PHASE COMPOSITION AND MICROSTRUCTURE OF Ti-6Al-4V ALLOY AFTER HYDROGEN-PLASTIC WORKING

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Abstract. The influence of combination of thermohydrogen treatment and plastic working of Ti-6Al-4V (VT6 Ru) titanium alloy on its microstructure and phase composition has been investigated. The possibility to form and fix the ordered α_2-phase (Ti$_3$Al) with the help of reversible hydrogen alloying is demonstrated. Regularities of the influence of warm plastic deformation of hydrogen-charged alloy VT6 on volume ratio of α_2-phase and its morphology as well as on the tensile strength at elevated temperatures have been investigated.

1. Introduction

About 50% of titanium used in the aerospace industry is the ($\alpha+\beta$) alloy Ti-6Al-4V, the analogue of which is Russian VT6 alloy. This alloy possesses a perfect combination of operational and technological properties [1,2].

One of the effective methods to control the ($\alpha+\beta$) structure of titanium alloys is reversible hydrogen alloying (RHA) [3,4,5]. Hydrogen is absorbed quite easily and in large quantities by many metals as well as can be easily removed at high-temperature processing in vacuum. This allows using hydrogen as a temporary alloying element in metallic materials at a given stage of manufacture of semi-finished and finished products including those of titanium alloys.

Historically, in 1972 V. Goltsov first represented a new paradigm of materials science according to which hydrogen should be considered not only as a harmful impurity but also as a useful alloying element [5]. Controlled and reversible hydrogen saturation of metal allows forming the structure and higher range of physical and mechanical properties, achievement of which is impossible by means of conventional types of thermal treatment.

In 1987 A. Ilyin [6] introduced a term of thermohydrogen treatment (THT) of titanium alloys. It is based on the capability of controlling the mechanism and the kinetics of existing or new hydrogen-induced phase and structural transformations through rational selection of temperature-and-hydrogen concentration conditions of influence on the metal.

THT allows to control the mechanism of phase transformations and structure formation in titanium alloys and includes three main operations:

a) hydrogenation of metal up to a specified concentration of hydrogen;

b) thermal influence on hydrogen-charged metal;

c) vacuum annealing up to safe hydrogen concentrations, at which the development of hydrogen embrittlement of any kind, while constructions are in service, is impossible.

Combination of THT and plastic working (let us call this process hydrogen-plastic working in shot – HPW) is of special interest since hydrogen alloying promotes the manifestation of hydrogen plasticization effect. At definite hydrogen concentrations, decrease of flow stresses and increase of deformation degrees up to first crack occur in metals.

Dependence of flow stress of titanium alloys on hydrogen content and deformation temperature in the two-phase ($\alpha+\beta$) area results from the interaction of the following processes: increase of β-phase volume ratio, its solid-solution hydrogen hardening and softening of α-phase by hydrogen [7-9]. As a result of HPW of titanium alloys, homogeneous dispersed microstructure with equiaxed particles of α-phase (down to 1 μm) which improves strength and plastic properties is formed [10].

Over the last decades the methods which allow forming submicrocrystalline (SMC) or nanocrystalline (NC) structure in metals and alloys have been intensively developed. First of all this is connected with the fact that SMC and NC metals and alloys possess unique physical and mechanical properties being essentially different from the relevant ones for materials with fine and coarse grain structure [11]. Some works [12-14] show that the formation of submicrocrystalline state in VT6 alloy is possible through reversible hydrogen alloying in combination with warm working. However, the disadvantage of such structures is that grain growth starts at relatively low temperatures (close to $0.4T_m$, T_m – melting temperature). In addition, under temperatures which are considerably lower than recrystallization temperature, activation of interface mass-transfer and grain boundary sliding connected with both large volume ratio of grain and phase boundaries and their non-equilibrium state causes the decrease of creep resistance [11,15,16]. So, if operating conditions for products of coarse-grained VT6 titanium alloy are restricted to temperatures 573 – 623 K [17,18], they can hardly exceed 523 K for alloy with submicron grains [19]. As it is known, high-temperature titanium alloys are less capable of softening at elevated temperatures due to intermetallic hardening effect. However, precipitation of α_2-phase (ordered Ti_3Al) in VT6 titanium alloy is complicated which is connected with insufficient aluminium content. On the other hand, it was shown in [20-22] by the example of VT20 and VT9 titanium that thanks to THT controlled precipitation of the α_2-phase (partial ordering of hcp lattice) is possible.

Therefore, researches into influence of hydrogen-plastic working on the α_2-phase (Ti_3Al) formation in titanium alloy VT6, changes in its volume ratio and morphology depending on the degree of warm plastic deformation of hydrogen-charged alloy have been carried out in this work. In addition, the influence of various types of treatment on tensile strength of HPW-processed alloy at elevated temperatures has been studied.

2. Material and experimental procedures

Ti-6Al-4V (VT6 Russian grade) titanium alloy, produced by JSC VSMPO-AVISMA Corporation (Verkhnaya Salda, Russia) was used in the work. Chemical composition of the alloy is given in Table 1.

Table 1. Chemical composition of titanium alloy VT6.

	Chemical composition, wt.%							
	Al	V	Zr	Si	Fe	N	H	Others
VT6	6.46	3.84	0.02	0.01	0.083	0.003	0.003	0.043

Hydrogen enrichment was conducted by thermodiffusion method at a temperature of 1073K with a concentration in the alloy as high as 0.8 – 1.0 wt. % of hydrogen. Sheet rolling was done in flat mills at a temperature interval of 623 – 723K. The alloy for investigation was treated by several modes which are given in Table 2.

Vacuum annealing was carried out at a temperature of 873K during the time required for hydrogen impoverishment in the material down to 0.002 wt.% or less according to the calculations specified in [22].

Table 2. Treatment regimes of the alloy VT6.

State	Mode							
	Hydrogen charging at 1073K	Deformation, %			Annealing in hydrogen-charged state at temperature, K				Vacuum annealing at 873K
		0	20	50	773	873	973	1023	
RHA	✓	✓							✓
THT1	✓	✓			✓				✓
THT2	✓	✓				✓			✓
THT3	✓	✓					✓		✓
THT4	✓	✓						✓	✓
HPW1	✓		✓						✓
HPW2	✓			✓					✓
HPW3	✓		✓				✓		✓
HPW4	✓			✓			✓		✓

Microstructure was examined by the methods of optical microscopy with Olympus GX71 optical microscope, scanning electron microscopy with FEI Quanta 600 FEG (exposure modes: in back-scattered electrons and secondary electrons), transmission electron microscopy with FEI Tecnai G2 F20 S-TWIN microscope at an accelerating voltage of 200 kV. Phase composition was examined by the method of X-ray diffraction with "Thermo Scientific" ARL X'TRA diffractometer using monochromatized copper radiation CuKα. Volume ratio of phases and parameters of crystal lattices were determined by means of calculation procedures of dependencies of peak intensity correlation and PowderCell v2.4 full profile analysis software.

Polishing paper of different coarseness was used to prepare polished specimens for optical microscopy, scanning electron microscopy, X-ray analysis. Finishing polishing was done by diamond water-base solution. At the final stage polished specimens were exposed to electrolytic polishing or etching. Electrolyte composition: H_2SO_4-60%, HNO_3-30%, HF-10%, etching agent: H_2O-90%, HF-10%.

The jet polishing method was used to produce thin foils (Struers TenuPol-5). Electrolyte composition: 20% $HClO_4$+80% CH_3CO_2H.

1246P-2/2300-I vacuum tensile machine was used for testing at elevated temperatures at tensile rate $2\cdot10^{-3}$ c^{-1}. Not less than 3 samples were taken for each state while performing mechanical testing. Nominal error in determination of ultimate tensile strength σ_B did not exceed 5%. Test samples were cut out of sheets by electrospark method in longitude direction of rolling.

3. Experimental results and discussion

Initial microstructure of VT6 alloy in as-received state is represented by equiaxed grains of primary α-phase of about 20 μm, as well as β-transformed structure with α-phase lamellas with a thickness of 4 μm (Fig. 1).
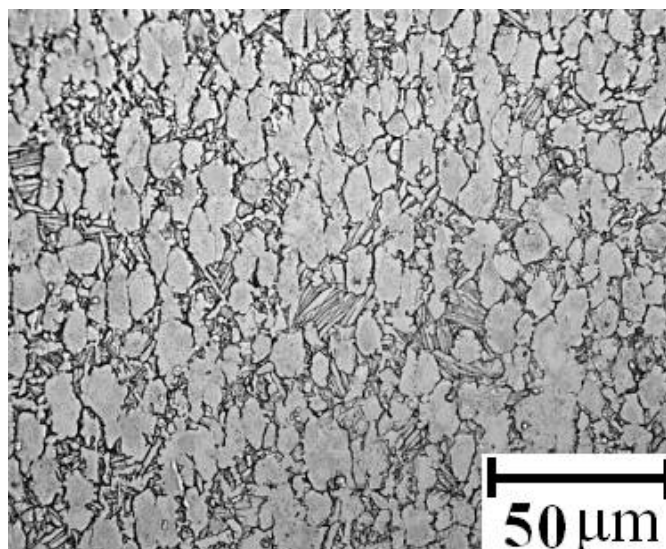
Fig. 1. VT6 alloy structure in as-received state. Optical microscopy.

According to X-ray analysis data, volume ratio of α and β-phases amounts to 87 and 13%, respectively. Crystal lattice parameters for hcp-modification (of α-phase) α_a=2.92 Å, α_c= 4.66 Å, for body-centered cubic (β-phase) a=3.21 Å.

Hydrogen charging was performed at a temperature of 1073K, which is higher than that of polymorphic transformation (α+β→β) of VT6 alloy with a hydrogen content of 0.8–1.0 wt.%. As a result, the alloy with hydrogen was practically represented by the only β-phase (primary) with a grain size of about 150 – 200 μm (Fig. 2).
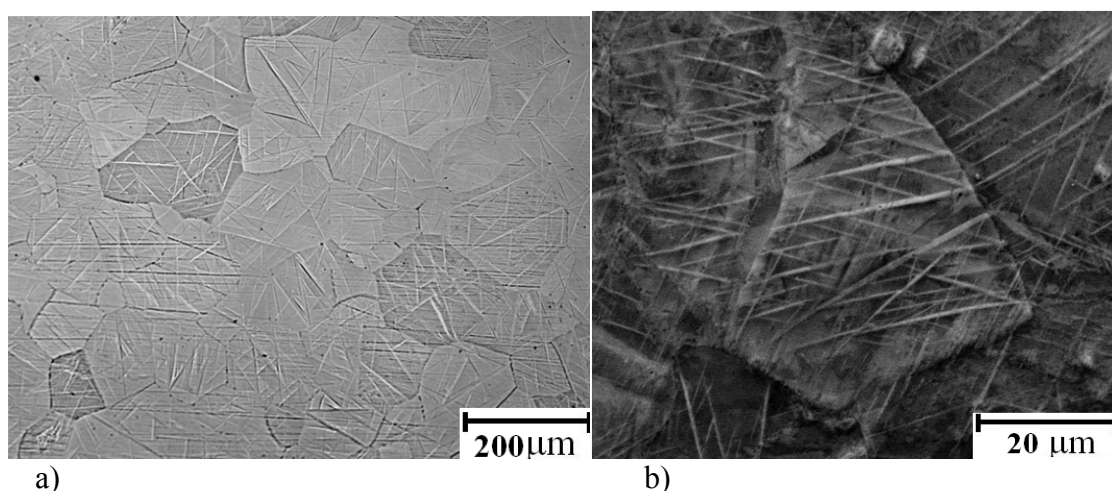

a)   b)

Fig 2. Microstructure of titanium alloy VT6 in hydrogen-charged state: a) optical microscopy; b) SEM.

After vacuum annealing, which was done immediately after hydrogen absorption, (HRA state according to Table 1), the alloy structure was characterized with even fine precipitation of α-phase with a size of about 0.3 – 0.7 μm in all volume of primary β-phase. According to the data from X-ray analysis, lattice parameters of α-phase are α_a=2.92Å, α_c= 4.67 Å, β-phase a=3.21 Å, which are the same for the initial state of the material.

In case of thermohydrogen treatment (combination of reversible hydrogen alloying with annealings in hydrogen-charged states) chaotically directed crystallites in the form of plates (Fig. 3) of different size are observed: small ones (with a thickness of about 0.15 μm) and large (with a thickness of more than 1 μm).
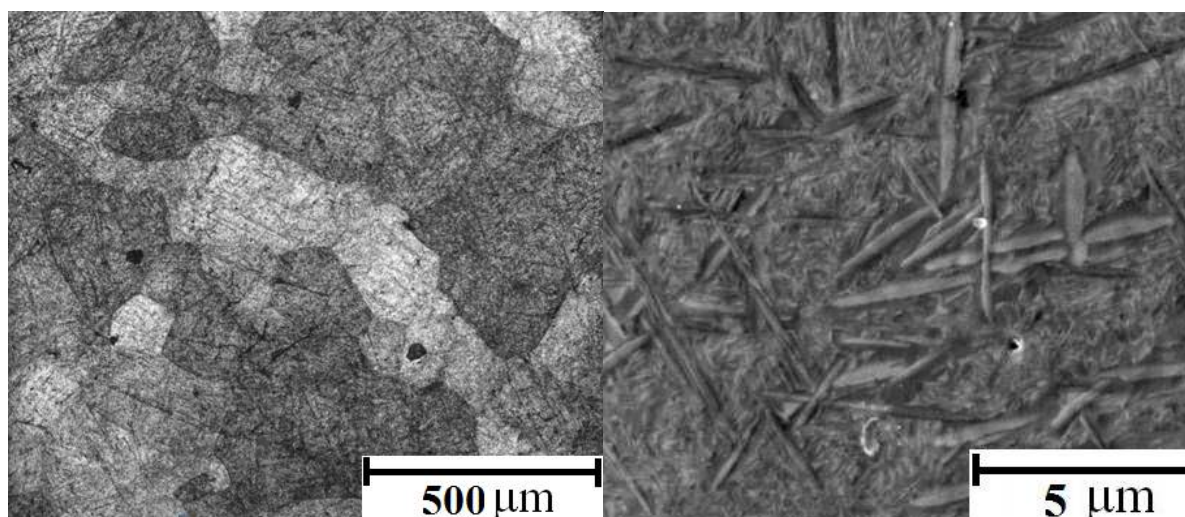
Fig. 3. Microstructure of the titanium alloy VT6 processed by thermohydrogen treatment (THT3): a) optical microscopy; b) scanning electron microscopy
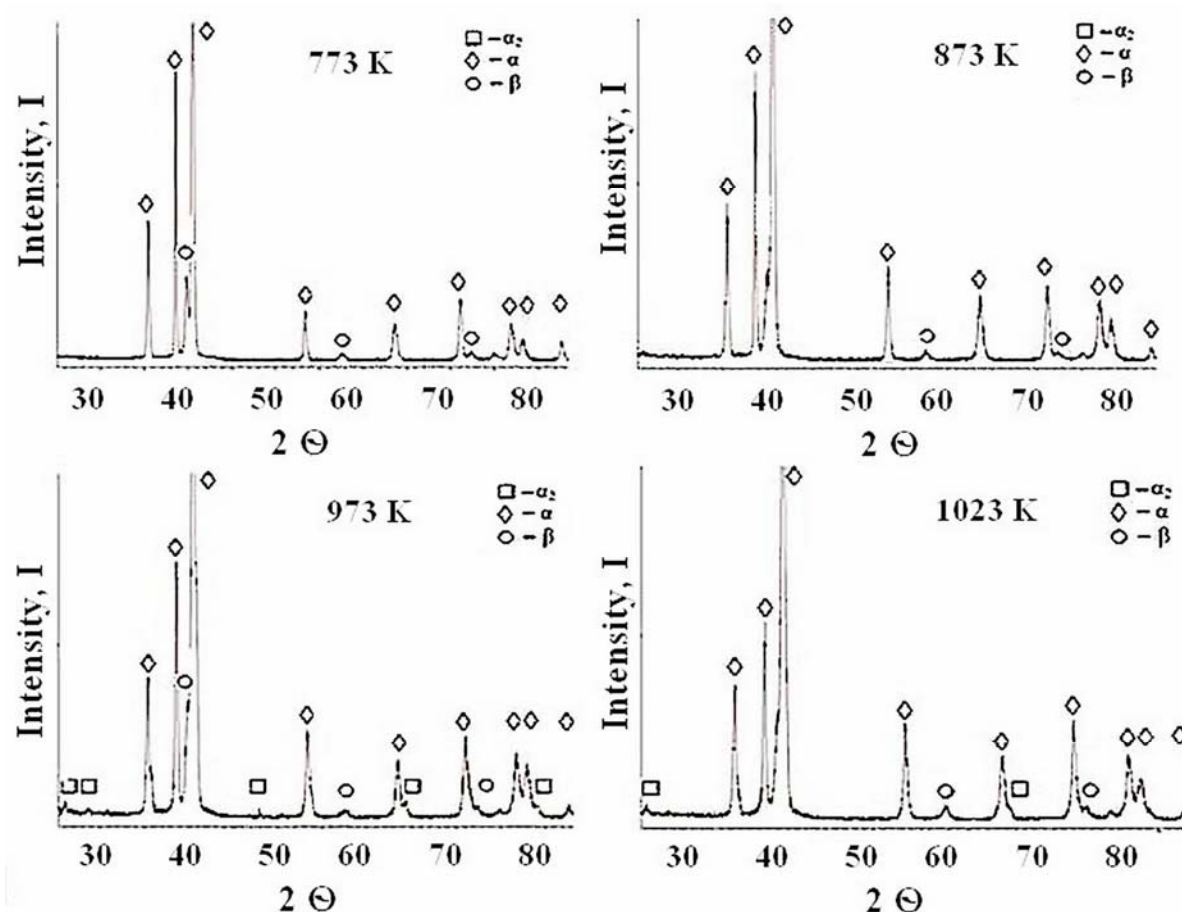

Fig. 4. XRD patterns of the alloy VT6 after thermohydrogen treatment (THT1-THT4, see Table 1) with decoding of the phases.

The data from X-ray analysis of the samples treated by THT are given in Fig. 4. XRD peaks of ordered α_2-phase (Ti$_3$Al) are found in thermohydrogen treated alloy which was annealed in hydrogen-charged state in the temperature interval of $973 - 1023$K (states THT3 and THT4). Since some peaks of α_2-phase coincide with peaks of α-phase, asymmetry of

peak shapes and their widening are observed. In Table 3 we have given the values of crystal lattice parameters and volume ratio of α_2-phase in VT6 titanium alloy after thermohydrogen treatment.

Table 3. Crystal lattice parameters and a volume fraction α_2-phase in titanium alloy VT6 after thermohydrogen treatment.

State	Annealing temperature in hydrogen-charged state, K	HCP (α-phase)		HCP (α_2-phase)		Volume ratio of α_2-phase, %
		A	c	a	c	
THT1	773	2.920	4.660	--	--	--
THT2	873	2.925	4.660	--	--	--
THT3	973	2.930	4.660	5.785	4.660	13±3
THT4	1023	2.925	4.660	5.785	4.660	9±2

It is found out that warm rolling of the material in hydrogen-charged state leads to the change of microstructure morphology. Scanning electron microscopy pictures of typical microstructures of VT6 titanium alloy after dehydrogenization which were obtained as a result of warm plastic deformation by rolling at a degree of 20 % and 50 % in hydrogen-charged state are shown in Fig. 5. Lamella crystallites of α-phase dominate within grains at a deformation degree of 20 %. Globular crystallites are found at deformation of 50 %.
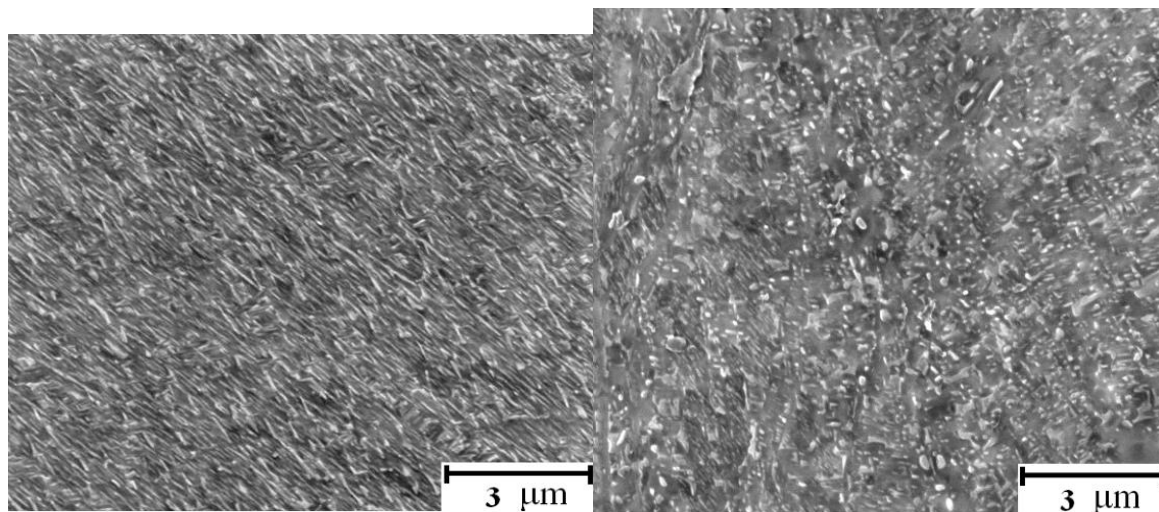

Fig. 5. The images of titanium alloy VT6 microstructures after hydrogen-plastic working a) HPW1 state (20 % of rolling) and b) HPW2 state (50 % of rolling). Scanning electron microscopy.

Hydrogen-plastic working lead to the increased volume ratio of α_2-phase relative to thermohydrogen processing. Such effect of warm deformation by rolling of the alloy in hydrogen-charged state on its phase composition according to the data from X-ray analysis is presented in Table 4. Meanwhile, the parameters of crystal lattices of phases vary insignificantly.

Table 4. Volume ratio of phases in titanium alloy VT6 after hydrogen-plastic working.

State	Deformation, %	Volume ratio, %		
		α-phase	β-phase	α_2-phase
THT3	0	82±3	5±3	13±3
HPW3	20	73±2	8±2	19±2
HPW4	50	73±2	9±2	18±2

TEM data is also indicative of ordered α_2-phase formation after HPW (Fig. 6). Microdiffraction pictures of thin foils contain extra-reflexes of ordered α_2-phase, which is homogeneously distributed in the material according to dark-field images.
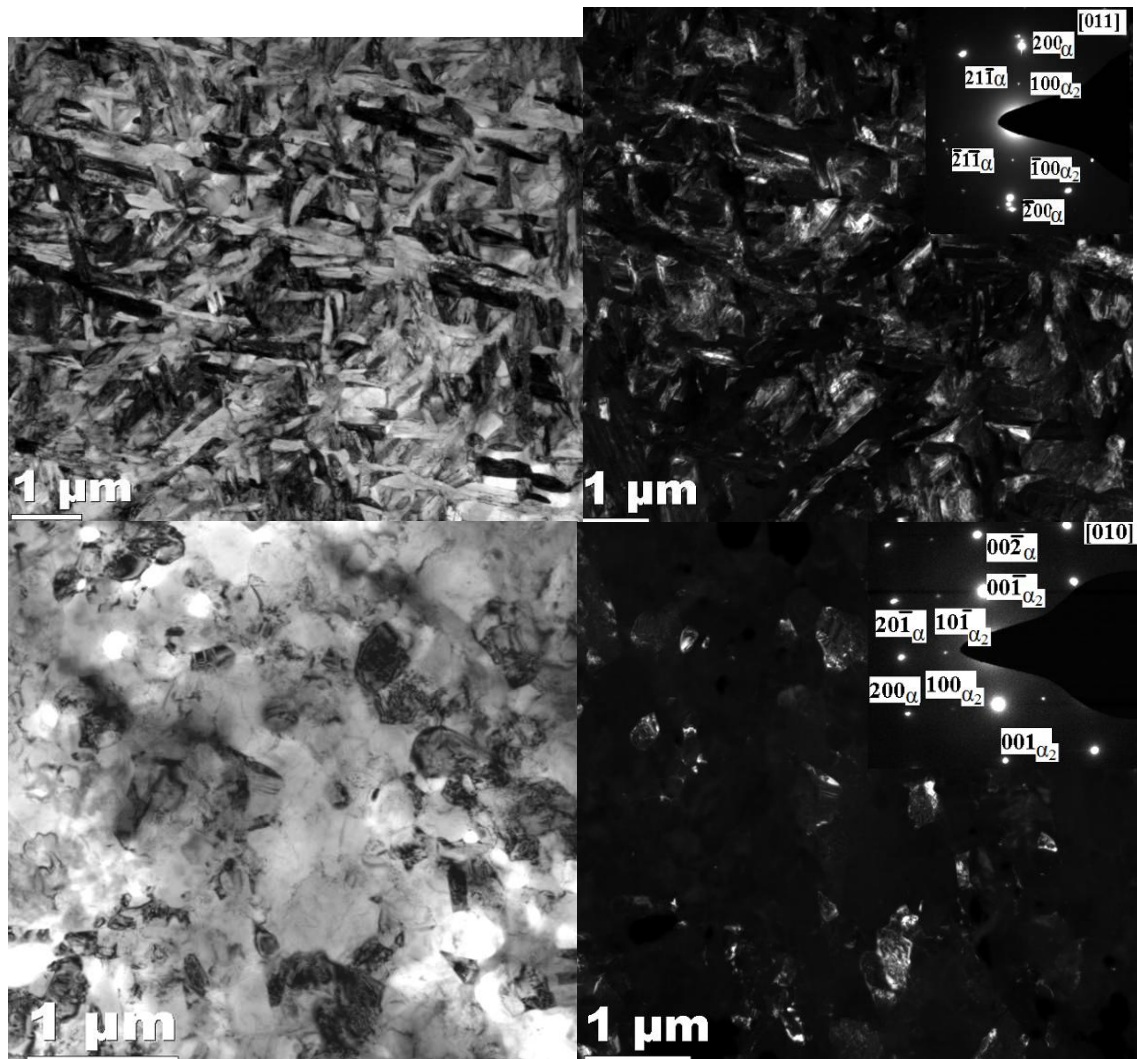

Fig. 6. The images of titanium alloy VT6 microstructures after hydrogen-plastic working (a-b) HPW3 state (20 % of rolling) and (c-d) HPW4 state (50 % of rolling). Transmission electron microscopy (microdiffraction is received from the area S=0.25 μm^2). Longitudinal section of the samples after rolling: light field (a, c); dark field obtained with extra-reflex (100)α_2 of zone axis [011] (b) and with extra-reflex (10-1)α_2 of zone axis [010] (d).

It is known that alloys containing Ti_3Al in its structure have the enhanced high temperature strength since the α_2-phase particles block the dislocation motion intensively and

promote the improvement of creep resistance of titanium alloys [1]. Indeed, mechanical testing at elevated temperature has shown the increase of strength properties of VT6 alloy undergone THT and HPW treatment. Meanwhile, the reinforcing effect is observed only in those samples in which occurrence of intermetallic α_2-phase is found by X-ray and TEM (Fig. 7).
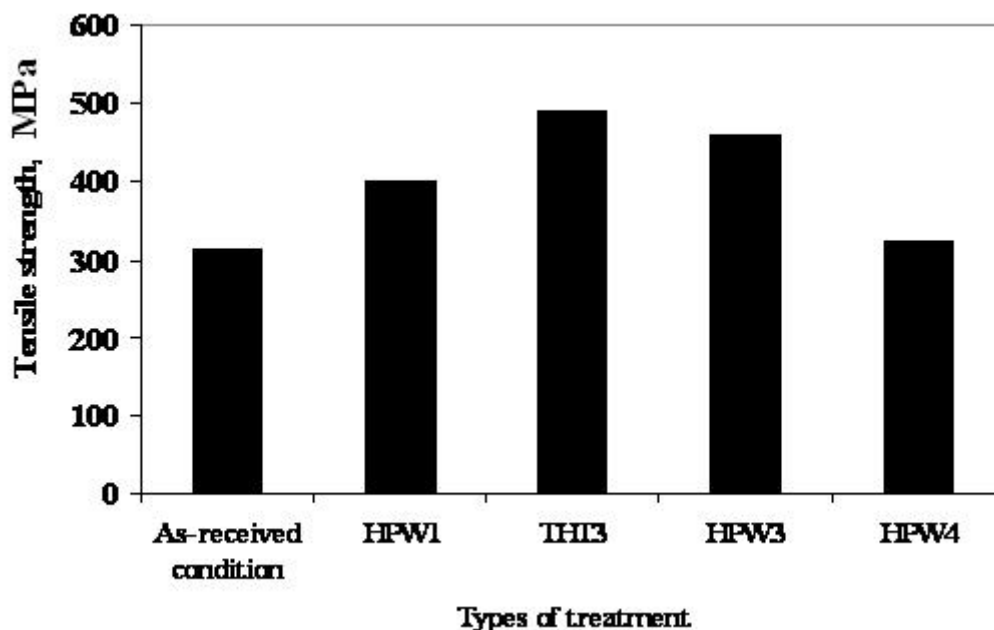

Fig. 7. Tensile strength at 873K of the alloy VT6 in various states.

4. Discussion

Earlier in [23,24] for VT6 titanium alloy it was shown that α_2-phase can form in low quantities and as a result of conventional isothermal annealing, at a holding duration of up to 200 – 300 hours. By now a series of works about possibility of creating new structure types in titanium alloys with application of reversible hydrogen alloying which cannot be formed by conventional methods has been published [25,26].

The hydrogen, being a strong β-stabilizer, decreases the temperature of polymorphic transformation (by 200 – 250K) as well as temperatures of martensitic transformation and critical cooling rates [7]. It enables to realize the quenching effect and obtain more metastable phases at "mild" temperature-and-rate conditions of treatment. The hydrogen shifts the state diagram towards the increase of volume ratio of β-phase, and finally, it leads to the increase of aluminum concentration in α-phase up to values at which it's ordering becomes possible. It is this effect that has been observed earlier in VT20 alloy [17] and has been revealed in this work by us while annealing VT6 hydrogen-charged alloy.

It should be noted that vacuum annealing with dehydrogenization must lead to leveling the phase composition (restoration of phase equilibrium according to the diffusion mechanism). However, the big difference between hydrogen diffusion coefficients and alloying elements enables to fulfill the transformation of metastable β-phase into α-phase (which contains high quantity of β-stabilizing elements and little aluminum) at low temperatures of gas removal. In addition, when removing hydrogen, "dissolution" of α_2-phase (disordering due to the lack of aluminum) formed in hydrogen-charged material at higher temperatures is unlikely, at least for kinetic reasons. Thus, it is possible to fix α_2-phase in VT6 alloy with the help of THT and HPW.

Dissolving unequally (mainly in β-phase), the hydrogen enhances the capability of plastic formation of material [23] which effectively helps to process difficult-to-form

titanium alloys at lower temperatures and rates. For example, integrated approach to alloy development and technology of its treatment (basically, development of alloy composition was carried out directly for the hydrogen technology) has enabled to create new alloy 7115 based on Ti_3Al with Ti-14Al-3Nb-3V-0.5Zr chemical composition in "MATI" – K.E. Tsiolkovsky Russian State University of Aviation Technology [27]. This example does not exactly correspond to the situation realized in this work where the alloy with hydrogen is a pure β-phase. Nevertheless, the alloy is easily deformed by rolling at a temperature of over 573K remaining bcc structure at the same time. It is natural that the increase of defect density after rolling (twins, dislocations, small-angle boundaries, etc.) promotes precipitation of the ordered $α_2$-phase at a subsequent annealing. The higher deformation degree is, the more transformation completeness and decomposition homogeneity are. At the same time another tendency is observed: with the increase of strain, subgrains both of $α_2$- and α-phase become less elongated. In addition, misorientations between crystallites increase. As a result, the best high temperature strength properties are demonstrated in the state characterized by the presence of α- and $α_2$-phase of lamella morphology with mainly small-angle misorientations between α-phase crystals of high dispersion.

5. Conclusions

- It has been established that it is possible to form ordered $α_2$-phase (Ti_3Al) in VT6 alloy as a result of thermohydrogen treatment and hydrogen-plastic working. Meanwhile, warm plastic deformation of hydrogen-charged material leads to the increase of volume ratio of this phase in dehydrogenated alloy.
- It has been shown that it is possible to fulfill the controlled creation of several types of microstructures with different $α_2$-phase volume ratio by varying parameters of hydrogen-plastic working (strain, annealing temperature).
- VT6 alloy states characterized by the presence of ordered $α_2$-phase of lamella morphology and small-angle misorientations of α-phase crystallites possess the highest tensile strength at temperatures of up to 873K.

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