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Nanostructuring and Physical Properties of Metal-Ceramic Composites With a Different Content the Ceramic Components

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Abstract. A comparative analysis of the microstructure and durability of hard-alloy plates treated with high-energy pulsed electron beam generated from the plasma of argon or xenon in steel cutting was conducted. It is shown that the choice of the plasma gas to generate electron from the cathode plasma-filled setting for pulsed electron-beam irradiation has a significant influence on the formation of structural-phase state in the surface layer and the durability of hard-alloy plates in steel cutting.

1. Introduction

A generally accepted strategy in developing new methods for increasing the mechanical strength of metal-cutting hard-alloy plates is the improvement of the metal-ceramic structure of the plates to be achieved through a proper doping of metal binder and a proper choice of both the ceramic component and powder-mixture sintering conditions. The latest achievement in this field is the sintering of hard alloys from nano-powders forming the starting metal-ceramic composition. 3D-nanostructured hard alloys feature an enhanced mechanical strength, hardness, crack growth resistance, and wear resistance [1-3]. The main drawback of such alloys is their high cost, defined by the high cost of the nano-powder components of the metal-ceramic composition and by some specific features of the sintering technology; this drawback seriously hampers the use of the above strategy in national industry.

An alternative solution of the problem on improving the mechanical strength of metal-cutting hard-alloy plates produced in Russia is the hardening of the surface layer of the plates based on the concept of formation of a multi-level phase-structural state of the material in

micro-, submicro-, and nano-size regions. As it was shown in [3], the physics behind the formation of the multi-level alloy structure consists in realization of conditions permitting localization of plastic deformation in the material volume at the lowest possible scale of the internal structure. The latter in turn provides for a more uniform distribution of elastic stress in the material and increases the energy required for nucleation of critical stress concentrators. The above-said is of special significance for the discussion of the mechanisms of surface hardening of brittle materials such as hard alloys intended for applications in tools, in which the outer surface comes as a nucleation source of rupture microcracks.

A metal-ceramic alloy in the initial, as-sintered state involves three phase-structural-state levels: mesoscopic-scale particles of ceramic component with 1-10 μm sizes (carbides, carbonitrides, borides, etc.), interparticle metal-binder layers about 4 μm thick, and particle-binder transition zones of width ~1 μm (Fig. 1).

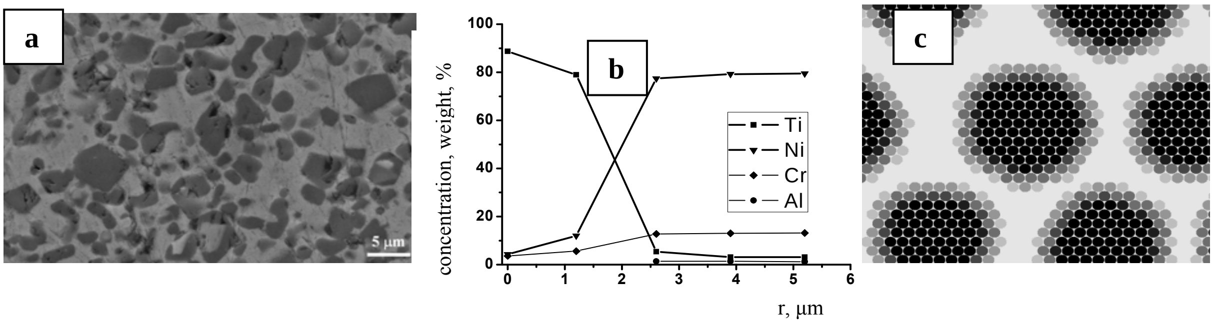

Fig. 1. The microstructure of the surface layer of 50 vol.%TiC – 50 vol.% (Ni-Cr) alloy (a); the distribution of the elemental composition of the metal-ceramic alloy at the interface between the carbide particles and the metal binder (b); and a computer model of the structure of the hard alloy with carbide particle-to-metal binder transition zones (c).

A numerical modeling of the effects due to individual phase-structural state levels on the strength of hard alloys under dynamic loading at a given volumetric proportion between the components of metal-ceramic composition has showed that, within the three-level structure, the mechanical strength of hard alloys is primarily defined by the mechanical strength and geometric sizes of the zone of transition from carbide particles to the metal binder: on increasing the strength and width of the transition regions within the actual range of parameters, a three-fold increase of the mechanical strength of hard alloys can only be achieved. In other words, the presently available possibilities in improving the material characteristics (physical, strength, and wear properties) of hard alloys with a metal-ceramic structure involving three levels of the phase-structural state by means of powder metallurgy (sintering of metal-ceramic powder compositions) are rather limited.

A cardinal improvement of the mechanical strength of traditional hard alloys is only possible via the formation of additional phase-structural-state levels in the metal binder of metal-ceramic compositions in submicro- and nano-size regions and via the dispersion of the particles of ceramic component down to nano-size state. An efficient method for such modification of the phase-structural state of the surface layer of hard alloys is the irradiation of the hard-alloy surface with a high-intensity, low energy electron beam with submillisecond duration of its action in plasma-forming gases with different values of ionization energy, which allows a cardinal modification of the structure of the surface layer several ten micrometer thick achieved through transferring the layer in a multimodal phase-structural state without any substantial modification of the phase-structural state of the material volume [4].

The purpose of this work was to study the laws of the formation of structural levels in the surface layers of the metal-ceramic composites with different ratios of the ceramic and metal components under pulsed electron-ion-plasma irradiated surface and influence the formation of additional structural levels of the physical properties of the surface layer of the composites.

2. Materials and methods of research

Studies were conducted on the sintered composite with a low content of ceramic component - 50% TiC / 50% (Ni + Cr + Al) and a high content of ceramic component - (75% WC + 14% (Ti, Ta, Nb) C) / 11 % Co. Pulsed electron-ion-plasma irradiation composite sample was performed at an energy density of the electron beam 20 ... 100 J / cm2 with a duration of irradiation pulses 50 ... 200 µs with a pulse repetition rate up to 10-1s. Irradiation was carried out in inert gas discharge plasma (argon, xenon) and reactive (nitrogen) gas.

The microstructure of the surface of a solid alloy after electron beam treatment was investigated in the scanning electron microscope SEM-515 «Philips» with energy-top box for the local elemental analysis EDAX ECON IV. Investigations of the phase composition and defect substructure was carried out with an electron microscope «Jeol - 200", phase composition was analyzed by indexing mikroelektronogramm using standard techniques of electronic diffraction microscopy.

Results and Discussion

It was found that, during pulsed electron-beam irradiation of hard alloys with a high content of metal binder in the metal-ceramic composition (50.0 vol.%TiC-50.0 vol.% (Ni-Cr)-alloy) in Ar-containing gas-discharge plasma (ionization energy of Ar 1519.6 kJ/mole), in the metal binder of the hard-alloy surface layer, as a result of the decay of the titanium-carbon solid solution, in the binder solution secondary titanium carbide particles with sizes down to 200 nm, which form the fourth phase-structural-state level, appear. Similarly, during pulsed electron-beam irradiation of the alloy in (Ar+N)-containing gas-discharge plasma (ionization energy of N 1401.5 kJ/mole) in the metal-binder interlayers 50-nm nanoparticles of aluminum nitride AlN appear; such particles form the fifth phase-structural-state level of the hard-alloy surface layer (Fig. 2).

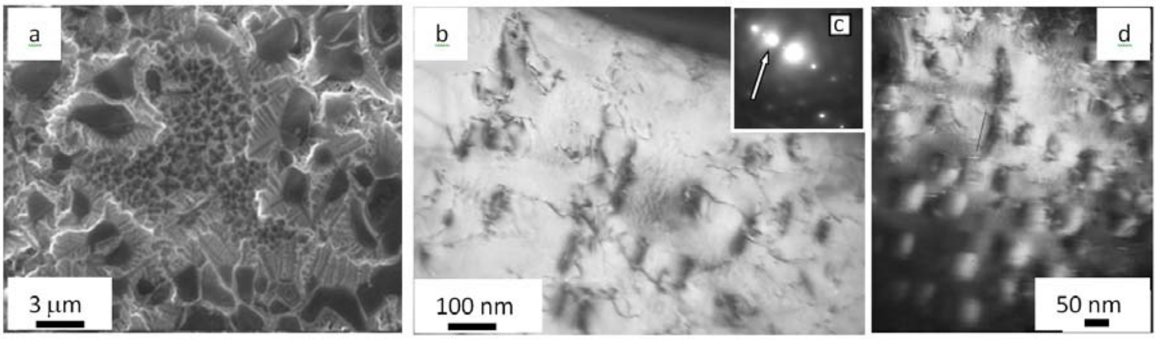

Fig. 2. The microstructure of the surface layer of TiC-(Ni-Cr) hard alloy subjected to electron-beam irradiation in Ar-containing gas-discharge plasma (electron-beam energy flux density 40 J/cm2, 15 pulses, pulse repetition frequency 1 s-1, width of irradiation pulses 200 µs) (a) and in (Ar+N)-containing gas-discharge plasma (40 J/cm2, 15 pulses, 1 s-1, 200 µs) (b-d). Scanning (a) and transmission (b - d) electron microscopy data.

Pulsed electron-beam irradiation of TiC-(Ni-Cr) hard alloy in plasma-forming gases with a smaller value of ionization energy (1350.0 kJ/mole for Kr and 1170.0 kJ/mole for Xe) exerts a more cardinal influence on the phase-structural state of the material in the surface layer. Like in the case of the irradiation of the material in Ar- and (Ar+N)-containing gas-discharge plasmas, at fixed regime of pulsed electron-beam irradiation nanostructuring of carbide-component particles occurs, - the carbide particles of the metal-ceramic composition get disintegrated in a multitude of nano-sized particles, thus forming a polycrystalline structure with a dendrite-like carbide skeleton in each crystal irradiated with electrons in Kr-containing plasma and with nano-dispersed distribution of the carbide component in crystals irradiated with electrons in Xe-containing gas-discharge plasma (Fig. 3).

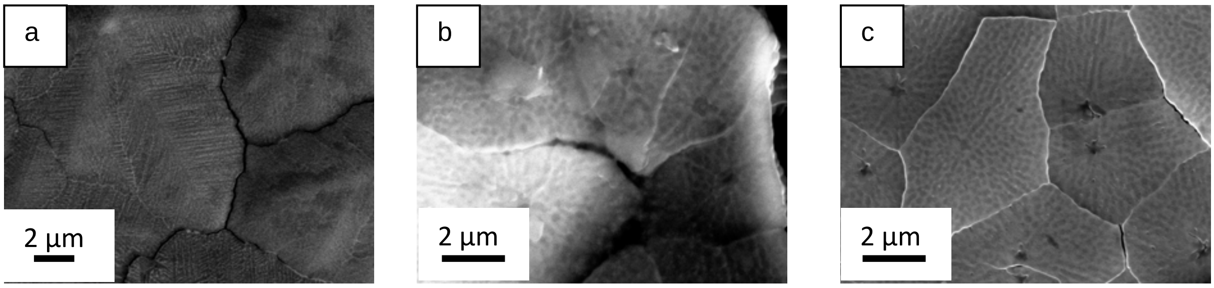

Fig. 3. The microstructure of the surface layer of TiC-(Ni-Cr) hard alloy subjected to pulsed electron-beam irradiation of the alloy in Kr-containing (a), Xe-containing (b), and (Xe+N)-containing (c) gas-discharge plasmas: a, b – 50 J/cм^2 , c – 40 J/cм^2; width of irradiation pulses - 150 μs, total number of pulses - 15.

By means of transmission electron microscopy, it was found that, right on the irradiated surface of hard-alloy samples, a two-phase mixture involving titanium carbide (TiC) nanocrystals and a (Ni-Cr) binder respectively sized 15…25 nm and 3…5 nm, forms (the circumference in Fig. 4, a singles out the foil area from which the electron-diffraction micropattern was taken).

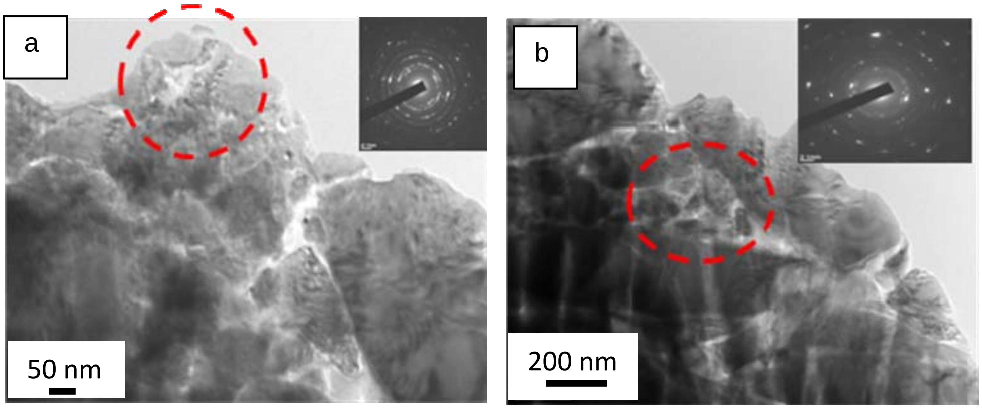

Fig. 4. The microstructures in the surface layer of TiC-(Ni-Cr) metal-ceramic alloy at depths 5-10 μm (a) and 25-30 μm (b) after processing the material in Xe-containing plasma.

With increasing distance from the extreme point of the outer surface (to 25-30 μm), fractured titanium carbide particles typical of the initial state of the material are observed (in the images, one such particle is singled out with the circumference), with regions involving carbide-phase particles sized 40…100 nm that occur at the junctions between the titanium carbide particles. In the electron diffraction micropatterns, reflections due to the carbide phase are only observed (Fig. 4, b). Further deepening to a depth of 50-60 μm has showed that the layer located at this depth contains comparatively large TiC carbide particles sized 0.5-1.0 μm and a (Ni-Cr) binder reinforced with secondary titanium carbide nanoparticles (Fig. 5, a). The deepening to depths in excess of 100 μm reveals coarse single-crystal titanium carbide particles and the (Ni-Cr)-binder in the initial state, i.e. without secondary titanium carbide nanoparticles (Fig. 5, b).

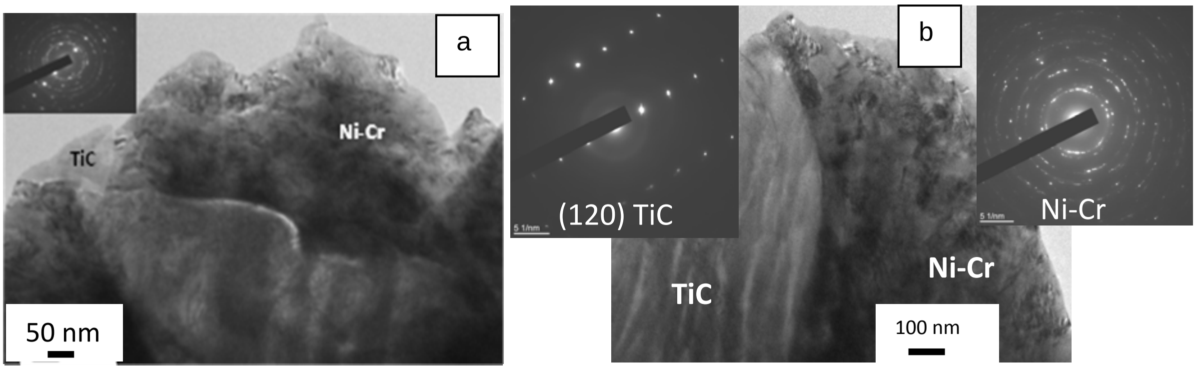

Fig. 5. The microstructure of the surface layer of TiC-(Ni-Cr) metal-ceramic alloy at depths 50-60 μm (a) and ~100 μm (b) after irradiation of the sample with electrons in Xe-containing gas-discharge plasma

The described formation pattern of the additional phase-structural-state levels of the surface layer of TiC-(Ni-Cr) hard alloys at pulsed electron-beam irradiation of samples in plasma-forming gases with different values of ionization energy has a direct relationship with the control of strength-defining properties of the surface layer of hard alloys used as tool materials. A kinematic diagram of a machine for performing abrasion tests according to ASTMG65, and also the rate of the abrasive wear of the surface layer of TiC-(Ni-Cr) hard-alloy samples prior to and after pulsed electron-beam irradiation of the samples in plasma-forming gases with different values of ionization energy versus the number of abrasive-disk rotations, are shown in Fig. 6. The planar sample under testing was pressed, with a 36-N force, to a 218-mm diameter rubbered disk rotating at a rotary speed of 200 rpm. To the friction surface, 13A-grade fused-alumina abrasive powder was supplied. The graininess of the powder was 20P according to GOST (Federal Standard) 28818-90 (particle size 200-250 μm). The abrasive consumption was 270-280 g/min.

At the initial time of the abrasion tests, the hard-alloy samples irradiated with the electron beam demonstrate a mechanical strength several times greater than the mechanical state of the initial (non-irradiated) alloy, this strength being the greater the larger is the number of the phase-structural-state levels available in the surface layer of the samples. With increasing the number of abrasive-disk rotations, the surface layer with increased mechanical strength becomes thinner, and the phase structural state of the material on the sample surface undergoes a variation with decreasing the number of phase-structural-state levels on the surface. As a result, the mechanical strength of the surface layer in irradiated samples approaches the mechanical strength of the hard alloy in the initial state of the material.

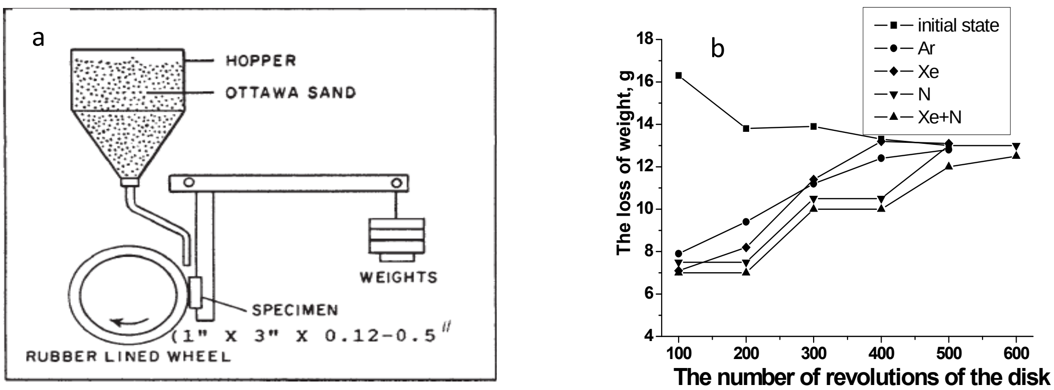

Fig. 6. A kinematic diagram of a machine used to perform abrasion tests according to ASTMG65 (a), and the rate of abrasion wear of TiC-(Ni-Cr) hard-alloy samples before and after pulsed electron-beam irradiation of the samples in plasma-forming gases with different values of ionization energy versus the number of abrasive-disk revolutions (b).

The above-said is in full measure confirmed by results of a study of the resistance of the surface layer of hard alloys during cutting of the samples with a diamond counter-body, and also by results of a study of the durability of the surface layer in cutting the samples with a metal hard-alloy plate on a turning machine. The temperature dependences of the resistance of the samples to cutting them with the diamond counter-body (as estimated from the depth of grooves cut on the sample surface) measured before and after pulsed electron-beam irradiation of the samples in Ar-, N-, and (Xe+N)-containing gas-discharge plasmas are shown in Fig. 7 (a). The same figure shows the durability of hard-alloy samples in metal cutting versus the energy flux density of the electron beam used for pulsed irradiation of the samples in gas-discharge plasmas based on Ar, N, Xe, and (Xe+N) gas mixtures (Fig. 7, b).

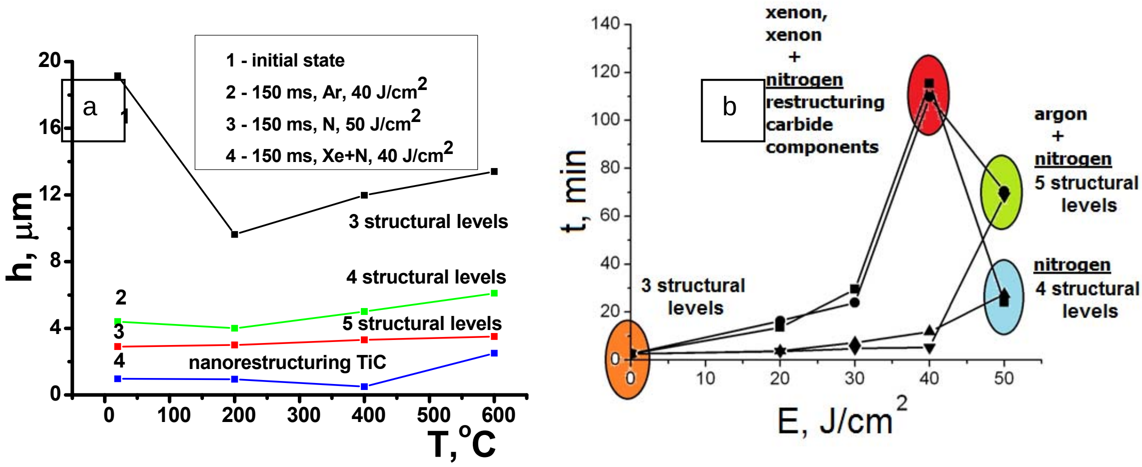

Fig. 7. The temperature dependence of the depth of grooves cut on the surface of samples with the diamond counter-body before and after pulsed electron-beam irradiation of the samples in Ar-, N-, or (Xe+N)-containing gas-discharge plasmas (a) and the durability of hard-alloy plates in steel cutting versus the energy flux density in electron beam during pulsed irradiation of the plates in Ar, N, Xe, and (Xe+N)-based gas-discharge plasmas (b)

The shown temperature dependences of the depth of grooves cut with the diamond counter-body on the sample surface sequentially reflect the influence of additional structural levels formed in the surface layer of hard alloy on the mechanical resistance of the layer during its interaction with the counter-body: with increasing the total number of structural levels the resistance of the hard alloy increases throughout the whole examined range of temperatures, and it reaches a maximal value on restructuring of the hard-alloy carbide component. Here, the mechanical strength of the hard alloy becomes comparable with the mechanical strength of the diamond counter-body. On increasing the total number of structural levels in the surface layer of the material from three levels in the initial state to four levels in the samples irradiated with electrons in Ar-containing gas-discharge plasma, the metal cutting power of the hard alloy increases by a factor of six. An increase of the total number of structural levels in the surface layer of the material from four to five levels in the samples irradiated with electrons in N-containing gas-discharge plasma increases the metal cutting power of the alloy material by a factor of 12. The nanorestructuring of the carbide component of metal-ceramic composition in the surface layer of the metal-ceramic alloy proceeding during the electron-beam irradiation of the alloy in Xe- or (Xe+N)-containing gas-discharge plasma increases the metal cutting power of TiC-(Ni-Cr) hard alloy by more than 20 times.

The data obtained in the present study have a direct bearing on the modification of the phase-structural state of the surface of hard alloys with a high content of ceramic component widely used in mechanical engineering. With the example of T40 hard alloy with composition (75%WC+14%(Ti,Ta,Nb)C)-11%Co it was established that, right on the irradiated surface, their forms a thin (80…140 nm) film of ternary carbide (Ti, W)Cx (Fig. 8, a) that passes into a cellular metal-ceramic structure (Fig. 8, b). The sizes of the cells formed by (Ti, W)Cx carbide particles with cobalt interlayers containing CoxWyC carbide inclusions and/or CoxWy compounds vary in the range 80…200 nm, and those sizes show an increase as we move deeper into the material from the side of its irradiated surface. The cells are separated from each other with cobalt interlayers of thickness 30…50 nm.

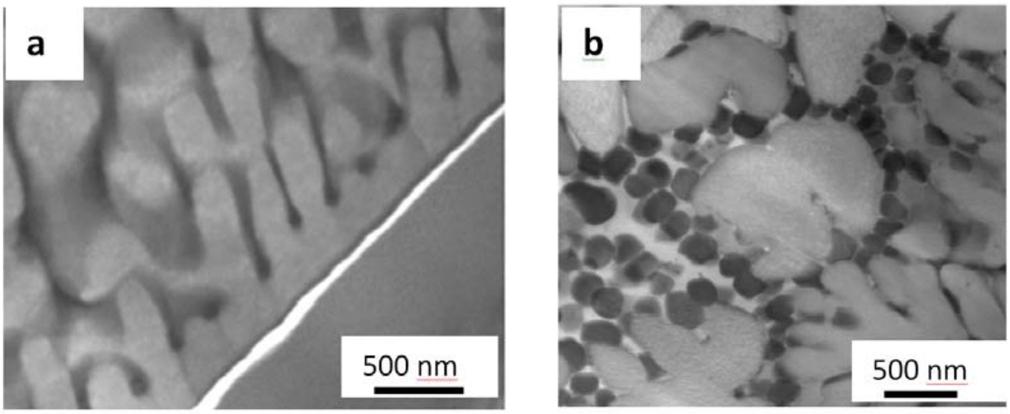

Fig. 8. The microstructure of the surface layer of T40 hard alloy processed with the pulsed electron beam in Ar-containing gas-discharge plasma

The durability of T40 hard alloy in metal cutting depends on the employed regimes of pulsed electron-beam irradiation and on the composition of the gas-discharge plasma (Fig. 9). A maximal improvement of the mechanical strength of T40 metal-cutting plates was achieved in plates irradiated with electrons in Xe-containing gas-discharge plasma.

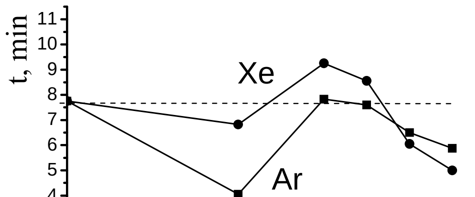

Fig. 9. The durability of T40 hard-alloy plates in steel cutting versus the energy flux density in the electron beam used for irradiation of the samples in Ar- and Xe-containing gas-discharge plasmas.

Conclusions

1. Formation of a multi-level structure in the surface layer of hard alloys offers a well-substantiated concept for increasing the mechanical strength of hard alloys as tool materials.

2. Pulsed (submillisecond time range) electron-beam irradiation offer a promising method for forming a multi-level phase-structural state in the surface layer of hard alloys in nano-size region.

3. The efficiency of pulsed electron-beam irradiation as a method for forming a multi-level phase-structural state in the surface layer of hard alloys depends on the choice of plasma-forming gases. With decreasing the gas ionization energy, the efficiency of the thermal action due to electron beam,

defining both the rate of phase transformations in the surface layer of hard alloys and the rate of formation of the multi-level phase-structural state in the material, grows in value.

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References

[1] Suryanarayana C, Al-Aqeeli N. Mechanically alloyed nanocomposites // Progress in Materials Science-2013.-V.58-No.4.-P.383-502.
[2] Chawla N, Chawla K K Metal matrix composites. –New York: Springer, 2006. 401p.
[3] Z Zak Fang, Xu Wang, Kyu Sup Hwang, H Y Sohn. Synthesis, sintering and mechanical properties of nanocrystalline cemented tungsten carbide – A review // International Journal of Refractory Metals and Hard Materials.-2009.- V.27, iss. 2.-P. 288-299.
[4] V E Panin (editor), Physical Mesomechanics and Computer-Aided Design of Materials / Nauka, Novosibirsk.- 1995.-Vol.1. – 298 p.
[5] Psakhie S G, Ovcharenko V E, Knyazeva A G, Shil'ko E V Formation of multi-scale structure in surface layers and the strength of metal-ceramic alloys under mechanical loads // Fizicheskaya Mezomekhanika.-2011.-Vol.14.-Iss.6.-P.23-34.