Protective Nanocomposite Vacuum Coatings Deposited by Separated Plasma Flows

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Abstract: The way of generation of protective nanostructure vacuum coatings by separated plasma flows was investigated. In order to limit the crystallite growth in the coatings the compound of the growing condensate was doped by Al. Nanocrystalline (Ti,Al)N coatings with grain size 10-20 nm and microhardness 35-40 GPa by means of vacuum-arc deposition technique from the separated plasma flows were obtained. It was determined that purposeful alloying improved operational coatings properties, and allowed using them as protective layers, deposited on the working surfaces of the cutting tools during timber-based material processing.
Keywords: nanocrystalline; coating; vacuum-arc; deposition technique; high-heat compounds.

1. Introduction

The construction industry along with biomedicine and electronics are seriously interested in nano-materials. Many areas are already widely used materials modified using nanotechnology. Carbon nano-tubes are used in the modification of the concrete, giving it greater mechanical strength, preventing the occurrence of cracks. They are used to improve thermal and mechanical properties of ceramic products, used for solar panels to increase their durability and efficiency. The use of nano-particles of silica in the concrete significantly increases its mechanical strength, and in ceramics and glass provides improved fire resistance and light transmission. When using the same materials of titanium dioxide leads to the appearance of these materials are self cleaning properties. Coating materials with such addition acquire resistance to UV light and significantly longer service life. Nano-particles of iron oxide, or as it is called, hematite increase the strength of concrete in compression and abrasion, and copper – corrosion resistance, weld ability and forming properties of steel. Nano-particles of silver in the coatings and paint products boost their antimicrobial properties.

But we want to mention another direction of development of nanotechnology, which is important for the construction industry. It is obtaining inexpensive metal-cutting tools with improved performance properties by modifying the surface layers, in particular the application of nanolayers or nanocomposite coatings on the material used for their manufacture, methods of ion-beam modification of or plasma technology. These methods open new possibilities to provide the surface properties independent of characteristics that define the entire mass of material.

Metal cutting tools are widely used in various kinds of work, and its main advantage is the opportunity to work with super-hard materials, therefore, these tools are used in various industries, including construction: concrete cutting, polishing gemstones, drilling, Metalworking, etc. the quality of cutting tools depends on the quality of work and safety of builders. In the manufacture of cutting tools used tool steel, superhard cemented material or hard alloy, and more recently, as noted above, manufacturers of cutting tools have begun to use new technologies aimed at the improvement of operational properties of the tool by modifying its surface layers.

Vacuum-arc deposition technique allows obtaining nanocrystalline coatings from high-heat compounds with much more finer grains in comparison with alternative nanotechnologies (super-dispersed powders compaction, amorphous phase crystallization, intensive plastic deformation, and etc.) [1-2]. However, vacuum arc monolayers coatings of high-heat compounds, for example TiN, CrN, MoN and etc., being super-dispersed in the direction of condensation surface, have a columnar structure in the direction of coating growth. So coatings deposition with nanosized dies is connected with the development of effective methods of the crystals growth control in the direction of the coatings growth.

Most protective coatings are the nitrides and carbides of the high-heat compounds of Group IV-VI transition metals of the periodic table of the elements. Functional properties of such coatings are considerably determined by their real structure – grain size, impurities concentration, texture, phase composition, internal stress level and etc. Particularly, the considerable changes in structure and properties of the nitride coatings can be achieved as a result of the alloying of Si, B, Al, Y, Cr, Ni and etc. [4-5].

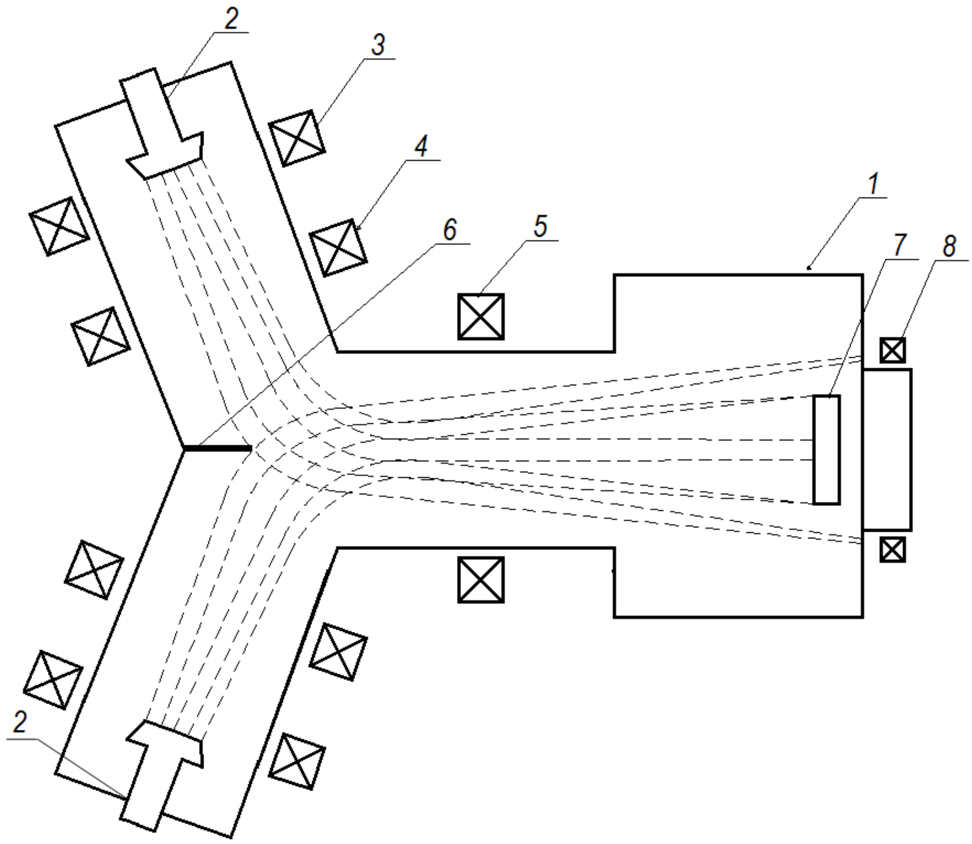
The generation of the multicomponent coatings may be done as follows: first of all, by coatings deposition from the alloys, secondly, by simultaneous sputtering of several materials. However, it is rather difficult to maintain the phase identity of the cathode and the coating material during the alloy sputtering. So the largest interest represents the alloying of coatings by different elements by means of simultaneous sputtering of several materials. The vacuum-arc (Ti,Al)N coatings have the greatest interest as protective layers, retaining a high hardness at higher temperatures, they have an increased coefficient of friction (in comparison with TiN), as well as an oxidation resistance at higher temperatures and comparatively high thermal conduction.

The control of structure and phase composition of the coating is realized by the selection of the deposition modes, the changing in the concentration of alloying element, the partial gas pressure, the temperature of deposition and the substrate bias. Most investigations in this direction are connected with the deposition of the condensates from the unseparated flows. However, the existence of macroparticles (drops and solid cathode material fragments) in the plasma flow is the main disadvantage, which limits the sphere of the application of vacuum-arc erosion plasma sources. Different types of the electromagnetic rotation systems of charged particles are used to withdraw the macroparticles from the flow of the condensable material during their motion from the cathode to the condensation surface.

In this paper, it is suggested to use a complex approach to the generation of the protective layers, including the coatings deposition of the multicomponent composition ((Ti,Al)N coatings) using separated plasma flows.

2. Testing Procedure

The coatings deposition was carried out on the modernized vacuum-arc plant, equipped by Y-shaped macroparticles separator. (Fig. 1).



1 – vacuum camera; 2 – arc evaporators; 3, 4, 5, 6 – electromagnetic coils;
6 – screen for droplet phase withdrawal; 7 – substrate

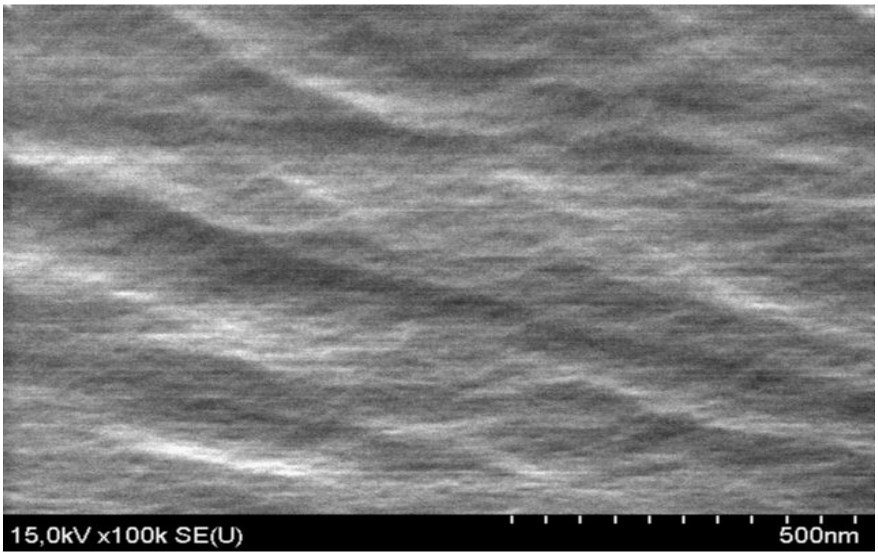
Fig. 1 - The scheme of multicomponent coatings deposition from the separated plasma flows

Two unlike arc evaporators (2) are placed symmetrically at an angle of 120º degrees relative to the incidence axis of the total plasma flow. The ionized components of plasma flows are deflected by 120º by means of electromagnetic coils (5, 8) and mixed plasma flows are deposited onto substrate. The focusing of the different plasma flows is controlled by the electromagnetic coils (3, 4). The screen (6) provides the droplet phase withdrawal from plasma flows and its deposition on the plasma-guide walls.

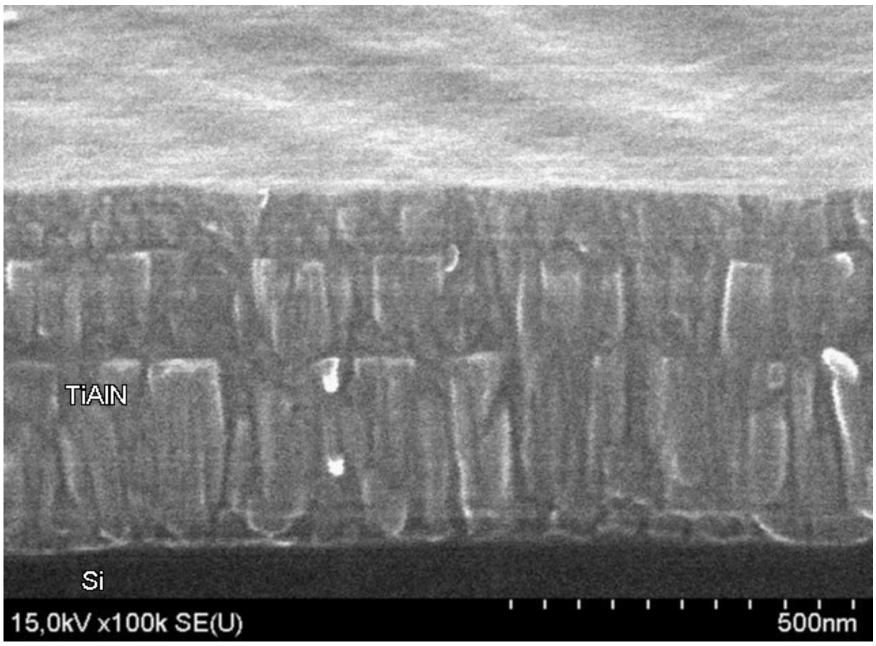
Titanium and aluminum (99.99%) cathodes were used to sputter the coatings. The deposition under the different modes was carried out on the substrates of stainless steel (12Cr18Ni10Ti), cemented carbide and silicium. The deposition time was chosen so that coatings thickness was 2.5±0.1 μm.

The morphology and structure of the deposited coatings were studied by means of scanning electron microscope. X-ray diffraction and X-ray phase analysis were carried out in the angular measuring range between 30° and 120° in the filtered Cu-Kα radiation. By using the main characteristics of the diffraction maximum allowed to estimate the lattice parameter (d), coherent-scattering region size (L). Microhardness was measured by nanoindenter Duramin under 0.25N load. In order to carry out the tribological investigations the «ball-on-disc» test was used.

As can be noted from the carried out investigations, coatings surface morphology is characterized by microcell structure similarly to the pure titanium-based coatings (Fig. 2). The drops absence on and in the coating surface is evidence of an effective separated system work.



a



b

Fig. 2 - Surface morphology (a) and fractograph of the deposited coatings (b)

The stepping (Ti,Al)N coating etching by means of high-energy argon ion beam showed that the element distribution into the depth of the (Ti,Al)N coating was uniform, and it can be stated about the achievement of the necessary mixing level of the separated plasma flows (Fig. 3).

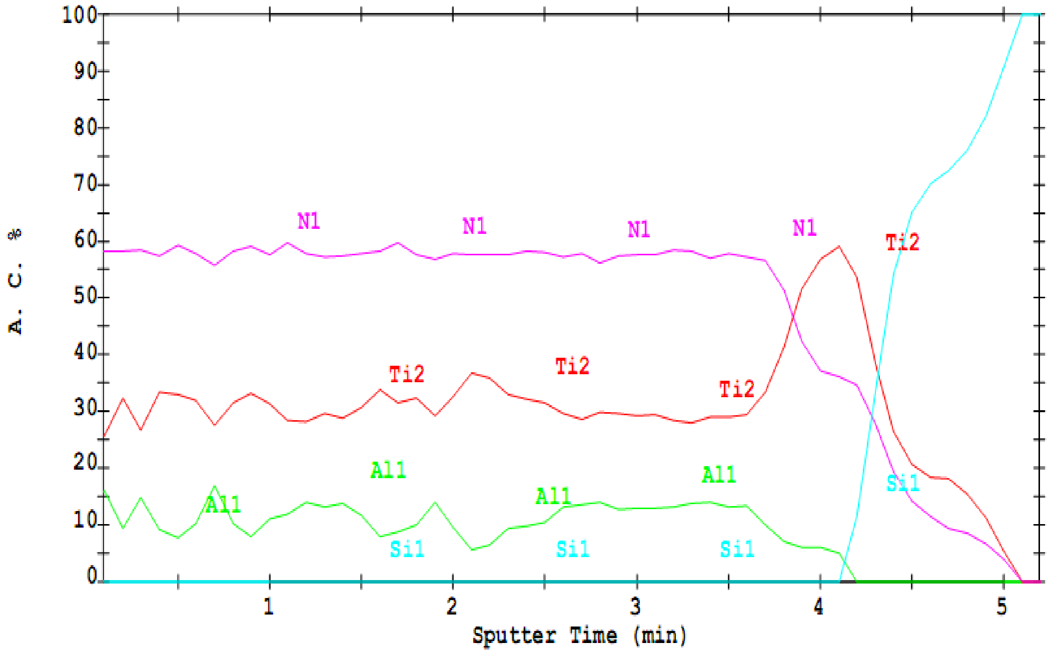
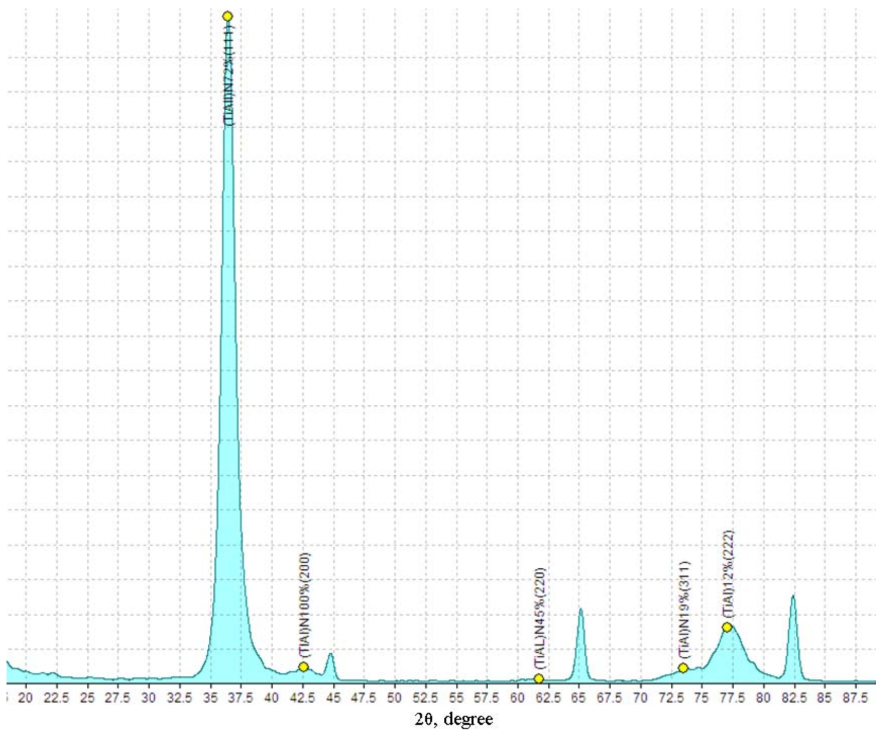


Fig. 3 - Element distribution into the depth of the (Ti,Al)N coatings

The phase composition analysis (Ti,Al)N coatings showed that the solid solution of Al in the TiN lattice with a cubic structure NaCl was the fundamental crystalline component in the initial post-condensation state for the coatings with aluminum concentration in the range of 5-30 at.% (Fig. 4 a). The (Ti,Al)N coatings with aluminum concentration over 30 at.% are characterized by the presence of two phases: cubic TiN phase and hexagonal AlN phase (Fig. 4 b).



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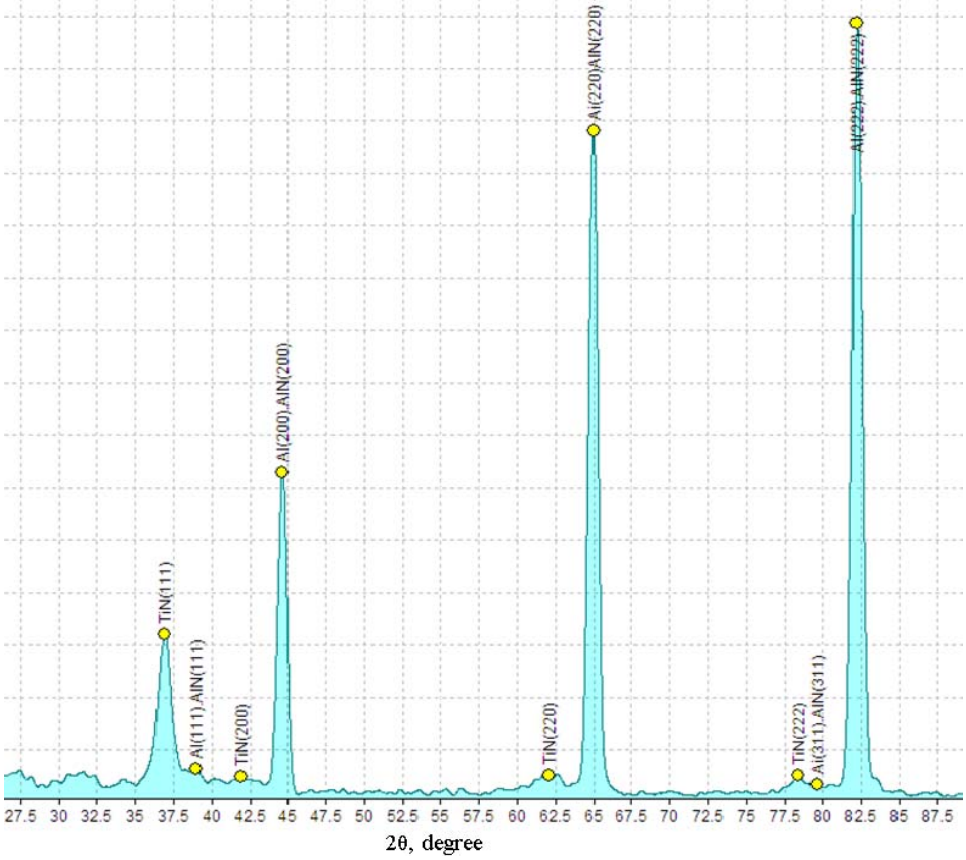


b

a – aluminum concentration 15 at.%; b – aluminum concentration 35 at.%

Fig. 4 - (Ti,Al)N coatings X-ray diffraction pattern

As can be seen from the results, lattice parameter decreases from 0.423 nm to 0.417 nm with the aluminum concentration increasing (Table 1). The obtained values of the lattice parameter are lower in comparison with massive TiN of stoichiometric composition (0.424 nm) and vacuum-arc TiN condensate deposited from the separated plasma flows.

Table 1 - Structural and mechanical characteristics of the composite coatings

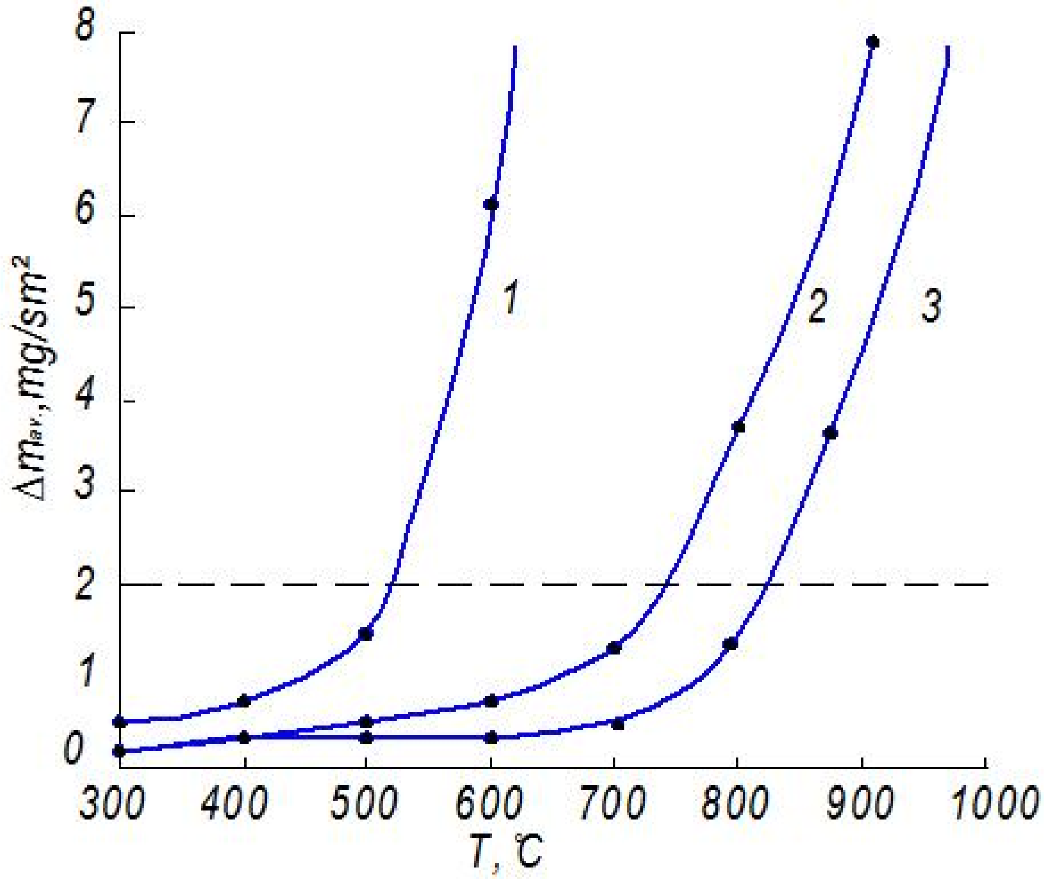
Coating	I_{Ti}, A	I_{Al}, A	Ti, at. %	Al, at. %	*d*, nm	*L*, nm	*H*, GPa
TiN	60	–	60.21	–	0.427	28	26.5
(Ti, Al)N	60	40	91.81	8.19	0.423	24	29.8
		50	84.19	15.81	0.421	20	34.9
		60	73.32	26.68	0.419	14	32.1
		70	64.79	35.21	0.417	15	36.1
AlN	–	60	–	58.23	–	76	19.2

Two mechanisms of hardening during the coating deposition can occur in case of alloying the nitride titanium based coating by Al. Which one takes place (solid solution or dispersion strengthening) depends on the Al concentration in the coating. The decrease of lattice parameter is caused by the substitution of Ti atoms in the TiN structure with smaller Al atoms. The given results are agreed with literature data, it is showed, that (Ti,Al)N coating is characterized by cubic TiN structure with decreased lattice parameter, provided atomic Al concentration is less 60%. However, the increasing of Al percentage in the coatings composition results in the decreasing of the microhardness of the coating.

It is known that it's impossible to decrease the temperature in the direct contact zone under high processing speed. In this case the oxidative wear mechanism, caused by the interaction between the oxygen and the coating material, takes place so it's necessary to control the high-temperature oxidation resistance of the deposited coatings. The (Ti,Al)N coatings oxidation characteristic when heating in the air in the temperature range 200–900 ºC and soaking 1 hour was studied (Fig. 5).

It's known, that the coatings oxidation is determined as the beginning of the coating mass change Δ*m* after thermal annealing owing to the oxide generation. The temperature, corresponding to the significant increase in $\Delta m \geq 20$ mg/sm^2, is determined as the maximum temperature when the coating has thermal stability.

When the temperature is lower 700 ºC the surface coating consists of homogeneous mixture oxides Al_2O_3+TiO_2, and when it's above 800 ºC the double-layered structure Al_2O_3/TiO_2 to be generated due to the enhancement of the aluminum atom diffusion towards the surface and the upper layer Al_2O_3 protects the coatings from the oxidation. It's found, that purposeful alloying of the titanium nitride coatings by aluminum had a positive influence on the thermal stability, the best result being got for the coatings with aluminum concentration approximately 35 at.%.



1–TiN; 2–(Ti,Al)N (at. Al-15%); 3–(Ti,Al)N (at. Al-35%)
Fig. 5 - The mass increase of the vacuum arc coatings during heating in air under different aluminum concentrations

The friction factor of the carbide cutting plates coated by Ti-Al-N is in the range from 0.31 to 0.50 (Fig. 6), and it's essentially lower in comparison with TiN coated cutting plates (0.7-0.8) and uncoated cutting plates (0.9). It is connected with presence of the plastic material (Al), which has a significant influence on the friction factor in the case of dry friction. The decreasing of the friction factor gives the temperature drop in the cutting area and consequently leads to the increasing of the coated tool wear resistance.

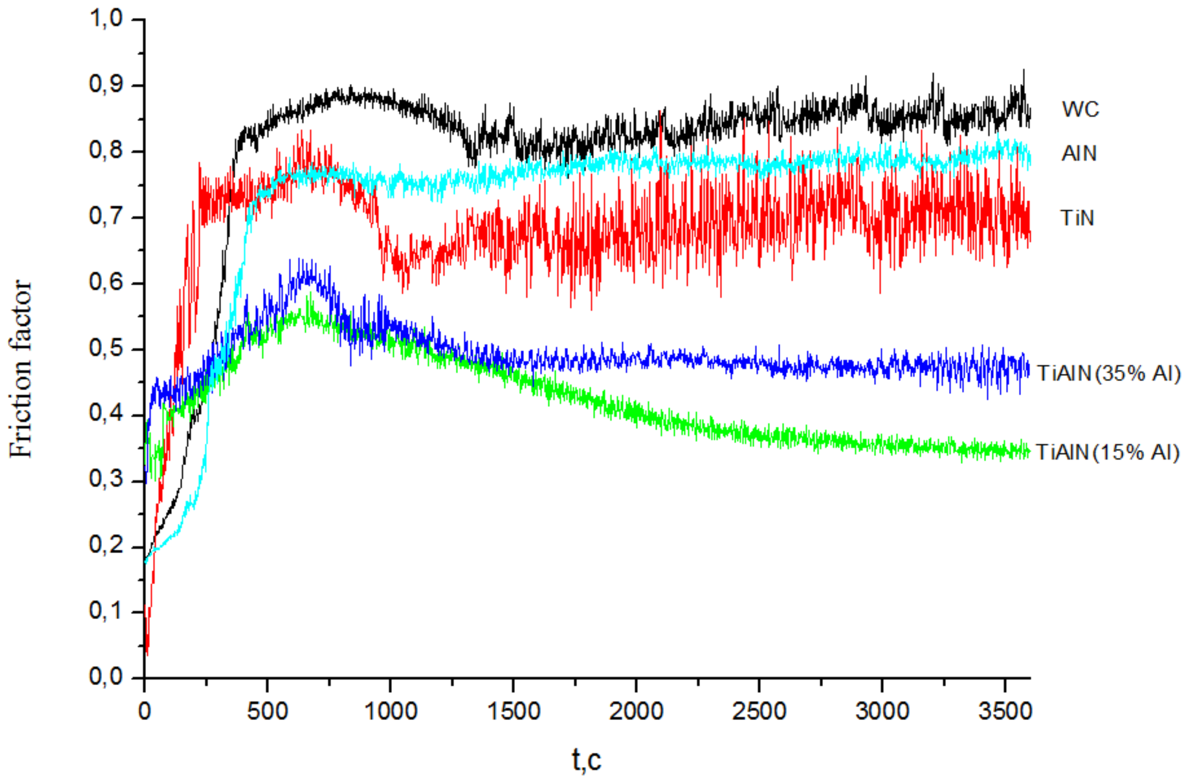
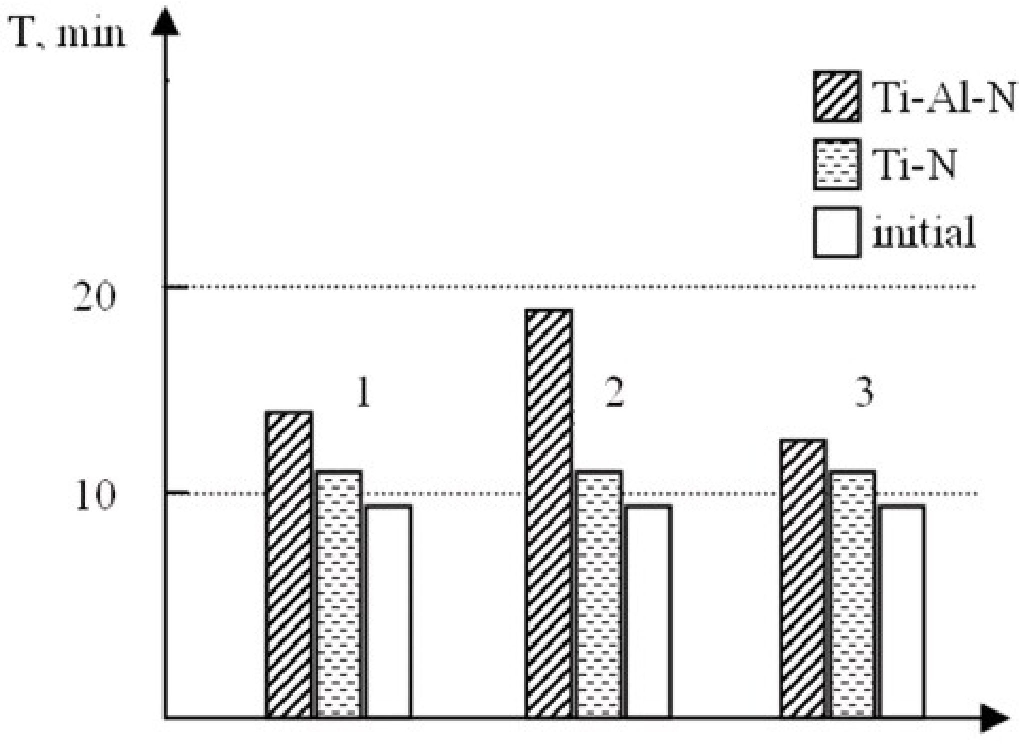


Fig. 6 - The friction factor of the vacuum arc coated cutting plates

The carbide cutting plates tests with (Ti,Al)N coatings during particle boards processing showed high working capacity at high speeds (temperatures) in comparison with TiN (Fig. 7). The resistance criterion was the clearance face wear.



1 – Al 15 at%, 2 – Al 35 at%, 3 – Al 50 at.% (literary data)

Fig. 7 - The dependence of the carbide cutting plates efficiency of (Ti,Al)N coatings on the aluminum concentration in the coating

3. Conclusions

Nanocrystalline (Ti,Al)N coatings with grain size 10-20 nm, microhardness 35-40 GPa, friction factor 0.31-0.50 by means of vacuum-arc deposition technique from the separated plasma flows were obtained. It is determined, that purposeful alloying improves operational coatings properties, and allows using them as protective layers, deposited on the working surfaces of the cutting tools during timber-based material processing.

4. References

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