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V.F. Bashev[1], O.E. Beletskaya[1], N.A. Korovina[2], N.A. Kutseva[1], A.A. Lysenko[1]

Influence of Rapid Cooling Methods by High-Energy Sources on a Phase Structure and Properties of Titanium Alloys

[1]*Dniepropetrovsk National University, ul. Nauchnaya 13, Dnepropetrovsk 49050 Ukraine,*
[2]*Dneprodzerdzginskii State Technical University, ul. Dneprostroevskaya 2, Dneprodzerdzginsk 51918 Ukraine*

The results of investigation of a phase structure and properties of serial titanium (α+β) alloys "BT3-1", "BT-8", "BT-16", treated by high-energy sources (HES) of electron-beam and laser radiation are presented. The cooling rates at laser processing were theoretically estimated and the thermal regimes of cooling in various melting zones were established. It was shown the products of martensitic transformation and titanium nitrides (Ti, Me)N (mainly) and $(Ti, Me)_2N$ forming in the upper horizons of laser-melted zone promote essential increase of microhardness in titanium alloys treated by HES.

Key words: electron-beam processing, laser processing, titanium alloys, cooling rate, quenching.

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The problems of processing, modifying and hardening of a material surface by high-energy sources are becoming more and more actual the last years. Therefore, further research of influence of rapid_cooling using HES on a phase structure, morphology and physical characteristics of constructional, serial titanium alloys is of considerable theoretical and applied importance. Laser (LP) and electron-beam processing (EBP) of a material surface are referred to the high-energy treatment.

The aim of this paper is to study effect of a chemical composition, processing methods and the rates of melt quenching on the phase composition and microhardness of rapidly cooled serial titanium alloys of the following initial composition (wt %): "BT3-1" (6% Al; 2,5% Mo; 2,0% Cr; 0,5% Fe; 0,25% Si); "BT-8" (6,5%Al; 3,3%Mo; 0,3%Fe; 0,5%Zr); "BT-16" (8,0%Al; 11,0%Zr; 1,0%Nb; 0,6%Mo; 0,15%Fe; 0,11%Si).

Titanium, similarly to iron, is a polymorphic metal: the hexagonal close-packed crystalline lattice α-Ti is stable up to 1155 K, the base-centered lattice β-Ti is stable above this temperature. Titanium and its alloys, as a rule, have increased corrosion resistance up to temperatures $\leq$ 873 K. All investigated alloys are related to α+β – alloys type, which are most suitable for practical application owing to realization of non-diffusional (martensitic) $\beta \rightarrow \alpha'$ transformation in conditions of reaching the critical cooling rates.

The industrial electron-beam plant (EBP) for processing of material surface in vacuum (at accelerating voltage 21,5 kV; electron beam currents 6 mA and 20 mA) and optical quantum generator "ГОС-1001" (LP) on neodymium glass working in a mode of free generation with the 3-rd multiple melting of material surface was used. The energy of pumping was 20 kJ, diameter of focusing spot was 16 mm.

The samples were examined by following methods: the X-ray diffraction (XRD) using a DRON-2.0 diffractometer with monochromatized copper K_α radiation, the measurement of microhardness using a "ПМТ-3" hardometer, the optical microscopy using a NEOPHOT-21 metallographic microscope. The lattice parameters of obtained phases were determined with an accuracy of $\pm$ 0,0002 nm, and the microhardness was determined with an accuracy of $\pm$ 100 MPa.

The dislocation density (ρ) in quenched samples was estimated by the formula [2]:

$$\rho\ [cm^{-2}] = A \cdot \beta^2, \qquad (1),$$

where β – is the integral width of x-ray (012) α-Ti line, A- is the factor for metals with a cubic lattice equal to about $2 \cdot 10^{16}$ cm^{-2}.

The formation of complex (Ti, Me)N nitride (table 1) follows from the reduced values of its crystalline lattice parameter in comparison with the lattice parameter of pure titanium nitride (a = 0,4232 nm). The reason can be connected with possible stehiometry deviation of nitride to the region depleted by nitrogen during obtaining of samples. It also can be connected with substitution of some part of titanium atoms by atoms of alloying elements as a rule with smaller nuclear radiuses in comparison with titanium atom [3].

First, in order to research the effect of melt-quenching by HES methods all samples were undergone the water quenching from solid state (from temperature of 1143 K). Then they were melt-quenched after melting

Table 1

Phase composition of the surface layers in titanium alloys, treated by HES

alloy	quenching from 1143 K	EBP (U=21,5 kV, I=20 мA)	LP (W=20 kJ)
"BT3-1"	α (a=0,2918 nm; c=0,4657 nm)+ 26% β (a=0,3255 nm)	α (a=0,2930 nm; c=0,4681 nm) +α' (a=0,2968 nm; c=0,4730 nm) +(<7%) β (a=3,201 nm)	α (a=0,2919 nm; c=0,4642 nm)+ α' (a=0,2938 nm, c=0,4675 nm)+ (<3%) β (a=3,201 nm)+ *(Ti, Me)N* (a=0,4228 nm)+ *(Ti, Me)$_2$N* traces
"BT-8"	α (a=0,2918 nm; c=0,4664 nm)+ 29% β (a=0,3260 nm)	α (a=0,2920 nm; c=0,4692 nm)+ α'(a=0,2928 nm; c=0,4834 nm)+ (11%) β (a=0,3236 nm)	α (a=0,2916 nm; c=0,4634 nm)+ α′ (a=0,2937 nm; c=0,4669 nm)+ (<3%)β (a=0,3230 nm)+ *(Ti, Me)N* (a=0,4220 nm)+ *(Ti, Me)$_2$N* traces
"BT-16"	α (a=0,2918 nm; c=0,4639 nm)+ (<7%) β (a=0,3250 nm)	α (a=0,2921 nm; c=0,4670 nm)+ α' (a=0,2928 nm; c=0,4681 nm)+ (<4%) β (a=0,3215 nm)	α (a=0,2918 nm; c=0,4664 nm)+ α' (a=0,2941 nm, c=0,4716 nm)+ (<3%)β (a=0,3230 nm)+ *(Ti, Me)N* (a=0,4210 nm)+ *(Ti, Me)$_2$N* traces

Notes: 1) α′ - is the metastable phase of a martensitic type with a hexagonal crystalline lattice; 2) (Ti, Me)N, (Ti, Me)$_2$N, - are the titanium nitrides, Me-alloying elements which are included in the composition of investigated samples.

of the local places on the titanium alloy surface by the mentioned above HES sources. The surface layers of rapidly melt-quenched titanium alloys were researched by the X-ray phase analysis. The results are given in the table 1. The X-ray layerwise analysis shows, that after EB-processing the titanium nitride with fine-grained structure places on the uppermost horizon. Under titanium nitride there is a narrow interlayer of (Ti_2N) nitride. It is indicated by very low integral intensity of (Ti_2N) lines on the X-ray diffraction pattern.

The quantity of residual β- phase was estimated by the experimentally established formula [1]:

$$\beta(\%) = \frac{100\%}{1 + 2{,}33(I_\alpha / I_\beta)}, \qquad (2)$$

where I_α, I_β – are the integral intensity of (012) α-Ti and (200) β-Ti x-ray lines respectively. The X-ray phase analysis has shown that after melt-quenching from 1143 K the samples of investigated titanium alloys contain the solid solutions based on α- and β- titanium modifications. The residual β- phase quantity in alloys "BT3-1", "BT-8" and "BT-16" reaches 26 %, 29 % and 7%, respectively.

Experimental results and discussion

1. The cooling rate evaluation of titanium alloys during laser processing.

The modeling of melt-quenching process at laser treatment of surface was carried out by the solution of a thermal equation for a semi-infinite plate using a numerical grid method. Fourier heat conduction equation was applied as follows:

$$C\rho\frac{\partial T}{\partial t} = \lambda\frac{\partial^2 T}{\partial t} + \rho L\frac{\partial \psi}{\partial t} \qquad (3),$$

where T, t, z – are the instant values of temperature, time, coordinate in a direction of a heat rejection; ψ – is the volume share of a liquid phase; C, ρ, λ, L – are the specific heat, density, thermal conductivity, specific heat of melting for Ti, accordingly.

The heat-physical characteristics of titanium are taken from [3]. The dynamics of cooling process in the laser-treated zone was investigated using worked out algorithm. The results of modeling are presented on fig. 1. Therefore it is possible to conclude, that all three layers are cooled in different regimes at initial instant of time: for example, the cooling rate (V_{cool}) of the central layer is less approximately on the order, than V_{cool} of the surface layer. The cooling rates of layers decrease with time. The tendency of transition of all melt volume in stage of regular cooling regime is observed at the end of process. It should pay attention to a specific feature of heating curve of surface layer, where the melting process of the laser-treated zone is exhibited as a fall on the curve T(t). This feature is probably due to the larger magnitude

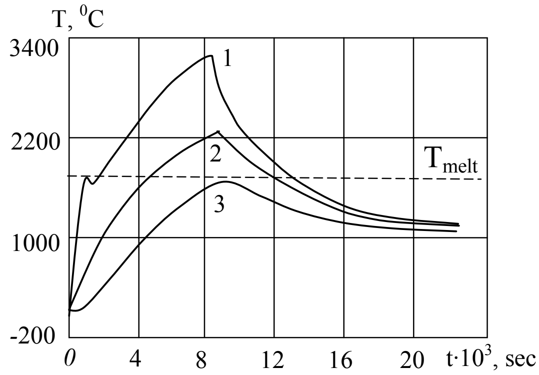


Fig. 1. Model curves of heating-cooling for titanium semi-infinite plate with maximum (specific power of laser impulse q=0,36·10^9 W/m^2) depth of melting:
1 – surface of melting zone;
2 – centre of zone;
3 – boundary of melting.

of specific titanium heat (~ 990 J/kg·K) than of other metal one.

The cooling rate estimation of the central layer of the melted titanium after laser impulse stopping was performed. The V_{cool} cooling rate reaches values from $3{\cdot}10^6$ up to $4{\cdot}10^5$ K/sec depending on melting depth (from 10 up to100 mu) (fig. 2). Therefore using obtained plot the cooling rates of Ti alloys can be estimated by melting depth magnitude (h). It also follows from fig. 2 that the cooling rates of melt achieved during laser processing, considerably exceed those critical V_{cool} (~ 950…1000 K/sec), which are necessary for realization of shift martensitic β→α′ transformation. Morphological evaluations of quenched structure show that the cooling rates of melt during electron-beam processing are smaller than during laser processing of titanium alloy surface. At laser processing the heating and melting of radiation zone are performed only during laser impulse influence. At electron-beam processing the continuous heating and melting of treated zone spreads in direct of electron beam passing. In this case each previous subzone is under influence of two opposite factors: on the one hand the material zone adjoining with thermally untreated surface is cooled intensively; on the other hand it is heated constantly from the side of following subzone which is still under electron beam influence. As a result the cooling rate of the whole melted zone naturally decreases on about of 25 % during electron-beam processing in comparison with laser treatment.

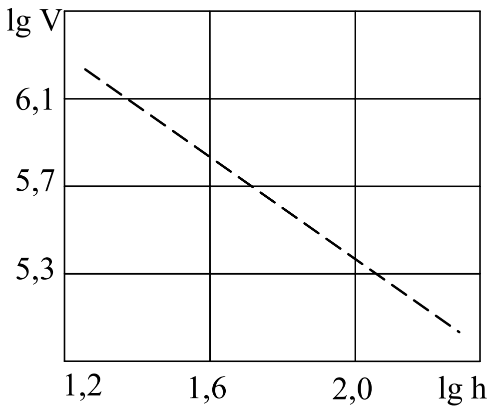


Fig. 2. The calculated cooling rate in central layer as a function of the melting depth of titanium sample at laser processing.

2. Phase transformations during processing of Ti-alloys by high-energy sources.

Research of influence of a structure and solid quenching from 1143 K has shown (tab.1), that the residual β-phase contents in alloys with the increased β-stabilizers amount is in an interval 25-30 %, and this one in "BT-16" alloy does not exceed 7%. This result corresponds to the established mechanism of forming of metastable phases during quenching of titanium alloys. According to this mechanism Ti-alloys can contain also residual β-phase simultaneously with martensitic α′-phase at cooling rates close to critical rates [1].

As experiments have shown the melt quenching of these alloys by EB and laser method allows changing purposefully the residual β-phase contents. Thus quantity of β-phase in alloys treated by electron-beam essentially decreases in comparison with alloys subjected quenching from 1143 K. The β-phase amount in these alloys after laser processing does not exceed 3-4 % and is already on the threshold sensitivity of the XRD method (table 1). The completeness of martensitic transformation passing directly influences on dislocation density in melt-quenched samples (and on microdistortion values, accordingly) and promotes the essential increase of microhardness in treated surface layers (tables 2, 3).

Table 2

Average microhardness of treated Ti-alloys, MPa

state	"BT3-1"	"BT-8"	"BT-16"
quenching, 1143 K	3600	3600	3500
LP	5800	6100	6100
EBP	5000	5100	5100

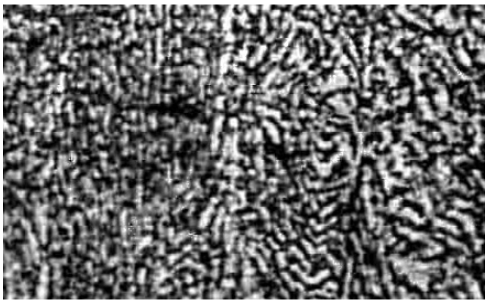
Table 3

Dislocation density in quenched Ti-alloys, cm^{-2}

state	"BT3-1"	"BT-8"	"BT-16"
quenching, 1143 K	$2{\cdot}10^{12}$	$3{\cdot}10^{12}$	$0{,}6{\cdot}10^{12}$
LP	$5{,}4{\cdot}10^{12}$	$8{\cdot}10^{12}$	$5{\cdot}10^{12}$
EBP	$3{,}8{\cdot}10^{12}$	$4{,}3{\cdot}10^{12}$	$3{,}6{\cdot}10^{12}$

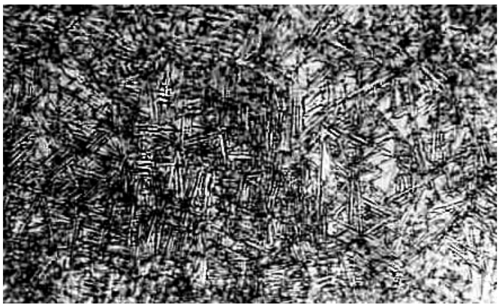
The changes of phase composition in laser-treated surface layers are accompanied by increase of microhardness ($H_μ$) as approaching to the surface horizon of melted zone. The magnitude of microhardness increases by a factor of about 1,7 in comparison with properties of quenched titanium alloys from 1143 K. The maximum values ($H_μ$) were fixed on the sample faces in uppermost horizons of zone treated by laser in the air. They reach values of 8700, 9200, 9000 MPa for "BT3-1", "BT-8", "BT-16" alloys respectively at the 50 g mass load. It connected with formation of titanium nitride layer as a reinforcing phase (microhardness of pure TiN is about 12000 MPa), fig. 3. The reduced $H_μ$ magnitudes (table 2) are explained by insignificant (50…60 microns) thickness of laser-treated layer. Microhardness was measured on the section from the upper horizons of melted zone to the matrix material. During testing the diamond pyramidion of microhardometer partially seizes zones with the continuously reducing contents of (Ti, Me)N, $(Ti, Me)_2N$ nitrides and martensitic phase of nitrogen solid solution in titanium. Thus the gradual decreasing of dislocation density and degree of lattice distortion (fig. 4) is observed. Note that using HES-methods does not allow fixing the formation of Ti_3N nitrides and TiC carbides in the composition of forming phase in comparison with impulse-plasma processing [5]. It is probably due to the presence of oxygen and the high diffusion rate of saturating nitrogen element which is determined by very high temperature in laser-radiated zone.

The research of morphology has shown (fig. 3b), that more fine-dispersed two-phase mixture is fixed in "BT3-1" alloy microstructure after quenching from 1143 K in

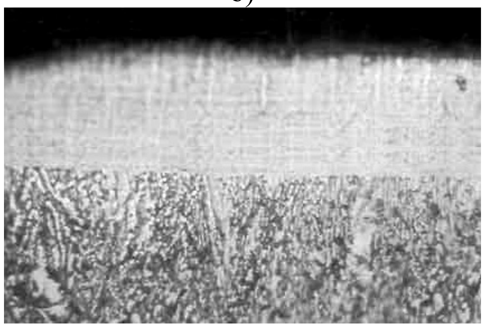


a)

b)



c)



d)

Fig. 3. Typical changes of "BT3-1" alloy morphology after different processing, (x500):

a) initial cast state (light segments –are the α-phase, dark segments – are the mixture of (α+β) - phases;
b) quenching from 1143 K;
c) electron-beam processing;
d) laser processing (light unetching stripe- is the titanium nitride (Ti, Me)N with narrow interlayer of $(Ti, Me)_2N$ nitride located under.

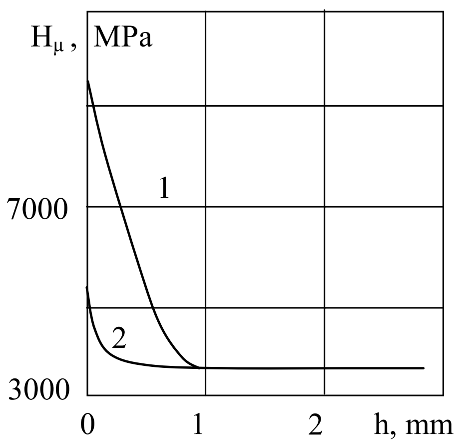


Fig. 4. Evolution of microhardness H_μ for "BT-16" alloy as a function of melting depth after treatment by laser (1) and electron beam (2).

comparison with initial (α + β) state (fig. 3a). The electron-beam processing promotes formation of metastable needle-shaped structure, which hinders shift processes, reduces plastic properties of alloy and essentially increases microhardness (fig. 3c). The greatest effect of influence of increased cooling rates on structure and properties of "BT3-1" alloy was fixed using laser processing of surface. In this case the fine-grained unetching layer is formed on the upper horizons of laser-treated surface. As XRD analysis shows this layer consists of mono- and heminitrides of titanium, which adjoin to the structure as needle-shaped (degenerated) dendrites of martensitic phase (fig. 3d). At laser processing the arising high cooling rates do not arrange the conditions for normal nucleation and growth of dendrites with higher order branches. The similar microstructure changes take place for "BT-8" and "BT-16" titanium alloys during HES-processing.

The obtained data evidence that laser melting in environmental air is more perspective technology than EB-treatment. Laser method has advantages for creating of wear-resistant and corrosion-resistant surface layers in products from serial titanium alloys without essential change of initial material plasticity.

Conclusions

1. Using Fourier heat conduction equation the temperature regimes of cooling in melting zones during laser processing are analyzed. It is established that in this case the cooling rates considerably exceed critical rates necessary for realization of martensitic $\beta \rightarrow \alpha'$ transformation in titanium alloys.

2. At heat treatment the laser method is more effective than electron-beam processing owing to formation of hard, wear-resistant surface layers consisting of titanium nitrides during laser melting in environmental air.

3. Using increased cooling rates of titanium alloy surface it is possible to adjust purposefully a completeness degree of martensitic transformation passing and microhardness values in treated surfaces of serial titanium alloys with abiding high plasticity in initial material.

Башев В.Ф. – доктор фізико-математичних наук, професор, завідувач кафедри металофізики;
Білецька О.Є. – аспірант кафедри металофізики;
Коровина Н.О. – аспірант кафедри твердого тіла;
Куцева Н.О. – кандидат фізико-математичних наук, асистент кафедри металофізики;
Лисенко О.О. – студентка 5 курсу кафедри металофізики.

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В.Ф. Башев[1], О.Е. Белецька[1], Н.А. Коровіна[2], Н.А. Куцева[1], А.А. Лисенко[1]

Вплив методів швидкого охолодження високо енергетичними джерелами на фазову структуру і властивості титанових сплавів

[1]Дніпропетровський національний університет, вул. Наукова, 13, Дніпропетровськ, 49050, Україна,
[2]Дніпродзержинський національний технічний університет, вул. Дніпропетровська, 2, Дніпродзержинськ, 51918, Україна

Представлено результати експериментів по фазовому складу та властивостям серійних титанових (α + β) сплавів ВТ3-1, ВТ-8, ВТ-16, оброблених високоенергетичними джерелами (ВЕД) електронно-променевого та лазерного випромінювання. Теоретично оцінено швидкості охолодження при лазерній обробці та встановлено теплові режими охолодження різних зон оплавлення. Показано, що продукти мартенситного перетворення та нітриди титану (Ti, Me)N (переважно) і (Ti, Me)2N, які утворюються у верхніх горизонтах оплавленої лазером зони, сприяють значному підвищенню мікротвердості оброблених ВЕД титанових сплавів.