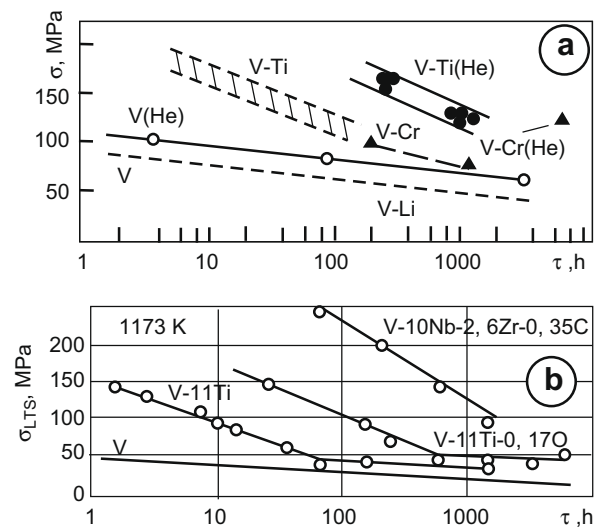


Fig. 8. Long-term strength of vanadium and vanadium alloys at 1073 K in vacuum (the initial state), lithium 1, and, after soaking at 1023 K, in helium 1 (a) and alloys with solid-solution-dispersion carbide hardening and solution-dispersion carbide and oxide hardening (b).

Table 6

Effect of media, temperature, and the time of isothermal soaking ( $t$ ) on the gas saturation of vanadium and vanadium-based alloys.

Alloy	Medium	T (K)	$\tau$ (h)	Concentration of interstitial elements		
				Carbon	Oxygen	Nitrogen
VnM2	Vacuum 1	1123	500	0.050	0.050	0.040
		1123	5000	0.045	0.052	0.040
VnM2	Vacuum 2	1123	120	0.050	0.100	0.040
VnM2	Helium 1	1023	2500	0.30	0.60	0.10
VT10		1023	2500	1.15	2.20	–
VTsuN1	Lithium 1	1023	2500	0.50	7.20	–
VnM2		Lithium 1	973	500	0.281	0.019
VT10	Lithium 2	973	500	0.304	0.034	0.036
	Lithium 3	973	500	0.304	0.025	0.028
	Lithium 1	973	500	0.374	0.037	0.029
VT30	Lithium 2	973	500	0.391	0.042	0.038
	Lithium 1	973	500	0.446	0.045	0.034
VnM2	Lithium 2	973	500	0.452	0.060	0.045
	Sodium 1	973	500	0.400	0.110	0.020
	Sodium 2	973	500	0.430	1.070	0.070
	Sodium 3	973	500	0.012	0.338	0.008

**Table 7**Effect of temperature and the time of tests in reactor media on the rate of corrosion ( $v$ ) and mechanical properties of new alloys as compared to VnM2 vanadium.

Alloy	$T_u^*$	$T$ (K)	$\tau$ (h)	$v$ , g/(m <sup>2</sup> ·h)	$\sigma_G$	$\sigma_y$	$\delta$ (%)	Medium
VnM2	298	873	1500	–	348	210	26.8	Flow of Na
	873	873	1500	3.8	245	100	12.5	
V + Nb + Zr	298	873	1500	–	483	335	30.0	
	873	873	1500	1.51	380	208	25.0	
VnM2	298	873	1500	–	–	–	0.8	Flow of Bi
	873	873	1500	–	–	–	4.5	
V + Ta + Hf	298	873	1500	–	–	–	9.1	
	873	873	1500	–	–	–	17.0	
VnM2	298	723	500	–	305	–	28.9	Vapor of Cs
	873	823	500	–	184	–	2.3	
V + Cr + Sc	–	723	500	–	–	–	31.0	
	–	923	500	–	–	–	21.0	
VnM2	–	533	1000	0.12	–	–	–	Water heat-transport medium at $p = 1.2$ MPa
	–	553	1000	0.02	–	–	–	

\* Temperature after corrosion tensile tests.

ponents, and changes in the chemical composition of the alloys and interstitial impurities (Table 6).

The analysis of the results obtained enables us to approach the consideration of the main methods of enhancing the high-temperature strength and corrosion resistance of promising vanadium alloys used in reactors, and of their realisation in practice. The rational alloying plays a specific role. The data on the high-temperature complex corrosion-mechanical tests in vacuum, helium, and lithium and sodium melts made it possible to establish the high efficiency of the solution–dispersion strengthening of vanadium as compared to the solid–solution strengthening (with both interstitial and substitutional elements) and dispersion strengthening (Fig. 8b) and to recommend its application with the aim of improving the high-temperature strength of low-alloyed vanadium alloys used in reactors for operation under conditions of controlled gas exchange with the corresponding media. As a rule, the elements of groups V and VI-A of the periodic table, guaranteeing a significant solid–solution hardening, and elements capable of forming thermodynamically stable precipitates of carbides and oxides in the vanadium matrix must enter into the compositions of such alloys. High-temperature alloys on the basis of the systems V–Nb–Zr–C, V–Mo–Zr–C, V–Ti–O, V–Ta–Hf, and V–Cr–Nd can be an example of the realisation of solution–dispersion strengthening (Table 7). It was found experimentally [16] that titanium, zirconium, hafnium, scandium, yttrium, and neodymium not only favor the formation of strengthening phases in the vanadium matrix but enhance its corrosion resistance under conditions of limited gas saturation from reactor media and improve the plasticity of the alloys (Table 7).

Besides alloying, appropriate heat treatment can ensure a significant strengthening of vanadium alloys. For instance, the introduction of oxygen into alloys of the V–Ti system makes it possible to enhance their high-temperature strength [16]. In this connection, we investigated prerequisites for the formation of interstitial phases in the process of thermochemical treatment of vanadium–titanium alloys, which consists of the oxidation of metal in air at temperatures of at most 948 K with the formation of oxide V<sub>2</sub>O<sub>5</sub> and a further two-stage vacuum annealing: at temperatures 1300–1500 K with the aim of dissolving an oxide film and homogenizing oxygen in the bulk of the metal and at 1100–1200 K for the formation of the optimum structure including precipitates of titanium oxides in its composition. The proposed thermochemical treatment enabled us to enhance the resistance to prolonged deformation of the alloy V–(5–11) mass% Ti by a factor of three for a test time of 5000 h.

The commonly accepted radical method of enhancing the corrosion resistance of metals is the application of coatings.

Therefore, to increase the refractoriness (above 1000 K) of vanadium and low-alloyed vanadium-based alloys and special steels, we tested their protection against gas saturation (oxidation) by applying multilayer diffusion coatings from melts of fusible metals. For example, by using melts of sodium with boron and silicon, we obtained, by stages, a two-layer boron–silicon coating on vanadium and VTsU alloy. In this coating, the silicide layer guarantees heat resistance, and the boride layer fulfills the function of a barrier preventing the dispersal of silicon and the penetration of oxygen into the matrix. Boron–silicide coatings of this type are characterized by high stability, since they retain their composition and structure unchanged for 5000 h at 1173 K.

#### 4. Conclusions

It follows from the aforesaid that, at present, there exists a great body of information concerning the possibility of enhancing the physicomechanical properties of vanadium, vanadium-based alloys (including low-activated alloys), similar materials for high-temperature application that operate under vacuum conditions, and a number of promising liquid–metal heat-transport media.

The most radical methods of improving the high-temperature strength of vanadium are both the combined alloying tested on alloys of the systems V–Nb–Zr–C, V–Mo–Zr–C, V–Ta–Hf, and V–Cr–Nd with the solution–dispersion mechanism of strengthening and the thermochemical treatment with the use of active gaseous components capable of oxidizing alloying elements in the matrix.

From the viewpoint of improving the refractoriness of vanadium, one should give preference to the protection with diffusion coatings, in particular, to boronizing and borosiliconizing.

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