

# Microstructure and Mechanical Properties of V–4Ti–4Cr Alloy as a Function of the Chemical Heat Treatment Regimes

M. M. Potapenko<sup>a</sup>, V. M. Chernov<sup>a</sup>, V. A. Drobyshev<sup>a</sup>, M. V. Kravtsova<sup>a</sup>, I. E. Kudryavtseva<sup>a</sup>,  
N. A. Degtyarev<sup>a</sup>, S. V. Ovchinnikov<sup>b, c</sup>, A. N. Tyumentsev<sup>b, c, d</sup>, I. A. Ditenberg<sup>b, c</sup>,  
Yu. P. Pinzhin<sup>b, c, d</sup>, and A. D. Korotaev<sup>b, c, d</sup>

<sup>a</sup>Bochvar High-Technology Research Institute of Inorganic Materials, Moscow, Russia

<sup>b</sup>Institute of Strength Physics and Materials Science, Siberian Branch, Russian Academy of Sciences, Tomsk, Russia

<sup>c</sup>Kuznetsov Siberian Physicotechnical Institute, Tomsk, Russia

<sup>d</sup>National Research Tomsk State University, Tomsk, Russia

e-mail: mmp@bochvar.ru

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**Abstract**—The regularities of the formation of a heterophase structure and mechanical properties of V–4Ti–4Cr alloy as a function of thermomechanical and chemical heat treatments are studied. The regimes of thermomechanical treatment which provide the formation of a heterophase structure with a homogeneous volume distribution of oxycarbonitride nanoparticles with a size of about 10 nm and an increase in the volume content and thermal stability of this phase and which provide an increase in the temperature of alloy recrystallization are developed. The formation of the heterophase structure results in a substantial (up to 70%) increase in the short-term high-temperature strength of the alloy at  $T = 800^\circ\text{C}$ . The increase in the strength is achieved while keeping a rather high level of plasticity.

**Keywords:** vanadium alloys, thermomechanical treatment, electron microscopy, microstructure, dispersed hardening, mechanical properties.

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## INTRODUCTION

Low-activation construction alloys of the system V–Ti–Cr (the basic alloy is V–4Ti–4Cr [1–10]) which are being developed for thermonuclear and nuclear power engineering do not provide the required level of high-temperature strength at a temperature higher than  $800^\circ\text{C}$ . This is associated to a substantial degree with the fact that in these alloys the formation of particles of oxycarbonitride phases responsible for the level of high-temperature strength is the result of not a well-directed doping with interstitial elements, but of uncontrollable contamination of these alloys with these elements in the process of melting and the subsequent cycle of treatment. Therefore, a relatively low concentration of interstitial elements substantially limits the volume fraction of nanodimensional particles of the nonmetallic phase and the efficiency of dispersed hardening, which determines the characteristics of the high-temperature strength of V–4Ti–4Cr alloy. The possibility of increasing the volume fraction of such nanodimensional particles by nanostructuring of the oxycarbonitride phase under the conditions of its formation from coarsely dispersed evolution of metastable vanadium carbide by variations in the regimes of thermomechanical treatment is shown in [11–15].

In this work, in order to solve the problem of increasing the high-temperature strength of V–4Ti–4Cr alloy, we used an additional chemical heat treatment (CHT) in which an increase in the volume content of the oxycarbonitride phase of TiV(C, N, O) in the alloy is achieved by increasing the concentration of interstitial elements in the process of its diffusion doping with oxygen.

## MATERIALS AND METHODS

The vanadium alloy VM-DPCh-9 (V–4.21Ti–4.36Cr–0.013C–0.02O–0.01N, wt %) was melted at the Bochvar High-Technology Research Institute of Inorganic Materials in the form of a boule with a weight of about 110 kg. Thermal treatments of semi-finished products were carried out in shaft vacuum laboratory resistance furnaces of SShVL type in vacuum of  $\sim 2 \times 10^{-5}$  Torr. The structural studies were carried out using optical metallography techniques on Olympus GX-71 and NEOPHOT-21 microscopes and transmission electron microscopy on Philips SM-30 and SM-12 electron microscopes at an accelerating voltage of 300 and 120 kV, respectively.

Thin foils for transmission electron microscopy were prepared by stream electropolishing in a 20% solution of sulfuric acid in methanol at a voltage of 20 V. The

samples for optical metallography were obtained by electropolishing in the same electrolyte on flat electrodes made of stainless steel at a voltage of 10–15 V and subsequent electrolytic etching in a 15% solution of oxalic acid in methyl alcohol at a voltage of 70 V.

The mechanical tests were carried out in a vacuum of  $\sim 2 \times 10^{-5}$  Torr with a rate of deformation of  $\dot{\varepsilon} \approx 2 \times 10^{-3} \text{ s}^{-1}$  by an active stretching of flat samples in the form of double blades with a size of working part of  $15 \times 2 \times 0.8 \text{ mm}$ .

## RESULTS

By developing practical regimes for a controllable diffusion doping of vanadium alloys with oxygen, the stability of the oxidative medium at the stage of saturation of alloys with oxygen plays an important role. Conventionally, in the processes of an internal oxidation type such saturation is implemented in media of decomposing oxides [17]. However, as the experience of work on internal oxidation of refractory alloys shows [18], the use of this technique is hampered by the necessity of purifying these oxides from extraneous impurities, in particular, from volatile compounds (e.g., lowest oxides), which contain oxygen and substantially affect the stability of the rate of diffusion saturation of alloys with this element. In order to increase this stability and simplify the operating cycle of treatment, we used in this work the method of diffusion doping with oxygen developed in [19] by applying annealings of vanadium alloys in air and subsequent transfer of the oxygen of surface scum into the sample inside in the process of thermal treatments in vacuum. As was shown in [20], the composition of vanadium alloys on other interstitial elements contained in air (C, N, etc.) remains practically unchanged in the process of such a treatment. Therefore, the concentration of oxygen absorbed by the samples was measured by precise weighing (not worse than  $10^{-4} \text{ g}$ ) on a VLR-200 analytical laboratory equal-arm balance. For the samples used in this work such a precision provided an error in the measurement of the oxygen concentration of  $\pm 3 \times 10^{-3} \text{ at. \%}$ .

As the basis of the method of treatment of boules and semifinished products proposed in this work, which includes both elements of TMT and CHT (TMT + CHT), a conventional TMT method (hereafter TMT-I) including series stages was taken [8, 9]:

(1) homogenizing baking of the boules at a temperature of  $1300^\circ\text{C}$  for 8 h;

(2) heating of the boules to a temperature of  $850\text{--}1000^\circ\text{C}$  with an exposure at this temperature for 1.5–2 h and extrusion on a press with the elongation ratio of 2–5;

(3) baking in a temperature range of  $950\text{--}1100^\circ\text{C}$  for 1 h and setting of sticks on a hydraulic press with a degree of deformation of not more than 50% with sub-

sequent annealing in a temperature range of  $950\text{--}1100^\circ\text{C}$ ;

(4) several “rolling  $\varepsilon = 50\%$  + annealing at  $T = 950\text{--}1100^\circ\text{C}$ ” cycles.

In the new method of treatment (TMT + CHT) presented here, between the third and final (fourth) stages of TMT-I, the following operations are performed:

(1) annealing of the alloy in vacuum of  $2 \times 10^{-5}$  Torr at  $T = 1400^\circ\text{C}$  for 1 h, which provides dissolution of the coarsely dispersed particles of the oxycarbonitride phase formed at the previous TMT stages;

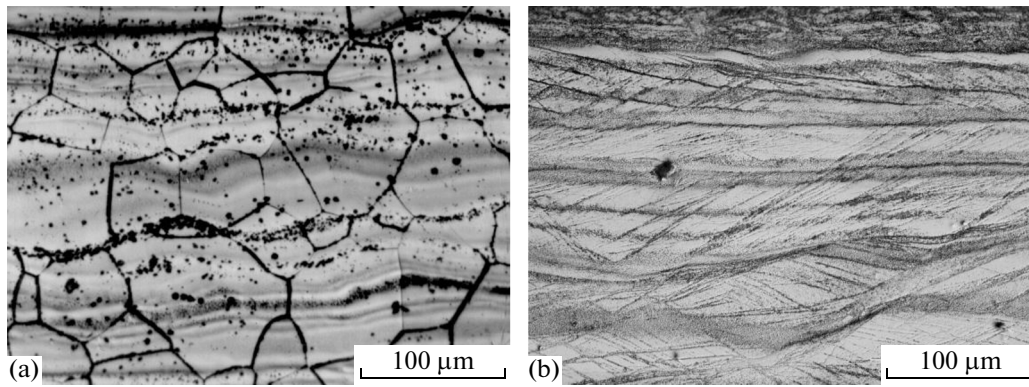
(2) diffusion doping with oxygen according to [19] with subsequent annealing in vacuum at  $1400^\circ\text{C}$ , which provides a homogeneous distribution of oxygen over the sample thickness;

(3) several (not less than three) cycles of TMT: deformation  $\varepsilon \approx 30\text{--}50\%$  plus annealings at  $T = 450\text{--}700^\circ\text{C}$  for 1 h.

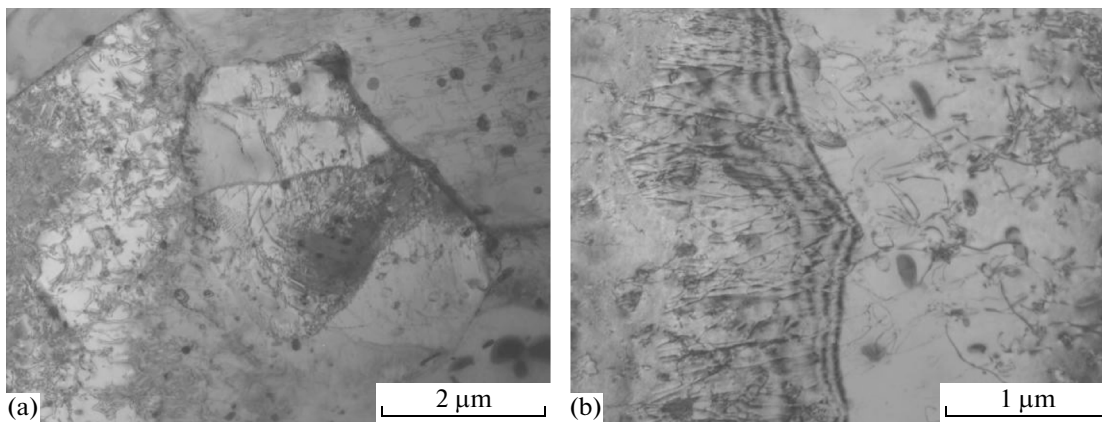
The last operation provides the kinetic conditions for the formation of particles of stable oxycarbonitride according to the mechanism of dissolution of coarsely dispersed evolvments of metastable vanadium carbide and subsequent evolvments of these particles from the solid solution. As was shown in [11–15], this results in the formation of a heterophase structure with a substantially higher, compared to conventional regimes of TMT-I, dispersity and homogeneity of distribution of the particles of the nonmetallic phase over the bulk.

By varying the duration of annealings in air, in this work, we have obtained samples with different oxygen concentration. The investigation into the microstructure by optical metallography has shown (Fig. 1) that, at an oxygen concentration in the alloy of 0.15–0.20 at. % and a total content of interstitial elements in the interval of concentrations of 0.2–0.3 at. %, the temperature of collective recrystallization is increased compared to the regime of TMT-I by  $100\text{--}200^\circ\text{C}$ . After a standard regime of TMT-I (Fig. 1a), an intense collective recrystallization is observed even in the process of an hour annealing at  $T = 1000^\circ\text{C}$ . The application of a combined (TMT + CHT) regime of treatment results in the suppression of the recrystallization to  $T = 1100^\circ\text{C}$  (Fig. 1b).

The electron-microscopic study has shown (Fig. 2) that in this case the particles of the nonmetallic oxycarbonitride phase are homogeneously distributed over the material bulk. The volume fraction of these particles increases with an increase in the concentration of oxygen and their most probable sizes amount to about 10 nm. The particles of such dimensions suppress the processes of recrystallization, fastening individual dislocations and the boundaries of disorientation. In this case, up to  $1100^\circ\text{C}$ , an imperfect substructure is formed, in which the regions of polygonization with a size of blocks of  $1\text{--}2 \mu\text{m}$  (Fig. 2a) interlace with the regions of primary recrystallization (Fig. 2b).



**Fig. 1.** Microstructure of V–4Ti–4Cr alloy after TMT-I (a) and TMT + CHT (b) with final annealings at 1000°C (1 h) (a) and 1100°C (1 h) (b). Oxygen content in alloys: (a) 0.06 at. %; (b) 0.15 at. %. Total concentration of interstitial elements (O, C, N): (a) 0.16 at. %; (b) 0.25 at. %.



**Fig. 2.** Microstructure of V–4Ti–4Cr alloy after TMT + CHT with a final annealing at 1100°C (1 h). Oxygen content in the alloy  $C_{[O]} \approx 0.15$  at. %; total concentration of interstitial elements is 0.25 at. %.

An increase in the volume content of the strengthening nonmetallic phase together with the stabilization of the imperfect substructure results in substantial effects of combined dispersed plus substructural hardening. The study of the characteristics of short-time strength and plasticity of V–4Ti–4Cr alloy carried out using the technique of active elongation at room tem-

perature and 800°C has shown (see table) that a consequence of the combined (TMT + CHT) treatment is a substantial increase in its yield strength at the temperatures indicated.

It is seen from the analysis of the data presented in the table that, in the process of TMT + CHT,

Yield strength  $\sigma_{0.1}$  and relative elongation to destruction  $\delta$  of V–4Ti–4Cr alloy after treatments according to various regimes

Regime of treatment	$C_{[O]}$ , at. %	$C_{[O, C, N]}$ , at. %	Temperature of tests			
			$T = 20^\circ\text{C}$		$T = 800^\circ\text{C}$	
			$\sigma_{0.1}$ , MPa	$\delta$ , %	$\sigma_{0.1}$ , MPa	$\delta$ , %
TMT-I	0.06	0.16	297–302	19–20	171–180	17–19
	0.12	0.22	371–392	17–21	246–257	7–9
TMT + CHT	0.15	0.25	383–398	18–20	262–273	8–10
	0.27	0.37	389–410	15–17	287–298	7–10

$C_{[O]}$  is the oxygen content in the alloy;  $C_{[O, C, N]}$  is the total concentration of interstitial elements.

- the yield strength increases when the concentration of oxygen in the alloy increases;
- the yield strengths at room temperature and at 800°C are about the same.

The latter, on one hand, indicates athermal mechanisms of strengthening and, on the other hand, results in the fact that the relative effects of hardening at  $T = 800^\circ\text{C}$  are much higher than those at room temperature. At room temperature, the maximum effects of hardening are  $\Delta\sigma/\sigma \approx 30\%$ , while at  $T = 800^\circ\text{C}$ , they are more than 60%.

The effects of this hardening increase are achieved while preserving a rather high level of plasticity. This can be associated with

- the formation in the process of treatment of a more homogeneous heterophase state excluding coarsely dispersed evolvments of oxycarbonitride phases as potential nuclei for localization of deformation and destruction;
- suppression of recrystallization of alloys, processes of grain-boundary sliding, and destruction at elevated temperatures.

The studies of CHT regimes carried out in this work, which provide values of concentration of oxygen higher than those shown in the table, have shown that, at the value  $C_{[\text{O}]} > 0.3$  at. %, an intense solid-solution strengthening by oxygen and a decrease in the plasticity of the alloy at room temperature are observed. This substantially limits the technological possibilities for performing the subsequent thermomechanical treatment. Therefore, the method of increasing the high-temperature strength proposed in this work is confined to an interval of oxygen concentration of  $C_{[\text{O}]} \leq 0.3$  at. % at a total concentration of interstitial elements of  $C_{[\text{O}, \text{C}, \text{N}]} \leq 0.4$  at. %.

We note that the presented increase in the thermal stability of the microstructure and high-temperature strength of V–4Ti–4Cr alloy with the use of CHT shows the possibility of achieving a similar result also by doping this alloy with oxygen at the stage of preparing the boule.

## CONCLUSIONS

Using the techniques of diffusion doping with oxygen for V–4Ti–4Cr alloy, the regimes of combined treatment (TMT + CHT) are developed which provide the formation of a heterophase structure with a distribution of nanoparticles of the oxycarbonitride phase with a size of about 10 nm homogeneous over the bulk, an increase in the volume content of this phase, and an increase in the temperature of alloy recrystallization.

With employment of the technique of transmission electron microscopy, the regularities of the formation of the heterophase structure and physicomechanical properties of V–4Ti–4Cr alloy have been studied in the process of its combined treatment (TMT + CHT).

The regimes of such a treatment with the application of diffusion doping with oxygen for this alloy are developed which provide the formation of a heterophase structure with a distribution of nanoparticles of the oxycarbonitride phase with a size of about 10 nm homogeneous over the bulk, an increase in the volume content of this phase, and an increase in the alloy recrystallization temperature.

The influence of the microstructure and regimes of the treatment mentioned above on the mechanical properties of V–4Ti–4Cr alloy at various temperatures is studied. It is shown that the formation of the aforementioned heterophase structure results in a substantial (maximum effect of hardening is about 70%) increase in the short-time strength of the alloy at  $T = 800^\circ\text{C}$  while keeping a rather high reserve of plasticity.

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