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ENHANCED STRENGTH AND SCRATCH RESISTANCE OF ULTRA-FINE GRAINED Ti64 ALLOY WITH (Ti+V)N COATING

I.P. Semenova[1], R.R. Valiev[1,2], K.S. Selivanov[1], Yu. M.Modina[1], A.V. Polyakov[1,2], M.K. Smyslova[1] and R.Z. Valiev[1,2]

[1]Ufa State Aviation Technical University, 12 K. Marx St., Ufa 450000, Russia
[2]Laboratory Mechanics of bulk nanostructured materials SPBU, 28 University Ave., Peterhof, St.Petersburg 198504, Russia

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Abstract. In the last decade a number of original works were published by Prof. I.A. Ovid'ko on the analysis of deformation mechanisms in nanostructured materials. It should be noted that in recent years nanostructuring of commercial alloys have been advanced for practical application. This work is devoted to improving the performance properties of Ti-6Al-4V alloy by hardening through the formation of ultrafine-grained (UFG) structure using severe plastic deformation and consequent application of the (Ti + V) N coating by vacuum - plasma deposition. The influence of the UFG structure on the enhancement of strength and adhesion properties of the coating was demonstrated. Mechanical tests at running temperatures of the alloy increased softening resistance was revealed for the coated UFG alloy in contrast with its CG and UFG counterparts without coating. The nature of the alloy behavior in terms of the "barrier effect" formation in the metal subsurface is discussed.

1. INTRODUCTION.

Professor Ilya Ovid'ko published several papers [1-4], which can be considered as an effective scientific basis to enhance mechanical properties of ultrafine-grained (UFG) metallic materials. Indeed, recent studies demonstrated that the formation of structures by severe plastic deformation techniques is a promising way to increase physical and mechanical properties of commercial metals and alloys. The SPD techniques allow achieving very high plastic strains at relatively low temperatures (usually 0.3…0.4 T_{melt}, K) in the conditions of high applied pressures [5,6]. Generally, the SPD-produced UFG metals and alloys have a grain size in the range of 100…500 nm but contain different nanostructural elements inside the grains, including nanotwins, nanoparticles, segregations etc., the latter producing a significant influence on their properties and therefore, such materials are related to the class of bulk nanostructured materials [7]. Formation of a bulk UFG structure in Ti alloys allows increasing their strength-to-weight ratio, fatigue resistance, fatigue life, which makes possible enhancement of service properties of items produced from them [8].

As is known, two-phase (alfa+beta) Ti alloys are used in a wide range of temperatures from -196 to 450 °C. Most commonly, in aircraft engineering and engine building a wide range of essential articles are constructed from the alloy Ti-6Al-4V, the operating temperature of which in in aircraft engine does

Corresponding author: R.Z.Valiev, e-mail: ruslan.valiev@ugatu.su and I.P.Semenova, e-mail: semenova-ip@mail.ru

not exceed 350 °C whereas the tensile strength usually constitutes 650-700 MPa [9]. To date, different SPD methods have been applied to process bulk UFG samples from the alloy Ti-6Al-4V alloy with a strength of up to 1200 ... 1500 MPa, whereas the strength of a conventional hot-rolled alloy does not exceed 1000 MPa [8,10].

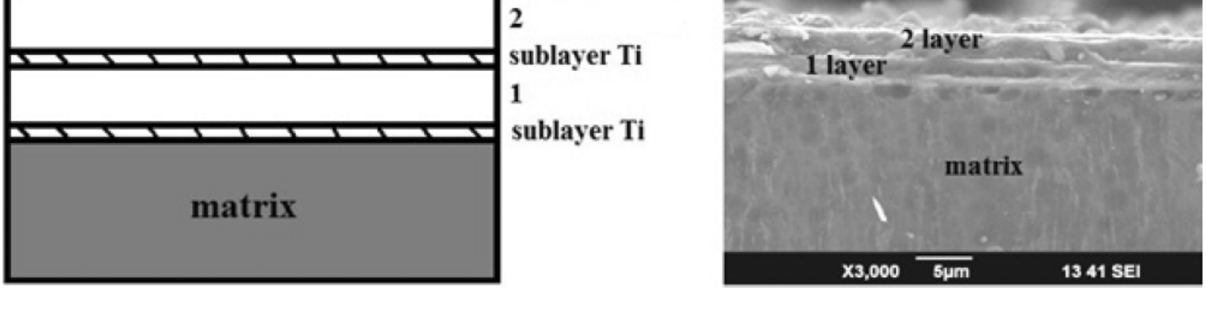
Special attention is paid to enhancement of such service properties of structural materials as corrosion and erosion resistance. It is achieved mainly at the expense of application of different protective coatings. There are several techniques dealing with the protection of a surface by applying the concentrated energy flow, including ion implantation [11-13], the vacuum-plasma coatings of nitrides and carbides [14,15]. Evidently impact of ion implantation and vacuum plasma coating application increase the role of the UFG alloy surface, as the structure, internal stresses, and finally service properties of coatings will depend on the surface condition (grain size, heat and physical properties, microgeometry).Recent studies show that the use of a substrate from pure SPD-processed Ti with ultrafine grain size can significantly improve the load-bearing capacity of TiN and diamond-like carbon (DLC) coatings as a result of increasing their hardness and adhesion strength [16,17].

Development and study of the combined strengthening techniques of Ti alloys are quite urgent for modern titanium material science and engineering. These techniques ensure enhancement of the necessary set of service properties, including strength, fatigue life, corrosion and erosion resistance. In this paper a combined approach was used to the Ti-6Al-4V alloy that has been successively subjected to severe plastic deformation for the formation of bulk UFG structure. In the subsequent vacuum-plasma application of a multilayer coating (Ti+V)N, the formation of a refractory vanadium nitride compound in the process of plasma chemical reaction during condensation additionally contributes to wear resistance. The Scratch test was used to analyze the influence of UFG structure on an adhesive strength of the coating. The mechanical behavior of the Ti-6Al-4V alloy subjected to combined treatment was studied at room and elevated temperatures for evaluation of its performance properties.

2. MATERIALS AND EXPERIMENTAL METHODS

The investigations were carried out on the Ti-6Al-4V alloy (Ti-basis, Al – 6.6%; V – 4.9%; Zr – 0.02%; Si – 0.033%; Fe – 0.18%; C – 0.007%; O_2 – 0.17%; N_2 – 0.01%; H_2 – 0.002%). The temperature of polymorphic transformation (TPT) in the alloy equaled to 975±5 °C. The initial samples with a diameter of 20 mm and 105 mm long were subjected to processing following the pre-developed technique consisting of preliminary heat treatment by quenching from T=950 °C (heating during 20 min) and consequent annealing at 675 °C during 4 hours, equal-channel angular pressing (ECAP) on a die-set with the channels intersection angle ψ=120° at a temperature of 700 °C and further extrusion at 300 °C.

The microstructure was studied by optical and transmission electron microscopy (TEM) on the microscope JEM-200B with an accelerating voltage of 200 kV. Thin foils for TEM were prepared by spark cutting of the plates with a thickness of 0.8-1 mm, mechanical thinning with subsequent electrolytic polishing at subzero temperatures.



a b

Fig. 1. Schematic illustration (a) and SEM image of microstructure of the coating (Ti+V)N on the surface of UFG Ti-6Al-4V samples.

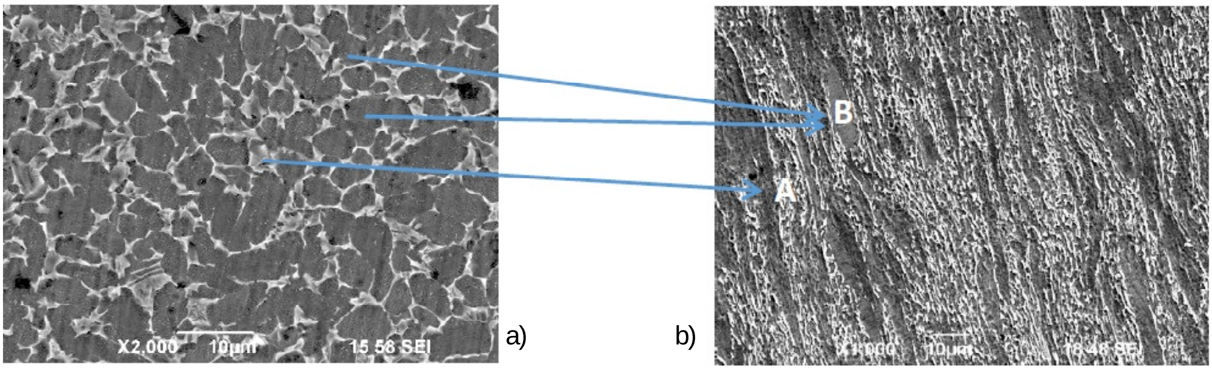


Fig. 2. SEM image of microstructure of UFG Ti-6Al-4V samples in the as-received state (a); after combined SPD-processing (b): regions A – (α+β) structure and B – primary α-phase grains.

The PVD coating (Ti + V)N was applied on the disk-shaped samples 5 mm thick in the installation WATT -900 3D simultaneously from two arc evaporators. The coating structure was formed by alternating the deposition time of each layer and the amount of material sprayed from each of the cathodes. Coating architecture (Ti + V)N consisted of Ti adhesion sublayer, two layers of (Ti + V)N (Fig. 1).

The «sin$^2\psi$» technique of X-ray diffraction (XRD) was applied to determine the residual stress in the coating [18,19]. The main parameters in calculating residual stresses are Young's modulus (E) and Poisson ratio (ν). For the (Ti + V)N coating E = 256 GPa and ν = 0.250 [20] The values of residual stresses are averaged over the entire depth of the X-ray transmission (up to 10 microns).

Inclined polished sections (Fig. 2) were prepared for metallographic studies of the coatings. Mechanical grinding was carried out on the sand paper with gradually decreasing grain size and followed by diamond-paste polishing for mirror-like surface of the section that was controlled with an optical microscope.

The thickness and lamination of coating layers were determined on the device "Calotest" (by CSEM Instruments Company). The system uses the abrasion of sample surface by a steel ball rotating at a constant speed until the dimple-shaped indentations are formed. The spherical polished section was prepared with the application of Calotest Hi-quality (0.5-1 and 0-0.2 μm) waterbase diamond suspensions.

Coating strength for the CG and UFG samples was analyzed by a scratching technique on the instrument Scratch Tester (CSM Instruments) [21]. The diamond indenter (with a radius of 0.02 mm and angle of taper 120°) was positioned to slide over the coating surface with the increasing load from 0.03 to 15 N. During the tests, the following data were determined: the loading of initial plastic deformation Lc_0, critical load of cohesive failure Lc_1 (from the first fractures on the surface) and critical load of initial adhesive separation of the surface from the substrate Lc_2. Four scratches were made on each specimen for statistical analysis and as a result, the standard error was calculated for each critical load. After the experiment, the scratches were examined with the use of an optical microscope at a magnification of 50X to 200X.

The microhardness was measured on an Omnimet (Buehler) microhardness tester with a load of 300 g and a holding time of 10 sec. Cylindrical samples with a gauge length 15 mm and diameter 3 mm were subjected to tensile testing on an Instron tensile machine at temperatures of 20….700 °C and strain rate $\varepsilon = 10^{-3}$ s^{-1}. At least 3 samples were tested for each state. The ultimate tensile strength (UTS), yield stress (0.2 YS) and relative elongation (Elongation %) were determined.

3.1. Microstructure of the Ti-6Al-4V alloy processed by SPD

Figs. 2 and 3 display the microstructure of coarse grained (CG) Ti-6Al-4V alloy. The microstructure was typical bimodal with the size of primary a-phase grains (15±5) μm and areas with the plate (α+β) structure. The fraction of the primary α-phase was about 65% (Fig. 2a). The fraction of the β-phase did not exceed 12% according to the X-ray study results. After the combined SPD-processing primary a-phase grains had an elongated form, the fraction

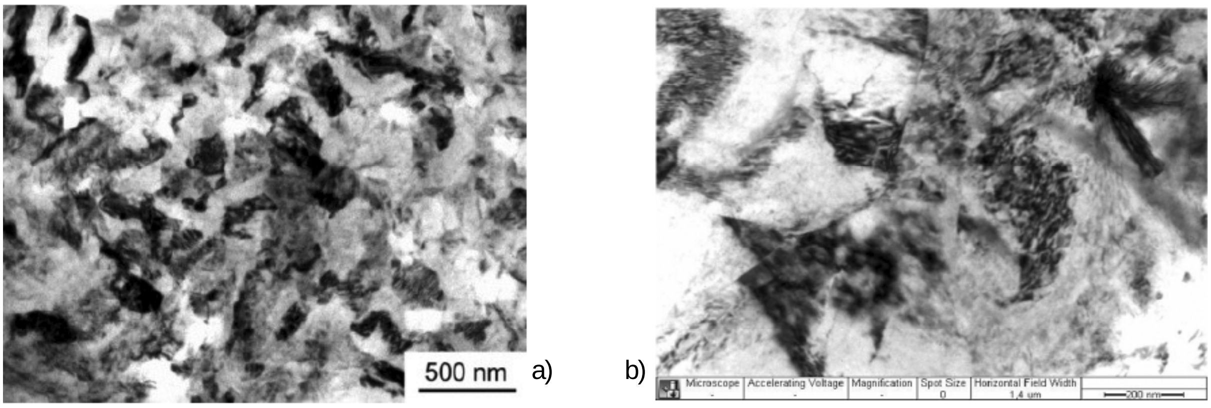


Fig. 3. TEM-image of the UFG structure of the region A (a) and region B (b).

of primary a-phase grains decreased to 25%, and its grain size reduced down to 5 μm (Fig. 2b).

In the areas with (α+β) structure (area **A** in Fig. 3a) the UFG structure was formed (Fig. 3d). The average grain/subgrain size of the α-phase was measured on the dark-field microstructure images and was about (240±60) nm. The formed UFG structure (Fig. 3) was characterized by high dislocation density (up to 17×10^{11} cm^{-2}), high internal stresses caused by strong distortions of the crystalline lattice, which is typical of various metals processed by SPD [5,6]. Fig. 3b shows typical TEM images of the fragmented primary α-phase (region **B**) after SPD processing. As a result of the processing by SPD, there is an increase in the dislocation density in the bodies of larger grains with the formation of weakly misoriented structures of a cellular type.The fraction of the β-phase reduced to 6% due to its partial dissolution and decay of $\beta \rightarrow \alpha_{pr} + \beta$, initiated by SPD [8].

3.2. Microstructure of a (Ti+V)N coating

Fig. 4 demonstrates the spherical polished section of the surface with a dimple-shaped coating formed with a steel ball of a 20 mm radius on the installation Calotest. Total thickness of the multilayer coating and the thickness of each layer were measured on this polished section. The image displays a two-layer coating (Ti+V)N with a total thickness of 5.5 μm, whereas Ti sublayer is not visible due to its very small thickness. Similar case is also observed for a CG sample with the same coating.

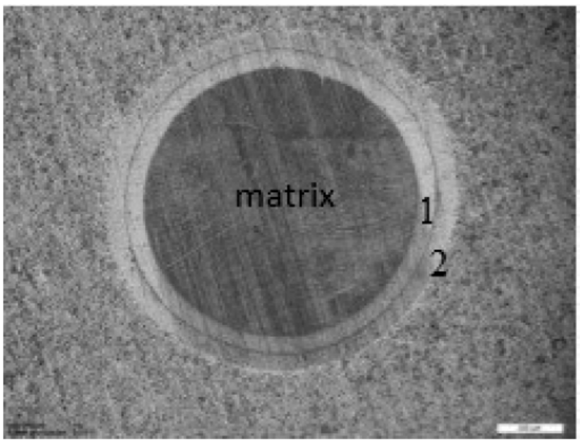


Fig. 4. Spherical polished section of the surface with a dimple-shaped coating formed with a steel ball on the installation Calotest.

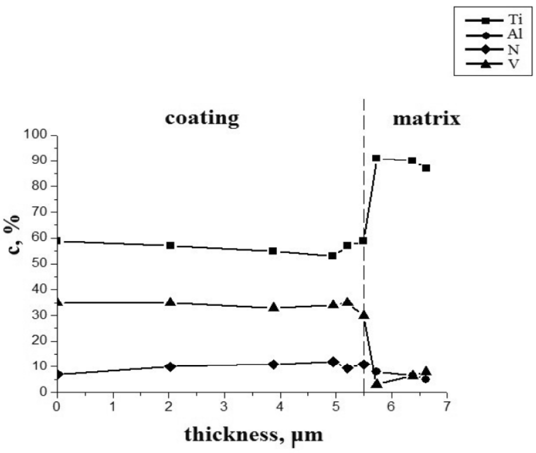


Fig. 5. Chemical composition change throughout the (Ti+V)N coating thickness on the UFG Ti-6Al-4V substrate.

Table 1. Evaluation of residual stresses by XRD analysis.

Sample	Young's modulusof matrix/coating E, GPa	Poisson ratio, ν	Residual stress, MPa
CGTi-6Al-4V + (TiV)N	112/256	0.250	-789 ± 37
UFG Ti-6Al-4V + (TiV)N	112/256	0.250	-1379 ± 28

Fig. 5 displays the diagrams for chemical composition change throughout the coating thickness obtained by the local X-ray analysis in a scanning electron microscopy. The data clearly illustrates the presence of an intermediate region, the chemical composition of which contains Ti and V nitrides, in the «matrix-coating» system as a result of mutual diffusion processes during deposition, such processes involving local heating of the surface in plasma. The content of Ti and V nitrides is more or less similar throughout the thickness the deposited coating layers (Fig. 5). The value of coating microhardness (HV) measured on the surface of CG and UFG samples was approximately the same and constituted 13±0.5 GPa, which was considerably higher than that of the CG and UFG alloys (3.2±0.1 and 4.2±0.1 GPa, correspondingly). Apparently, almost similar values of coating microhardness for the CG and UFG samples may be a result of the fact that the depth of penetration of an indenter under the loading of 100 g is less than the coating thickness.

As is known, the application of vacuum-plasma coatings with a different physical nature than that of a matrix leads the occurrence of residual stresses. Earlier, it has been demonstrated that the compressive stresses produce a favorable impact on fracture and wear resistance of the parts [20]. Here, the residual stresses are evaluated for the (Ti+V)N coating applied on the surface of the conventional CG and UFG alloy Ti-6Al-4V samples. The XRD analyses reveal the formation of compressive stresses in the (Ti+V)N coating, and the value being considerably higher in the UFG Ti alloy sample (Table 1).

3.3. Micro scratch-test

The readings for the depth of penetration of an indenter under loading, residual scratch depth after removing the load and the acoustic emission signal were also recorded during the course of the experiment. Fig. 6 shows the tracks (scratches) on the (Ti+V)N-coated samples from the Ti-6Al-4V alloy with the CG and UFG structure. The obtained data were used to define:

– the loading of initial plastic deformation (Lc_0),
– critical loading (Lc_1) corresponding to the initial cohesive failure of the coating in the form of separate fractures;
– critical loading corresponding to the initial adhesive separation of the surface from the substrate (Lc_2).

The experimental results are shown in Table 2 and Fig. 6. The latter demonstrates that the nature of the coating fracture is similar for the CG and UFG samples. The start of plastic deformation is earlier for the CG samples, which leads to an earlier microcracking and consequently, to a somewhat less cohesive failure load Lc_1 in comparison with the UFG samples. In addition, the UFG samples have an enhanced adhesive strength. Critical load of adhesive fracture on the UFG

Table 2. Results of Micro Scratch-test, Rockwell indenter with a radius of 20 μm.

Sample	Plastic deformation load, Lc_0, N	Cohesive failure load, Lc_1, N	Adhesive fracture load Lc_2, N
CG	0.4 ±0.05	3.8 ±0.12	6.8 ±0.18
UFG	0.7 ±0.01	4.4 ±0.05	14.1 ±0.32

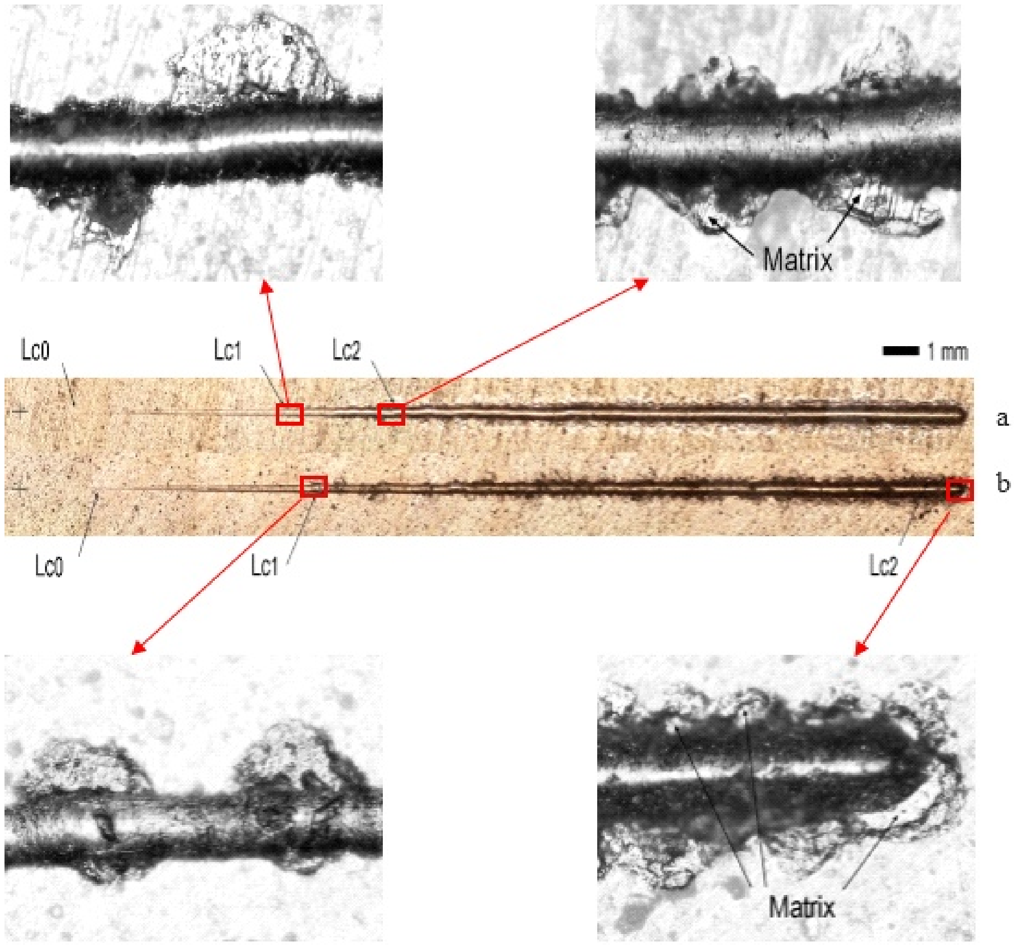


Fig. 6. Scratch tracks of (TiV)N multilayered coating on (a) coarse-grained Ti-6Al-4V and (b) ultrafine grained Ti-6Al-4V.

samples is almost twice higher than that for the CG counterparts (Table 2).

3.4. Mechanical behavior of the UFG Ti-6Al-4V alloy with and without (Ti+V)N coating at elevated temperatures

Fig. 7 presents the temperature-dependence plots of ultimate tensile strength (Fig. 7a) and total elongation (Fig. 7b) for the CG and UFG Ti-6Al-4V alloys. The mechanical tests of the samples conducted at room temperature showed that the UTS of the UFG alloy reaches 1320 MPa, which is almost 30% higher than the UTS value of the CG alloy (985 MPa) (Fig. 7a). As is seen, during the tests at working temperatures of 300, 350, and 400 °C the strength in both states is observed to decrease and the ductility enhances. At the same time within the temperature range from 20 to 400 °C, the UFG alloy retains higher strength values as compared to the CG alloy. The difference of these values for the CG and UFG alloy is almost 300 MPa (Fig. 7a).

The strength and ductility curve for the UFG samples with the coating (Ti + V)N is of a general pattern with that for the UFG alloy without coating (Figs. 7a and 7b). However, it should be noted that the coating hinders the softening process at temperatures 350 and 400 °C, as evidenced by a decrease in the slope of the curve (Fig. 7a). For example, the tensile strength at 400 °C of the coated UFG samples was 1070 MPa, whereas the uncoated samples had a strength of 900 MPa, which is significantly higher than the tensile strength demonstrated by the CG sample (780 MPa). The difference in total elongation values of the UFG samples with and without coating was minimal at 300 and 350 °C, whereas at 400 °C it constituted 25 and 35%, correspondingly (Fig. 7b.).

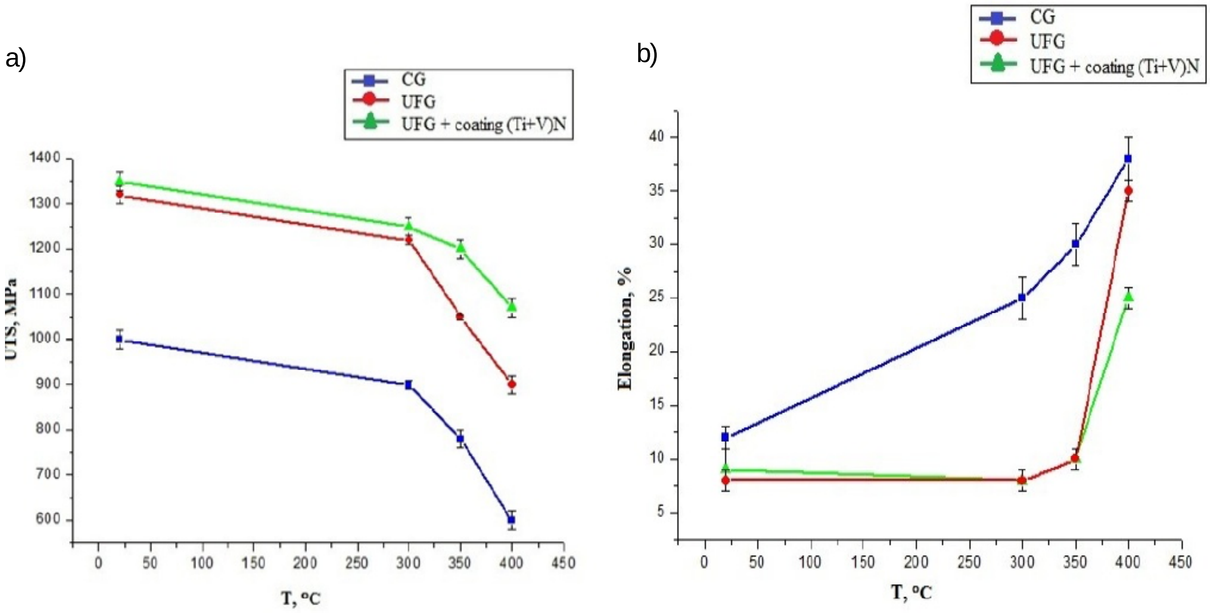


Fig. 7. Dependence of UTS (a) and Total Elongation (b) on test temperatures for the Ti-6Al-4V samples with CG structure, UFG structure and coating (Ti+V)N.

4. DISCUSSION

Thus, the use of severe plastic deformation for grain refinement in the alloy Ti-6Al-4V followed by application of a multilayer coating (Ti+V)N produces a considerable influence on the adhesion strength of the coating as well on the mechanical behavior of the «substrate-coating» system, especially at elevated temperatures.

As was revealed, the ultrafine grain in the substrate microstructure increases the adhesive strength of the coating by 10-20% in comparison with the CG matrix from the alloy Ti-6Al-4V A similar effect was observed in the work [17], where TiN and diamond-like carbon (DLC) coatings were deposited on pure Ti substrates with and without processing by high-pressure torsion (HPT). The revealed regularity clearly shows a direct dependence of coating adhesive properties enhanced by grain refinement. Since in the vast majority of cases, the «centers of crystallization» during coating deposition are the grain boundaries and the points of emergence of dislocations on the surface, in this case high density of grain boundaries and crystal defects in the UFG sample may obviously contribute to better support to the thin coatings [16].

The results of studies of mechanical properties demonstrated that the formation of UFG structure in the Ti-6Al-4V alloy led to increased strength not only at room temperature, but also at elevated temperatures. The possibility of achieving high strength in the Ti-6Al-4V alloy at room temperature through a-grain refinement was proved in the works by different researchers who used various SPD techniques, including isothermal forging [8,10]. The results of this work showed that the UFG alloy demonstrates also increased strength at a temperature of 400 °C (900 MPa) as compared to the conventional CG alloy with a strength of 600 MPa.

The coating (Ti+V)N was revealed to produce a positive influence on the strength of the UFG alloy during the tests at 300…400 °C. In particular, at 400 °C ultimate tensile strength of the UFG sample with coating was 1000 MPa, which considerably exceeds the values of the UFG and CG sample without coating (900 and 600 MPs, correspondingly) (Fig. 7a). As is known, at the stage of macroelastic straining, tensile plastic deformation occurs mostly in the surface layers with self-organization of dislocation substructure of the point and other defects [23-25]. This leads to the gradient dislocation density and the formation of an enhanced surface layer that serves as a «barrier» for the dislocations emerging from the material interior to its surface. Consequently, this brings to a redistribution of loading between the external and internal surfaces in metal and to the change in mechanical properties of a substrate.

The researchers consider several mechanisms dealing with the occurrence of the «barrier effect» that explain the influence of hard surface coatings on the mechanical properties of metals [21]: elastic rebound between the dislocations in the substrate with coating that has a larger value for an elastic modulus; suppression of surface dislocation sources by coating; blocking mechanism, when the coating prevents the emergence of dislocations to the surface, etc.

Generation of residual compressive stresses at the «matrix-coating» boundary is an important factor in the formation of the «barrier effect», as is attested by X-ray analysis in the present work (Table 1). Apparently, surface hardening with the creation of a high level of compressive stresses changes the pace of structure self-organization in the near-surface layers and, as a result, the breakthrough of a surface barrier layer will occur at a higher stress. At the same time, the dislocation mobility in the near-surface layer is affected by such factors as the film structure, its thickness and adhesion to the metal-substrate, the difference in the elastic moduli of the matrix and the film, residual stresses and other.

Complex approach to the material strengthening will also increase the fatigue life, which is evidenced by previous works on steels. For example, a considerable increase of fatigue strength in steel JIS S35C with a thin TiN coating (2-6 μm) deposited on the surface of the samples by vacuum-plasma technique is shown in [24]. A thin layer of TiN 3 μm thick on the surface of steel AISI 1045 improves its fatigue endurance by 40 MPa [25].

Thus, the above experimental data demonstrate the possibility in principle to increase the strength properties of the alloy Ti-6Al-4V with ultrafine-grained structure at working temperatures (up to 400 °C) by applying a highly rigid and strong coating of the (Ti+V)N system through plasma-vacuum technique. At the same time, the approach requires a more profound study of fatigue behavior of the alloy, especially at elevated temperatures, resistance to creep and surface wear, thus making it the object of further research.

Such complex approach to strengthening of the alloy Ti-6Al-4V is promising for the production of essential parts of GTE such as compressor rotor blades, to which the exclusive requirements for resistance to fatigue and erosion are imposed upon.

5. CONCLUSIONS

1. The formation of the UFG structure with a mean grain/subgrain size of 260 μm in the alloy Ti-6Al-4V processed through ECAP and subsequent extrusion resulted in a higher strength of 30% at room temperature, and of no less than 15% at elevated temperatures up to 400 °C in comparison with the coarse-grained structure.
2. The coating (Ti+V)N deposited by the vacuum-plasma technique on the UFG alloy surface and constituting of two main layers with a total width of 5.5 μm has a very high hardness (over 13 GPa) and improved adhesive strength as against the CG alloy.
3. Mechanical tests of the UFG samples with and without coating at temperatures of 300, 350, and 400 °C demonstrated that the samples with coating exhibit a higher strength compared to the samples without coating, which is, apparently, related to the occurrence of the «barrier effect» in the near-surface layer of the metal close to the coating.

The results of this work reveal significant prospects for improving the service properties of Ti alloys through the formation of UFG structure by means of SPD processing and subsequent application of vacuum-plasma coatings on the surface.

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