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Modification of the surface layer of the system coating (TiCuN)/substrate (A7) by an intensive electron beam

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Abstract. In order to study the conditions of modification of the surface layer of the system coating (TiCuN)/substrate (A7) an analysis of processes occurring in the surface layer of the system wear-resistant coating/substrate irradiated by an intensive pulsed electron beam at a submillisecond exposure time has been carried out on the example of aluminum and titanium nitride. Irradiation has been carried out under conditions ensuring melting and crystallization of the surface layer of the material by a nonequilibrium phase diagram. It has been experimentally established that irradiation of the system coating (TiCuN)/substrate (A7) by an intensive electron beam is accompanied by changes in the phase composition of the material. It is evident that nanostructuring of the aluminum layer adjacent to the coating, and formation in it of nitride phase particles will contribute to hardening of the surface layer of the material, creating a transition sublayer between a solid coating and a relatively soft volume. The carried out analysis shows that binary nitrides based on TiN_{1-x} are most likely to form under nonequilibrium conditions, since the homogeneity range of this compound is rather large. On the other hand, formation of the ternary compound Ti_3CuN , which can be formed after an arc plasma-assisted deposition of titanium nitride of the composition TiCuN and by the subsequent intensive pulsed electron beam exposure, cannot be excluded.

1. Introduction

In most cases, surface properties of materials and products define the life of machines, mechanisms, and aggregates in general. Thus, formation of coatings for various purposes on the surface of the material allows to significantly improve physicochemical and performance properties of products, not significantly changing properties of the volume of the part, as well as its size and shape [1]. The necessary condition for performance of the system coating/substrate is a high level of adhesion forces achieved using various methods. One such method is the irradiation of the system coating/substrate by an intensive pulsed electron beam for the purpose of melting the coating into the substrate [2]. As compared to the widespread laser technology, the electron-beam technology has great potential in monitoring and controlling of the amount of input energy, differs in the locality of energy distribution in the near-surface layer of the processed material, and a high efficiency coefficient [3–5]. Ultra high rates ($10^8 - 10^{10}$ K/s) of heating up to melting temperatures and the subsequent cooling of the thin



near-surface layer of the material ($10^{-7} - 10^{-6}$ m), a very small ($10^{-6} - 10^{-3}$ s) exposure time to high temperatures, formation of limiting temperature gradients (up to $10^7 - 10^8$ K/m) that provide cooling of the near-surface layer due to heat dissipation into an integrally cold volume of the material at a rate of $10^4 - 10^9$ K/s, create conditions for formation in the near-surface layer of an amorphous, nano- and submicrocrystalline structure. The purpose of this work is to analyze the processes occurring during modification of the surface layer of a wear-resistant coating/substrate irradiated by an intensive pulsed electron beam with a submillisecond exposure time.

2. Materials and methods of study

Commercially pure aluminum of the brand A7 was chosen as the modified material [6]. Titanium nitride was chosen as the wear-resistant hard coating. Electric-arc plasma-assisted deposition of titanium nitride of the composition TiCuN was carried out using the installation "KVINTA" (ISE SB RAS). The thickness of the coating was $\approx 0,5$ μm . The high-speed heat treatment under the mode of the surface layer melting was carried out by an intensive pulsed electron beam (installation SOLO, ISE SB RAS), varying the energy density of the electron beam in the range of 10 J/cm^2 up to 30 J/cm^2 ; the pulse duration of the electron beam exposure was (50–200) μs ; the pulse count was 3–5. The study of the phase and elemental composition, the defect substructure of the surface layer were carried out using methods of optical and scanning electron microscopy and X-ray diffraction analysis.

3. Model representation and evaluation

Numerical evaluations of the range of energy parameters of irradiation by an intensive pulsed electron beam of aluminum samples of the solid coating TiN ensuring melting and crystallization of the surface layer of the material by a non-equilibrium phase diagram with formation of a multiphase structure have been carried out: (1) temperature profiles of preheating of the surface layer of aluminum and the coating TiN, depending on the energy density of the electron beam and the duration of irradiation; (2) a comparative analysis of the calculated temperature profiles has been carried out, and an evaluation of the range of optimal values of irradiation parameters has been carried out for processing samples of aluminum and the system coating (TiN)/substrate (aluminum).

The problem of finding the temperature field in a certain range of the energy density of the electron beam is reduced to solving the heat equation. A one-dimensional case of heating and cooling of a plate with a thickness d is considered. The coordinate system is chosen so that the x axis is directed depth ward the sample. At $x = 0$ a heat flux is set, but on the back side of the plate the heat transfer is absent. In the coordinate form the heat equation takes the following form (1):

$$c\rho \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2}. \quad (1)$$

where c is the specific heat, ρ is the density, and λ is the thermal conductivity of the material.

Boundary conditions for the pulsed electron beam exposure have the form:

$$-\lambda \frac{\partial T}{\partial x} = q(t) \quad (2)$$

where the heat flux works its way depth ward the sample from the surface in the following form:

$$q(t) = \begin{cases} q_0, & 0 < t \leq t_0; \\ 0, & t > t_0. \end{cases} \quad (3)$$

where q_0 is the average value of the heat flux during the exposure time by the electron beam t_0 . The initial temperature $T(0, x) = T_0$ throughout the depth of the sample $0 < x < d$.

For numerical solution of the problem the difference grid in increments τ in time was used: $t_j = j\tau$ and in increments h in space: $x_i = ih$, where j is the number of the layer in time, i is the number of the layer in space. The temperature value is determined in grid points. Approximation of the differential equation of heat conductivity with the first order in time and the second in space is used, an explicit scheme is chosen:

$$T_{j+1,i} = T_{j,i} + \frac{\tau(T_{j,i+1} - 2T_{j,i} + T_{j,i-1}))}{c\rho h^2} \quad (4)$$

Based on the numerical solution of the heat equation the modeling of temperature fields during the electron-beam treatment of aluminum sample surfaces was carried out. Calculations were performed for an intensive electron beam with an energy density in the range from 5 J/cm² up to 40 J/cm², and a pulse duration of 50, 100, 150, and 200 μ s. The thickness of the surface layer for thermal calculations $d = 10^{-3}$ m, the observation time 300 μ s.

Accounting of melting and vaporization of the material was carried out from the following physical considerations [3]. When the cell reached the melting temperature T_m , its temperature was fixed and assumed equal to the melting temperature, and all the input heat

$$q = \frac{(T_{j,i} - T_m)c}{q_m} \quad (5)$$

where $T_{j,i}$ is the cell temperature, was supposed to go towards melting of the sample; $q = 1$ means transition of the substance into a liquid state. The crystallization process was simulated in the same manner, only the value q was decreased from 1 to 0. The process of vaporization and condensation was simulated similarly. When the cell reached the boiling point T_{boil} the temperature of the cell was fixed and assumed equal to the boiling point, and all the input heat

$$q = \frac{(T_{j,i} - T_{kum})c}{q_{kum}} \quad (6)$$

goes towards vaporization of the substance; $q = 1$ indicates transition of the substance into vapor.

The numerical solution was carried out for thermophysical values of aluminum and titanium nitride given in the table 1.

Table 1. Thermophysical values of aluminum and titanium nitride, taken at $T = 800$ K [7-10] ^a.

E_s , J/cm ²	Thickness of the film, μ m	$V_3 \cdot 10^{-6}$, mm ³ /(N*m)	V_0/V	$\langle \mu \rangle$	$\langle \mu_0 \rangle / \langle \mu \rangle$
0,0 (initial A7)	0,0	7590		0.48	
15	0,5	6080	1,3	0.39	1,5
15	1,0	6570	1,4	0.40	1,2
20	0,5	5470	1,4	0.35	1,4
20	1,0	4790	1,6	0.31	1,6

^a λ is the coefficient of thermal conductivity, c_{av} is the specific heat, ρ is the density, T_m is the melting temperature, T_{vap} is the vaporization temperature, q_m is the melting heat, q_{vap} is the vaporization heat.

The thickness of the vaporized layer of titanium nitride of the composition TiN was evaluated using the formula (7):

$$H = V_{ucn} \cdot t / \rho \quad (7)$$

where V_{vap} is the vaporization rate of the titanium nitride film equal to 1.168 10^{-5} g/(cm sec) at a temperature of 1987 K and 54.589 g/(cm sec) at a temperature of 2241 K [10], ρ is the density of

titanium nitride, t is the time during which the temperature on the surface of the titanium nitride film, or on the surface of aluminum on which the film is deposited, is not lower than 1987 K.

The calculation results of the condition of the studied materials are presented in Figure 1 – Figure 3. It has been established that the melting temperature of the aluminum surface is achieved at $E_s = 18 \text{ J/cm}^2$ for $t_0 = 150 \text{ } \mu\text{s}$ (Figure 1, curve 1) and $E_s = 15 \text{ J/cm}^2$ for $t_0 = 100 \text{ } \mu\text{s}$ (Figure 1, b, curve 1). The melting point of titanium nitride of the composition TiN under the specified in the work parameters of the electron beam has not been reached (Figure 1, curve 2); melting of titanium nitride with the composition $\text{TiN}_{0.84}$ is observed only at the density of the beam energy of 30 J/cm^2 with a pulse duration of $100 \text{ } \mu\text{s}$ (Figure 1b, curve 3). The maximum heating temperature of the aluminum surface (Figure 1, curve 1), attained at completion of pulse exposure, is always lower than of titanium nitride of both compositions (Figure 1).

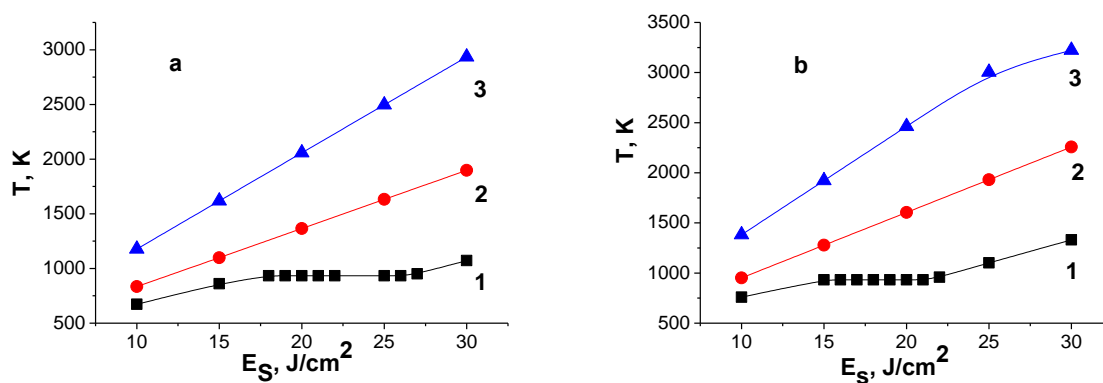


Figure 1. The dependence of the maximum heating temperature (considering melting and vaporization of the material) of the aluminum surface (curve 1) and titanium nitride of compositions TiCuN (curve 2) and $\text{TiN}_{0.84}$ (curve 3) irradiated by an electron beam on the density of the beam energy;

a – $t_0 = 150 \text{ } \mu\text{s}$, b – $t_0 = 100 \text{ } \mu\text{s}$

Thus, irradiation of the system coating/substrate will lead to formation of thermoelastic stresses. The difference in heating temperatures ΔT for titanium nitride is 300 K under the energy density of the electron beam $E_s = 10 \text{ J/cm}^2$ and 1000 K under $E_s = 30 \text{ J/cm}^2$ for $t_0 = 150 \text{ } \mu\text{s}$ (Figure 1, a) and a small difference for $t_0 = 100 \text{ } \mu\text{s}$ (Figure 1, b).

It is expected that the value of thermoelastic stresses in the system coating/substrate may decrease during formation of a certain transition layer comprising a liquid phase (the two-phase condition melt – solid body). Figure 2 represents the results showing that such a two-phase layer under the pulse length of the electron beam $t_0 = 100 \text{ } \mu\text{s}$ begins to form at the electron beam energy density of 15 J/cm^2 (the lifetime of such a condition $\Delta t = 6 \text{ } \mu\text{s}$ (Figure 3, curve 1)); for $t_0 = 150 \text{ } \mu\text{s}$ – at 18 J/cm^2 ($\Delta t = 7 \text{ } \mu\text{s}$ (Figure 3, curve 2)). A single-phase transition layer (liquid phase) (Figure 2, b) begins to form at the electron beam energy density of 23 J/cm^2 for $t_0 = 100 \text{ } \mu\text{s}$ ($\Delta t = 6 \text{ } \mu\text{s}$ (Figure 3, b, curve 1)) and at 28 J/cm^2 for $t_0 = 150 \text{ } \mu\text{s}$ ($\Delta t = 10 \text{ } \mu\text{s}$ (Figure 3, b, curve 2)).

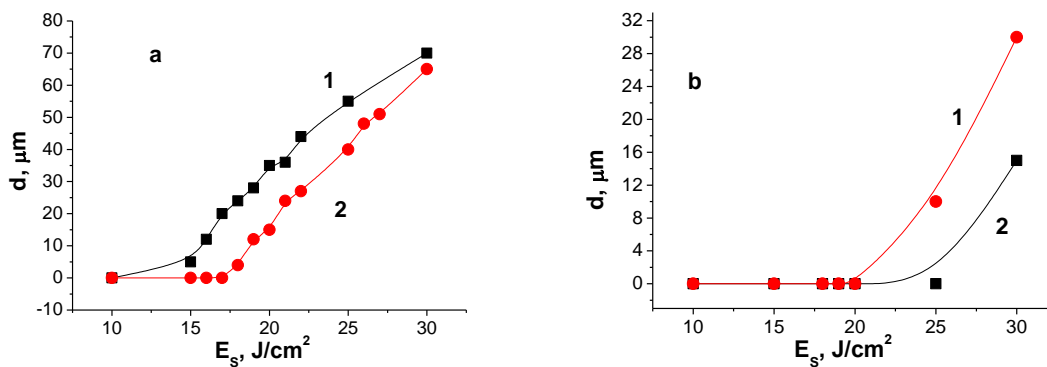


Figure 2. The dependence of the maximum thickness of the layer of the two-phase range (liquid solid + solid phase) d (a) and the melt layer d (b) on the surface of titanium on the energy density of the electron beam E_s at the exposure time of the beam 100 μs (curve 1) and 150 μs (curve 2).

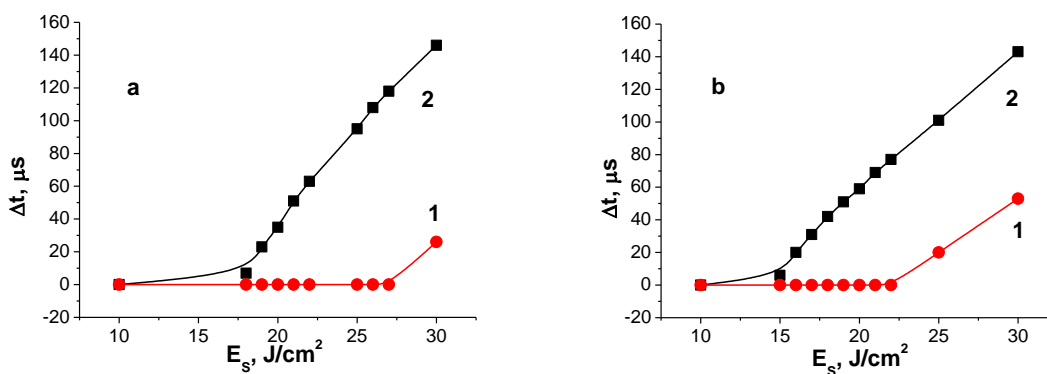


Figure 3. The dependence of the lifetime of the two-phase condition (liquid + solid phase) (curve 2) and the melt (curve 1) on the surface of aluminum on the energy density of the electron beam at the exposure time of the electron beam of 150 μs (a) and 100 μs (b).

Thus, the carried out numerical evaluations of the range of energy parameters of irradiation by an intense pulsed electron beam of the surface of aluminum and titanium nitride providing for melting and crystallization of the surface layer of the material by a non-equilibrium phase diagram allowed to construct temperature profiles of heating of the surface layer of aluminum depending on the energy density of the electron beam and the duration of irradiation pulses; to carry out a comparative analysis of the calculated temperature profiles; to assess the values of irradiation parameters of aluminum samples and the coating TiN.

4. Experimental results and their discussion

Irradiation of the system coating (TiCuN)/substrate (A7) by an intensive electron beam, as shown by thermal calculations, allows both to melt the coating into the substrate for improvement of adhesion forces and to destruct the coating (to remove the coating worn out during the operation of the part). Figure 4 shows the analysis results of the structure of the system coating (TiCuN)/substrate (A7), treated by an intensive electron beam in the mode of coating destruction. The coating is fragmented by a system of microcracks, delamination of the coating from the substrate is revealed. Melting of the coating into the substrate is not detected.

The carried out calculations show that the cooling rate of the surface layer of aluminum subjected to a pulsed electron beam irradiation at the energy density of $(10\text{--}30)\text{ J/cm}^2$, varies in the range of $(2,7\text{--}8,1)\cdot 10^8\text{ K/s}$ during the electron beam pulse duration of $50\text{ }\mu\text{s}$ and $(0,7\text{--}2,1)\cdot 10^8\text{ K/s}$ during the electron beam pulse duration of $200\text{ }\mu\text{s}$. Thus, formation of a nanoscale substructure in the surface layer of aluminum can be expected. Indeed, the studies carried out using electron microscopy methods revealed in the surface layer of aluminum, treated by an intensive electron beam (20 J/cm^2 , $50\text{ }\mu\text{s}$, 3 pulses, $0,3\text{ s}^{-1}$), a structure with sizes of crystallites varying in the range of $(60\text{...}100)\text{ nm}$ (Figure 4, *d*, inset).

Irradiation of the system coating (TiCuN)/substrate (A7) by an intensive electron beam is accompanied by changes in the phase composition of the material. The studies carried out using X-ray analysis revealed formation in the system coating (TiCuN)/substrate (A7) of aluminum nitrides AlN, the volume fraction of which, depending on parameters of the electron beam, varies from 2 % up to 16 %. It is obvious that nanostructuring of the aluminum layer adjacent to the coating and formation in it of the nitride phase particles will contribute to hardening of the surface layer of the material, creating a transition sublayer between a solid coating and a relatively soft volume.

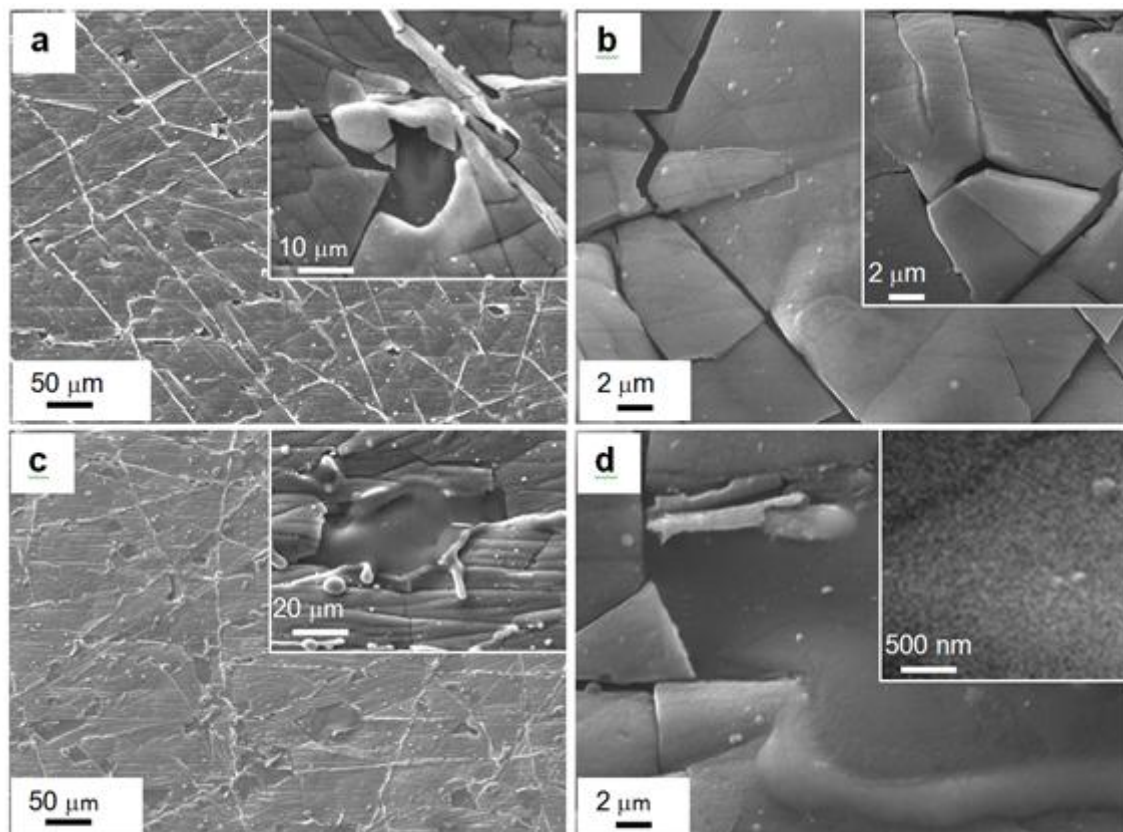


Figure 4. The electron microscopic image of the surface of the system coating (TiCuN)/substrate (A7) treated by an intensive electron beam: a, b – 20 J/cm^2 , $200\text{ }\mu\text{s}$, 3 pulses; c, d – 20 J/cm^2 , $50\text{ }\mu\text{s}$, 3 pulses.

In the system Cu–Ti–N titanium belongs to transition metals [11, 12]. Titanium is in the middle portion in the row of electronegative metals, and formation of limited solid solutions and compounds with many elements is characteristic to it. For copper the value of electronegativity is located at the boundary between transition metals and electronegative metals (Zn, Cd, Al, Be). This ensures that copper equally well forms solid solutions and compounds with other elements. Formation of six

intermetallic compounds takes place at melting of titanium with copper, two of which melt congruently (Figure 5) [13]: γ -CuTi₂ (prototype MoSi₂, Pearson symbol *tI6*, space group *I4/mmm*) at a temperature of 1010 °C and δ -CuTi (CuTi, *tP4*, *P4nmm*) – at 984 °C. Four other compounds: β -Cu₄Ti (ZrAu₄, *oP20*, *Pnna*), α -Cu₄Ti (MoNi₄, *tI10*, *I4/m*), λ -Cu₂Ti (VAu₂, *oC12*, *Amm2*), Θ -Cu₃Ti₂ (Cu₃Ti₂, *tP10*, *P4/mmn*) and ϵ -Cu₄Ti₃ (Cu₄Ti₃, *tI4*, *I4/mmm*) are formed by peritectic reactions [13]. Compounds λ and Θ exist in narrow temperature ranges and decomposition by eutectoid reactions. Compounds ζ , ϵ , δ and γ have narrow homogeneity ranges in composition. In addition, a number of studies revealed the existence of the compound Cu₇Ti₃, which melts congruently at a temperature of 905 °C, but at a temperature of 865 °C decompositions by eutectoid reaction on Cu₇Ti₂ and Cu₃Ti₂ (Figure 5).

The third element of the system Cu–Ti–N, nitrogen, is significantly different in chemical properties from metals forming this compound. Nitrogen with transition metals can form compounds with an ordered structure.

Nitride TiN_{1-x} has a cubic structure B1 (prototype NaCl, Pearson symbol *cF8*, space group *Fm3m*). Compound TiN_{1-x} belongs to the class of disordered nonstoichiometric nitrides with a wide range of homogeneity (Figure 5) [14]. In compound TiN_{1-x} atoms of Ti form a FCC metal sublattice, the octahedral interstices of which may contain interstitial atoms N or vacancies. Retention of the type of the crystal structure of a nonstoichiometric disordered compound when changing the concentration of structural vacancies determines the presence of the homogeneity range. The homogeneity range of the binary compound TiN_{1-x} is wide.

The condition diagram of the system Cu–N has not been found in the literature. It is known that there are two nitrides based on copper: CuN₃ with a cubic system (prototype ReO₃, *cP4* and space group *Pm3m*) with the lattice parameter $a=0,3814$ nm, and the compound Cu₃N with a tetragonal structure (*I4₁/a*) with lattice parameters $a=0,8653$ nm and $c=0,5594$ nm [14].

The ternary nitride system Cu–Ti–N is characterized by only one ternary compound Ti₃CuN (Pearson symbol *tP**) with lattice parameters $a=1,11968$, $c = 0,30217$ nm [15].

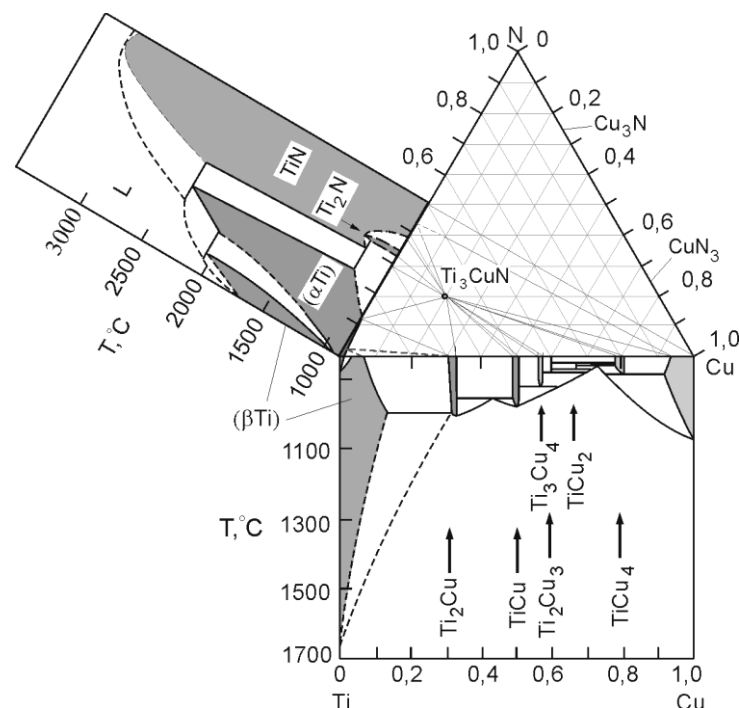


Figure 5. Binary diagrams of systems Cu–Ti, Cu–N, Ti–N [13], and an isothermal section of the ternary system Cu–Ti–N at 1000 °C [15]. Single-phase ranges on diagrams are highlighted in grey color.

Thus, the presented phase diagrams indicate that under nonequilibrium conditions formation of binary nitrides based on TiN_{1-x} is most likely to happen, since the homogeneity range of this compound is rather wide. On the other hand, it is impossible to exclude formation of the ternary compound Ti_3CuN which may be formed after an arc plasma-assisted deposition of titanium nitride of the composition TiCuN and the subsequent exposure to an intensive pulsed electron beam.

5. Conclusion

In order to study the conditions for modification of the surface layer of the system coating (TiCuN)/substrate (A7) by an intensive electron beam within the framework of a one-dimensional model the problem on finding the temperature field formed by irradiation of aluminum and titanium nitride by an intensive pulsed electron beam has been solved. Based on the numerical solution of the heat equation the modeling of temperature fields during the electron-beam treatment of sample surfaces has been carried out. The numerical solution has been carried out for thermophysical values of aluminum and titanium nitride. It has been shown that irradiation of the system coating/substrate will lead to formation of thermal stresses. The difference in heating temperatures ΔT for titanium nitride is 300 K at the electron beam energy density of $E_s = 10 \text{ J/cm}^2$ and 1000 K at $E_s = 30 \text{ J/cm}^2$ for $t_0 = 150 \mu\text{s}$ and rather big difference for $t_0 = 100 \mu\text{s}$.

It is expected that the value of thermoelastic stresses in the system coating/substrate may decrease during formation of the transition layer comprising a liquid phase (the two-phase condition melt – solid body). The presented results demonstrate that the two-phase layer at the pulse duration of the electron beam of $t_0 = 100 \mu\text{s}$ begins to form at the energy density of the electron beam of 15 J/cm^2 (the lifetime of such a condition is $\Delta t = 6 \mu\text{s}$); for $t_0 = 150 \mu\text{s}$ – at 18 J/cm^2 . The single phase transition layer (liquid phase) begins to form at the energy density of the electron beam of 23 J/cm^2 for $t_0 = 100 \mu\text{s}$ ($\Delta t = 6 \mu\text{s}$) and at 28 J/cm^2 for $t_0 = 150 \mu\text{s}$ ($\Delta t = 10 \mu\text{s}$).

It has been experimentally established that irradiation of the system coating (TiCuN)/substrate (A7) by an intensive electron beam is accompanied by changes in the phase composition of the material. The carried out studies using X-ray analysis revealed formation in the system coating (TiCuN)/substrate (A7) of aluminum nitrides AlN , the volume fraction of which, depending on parameters of the electron beam, varies from 2 % up to 16 %. It is obvious that nanostructuring of the aluminum layer, adjacent to the coating, and formation in it of the nitride phase particles will contribute to hardening of the surface layer of material, creating a transition sublayer between the solid coating and the relatively soft volume.

The carried out analysis shows that under nonequilibrium conditions the formation of binary nitrides based on TiN_{1-x} is most likely to happen, since the homogeneity range of this compound is rather wide. On the other hand, formation of the ternary compound Ti_3CuN , which can be formed after an arc plasma-assisted deposition of titanium nitride of the composition TiCuN and by the subsequent intensive pulsed electron beam exposure, cannot be excluded.

The ranges of irradiation parameters of the system coating (TiCuN)/substrate (A7) by a pulsed electron beam, allowing to destruct the coating by means of a fragile scabbing and to melt the coating into the substrate creating a transitional reinforced sublayer, have been established.

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