# Nanostructured Titanium Nitride Coatings Produced by Arc Sputtering of Composite Cathodes.
# I. Cathodes Structure, Phase Composition and Sputtering Peculiarities[1]

G.A. Pribytkov, E.N. Korosteleva, S.G. Psakhie, I.M. Goncharenko*, Yu. F. Ivanov*,
N.N. Koval*, P.M. Schanin*, A.V. Gurskih, V.V. Korjova, Yu.P. Mironov

*Institute of Strength Physics and Materials Science, Siberian Branch, Russian Academy of Sciences,
2/1 Academichesky Ave., 634021, Tomsk, Russia; Tel.: (3822)286-967; E-mail: gapribyt@mail.ru*
*Institute of High Currant Electronics, Siberian Branch, Russian Academy of Sciences,
4 Academichesky Ave., 634055, Tomsk, Russia*

**Abstract – The coatings, produced by arc sputtering of the multicomponent cathodes Ti–Cu and Ti–Cu–Al in medium of ionised nitrogen are investigated. Two different types of the cathodes were used: mosaic type and fabricated from the powders. The coatings, produced by concurrent arc sputtering of Ti and Cu cathodes, were investigated for a comparison. Arc sputtering of mosaic type Ti–Cu and Ti–Cu–Al cathodes resulted in cathodes composition dependent hardness of the coatings. The maximum hardness was twice as much compared with those produced by arc sputtering of Ti cathode. The rate of arc erosion of the cathodes is composition dependent. High arc erosion of powder made Ti+30% at.Cu cathode gave rise to porous, drop type coating. A likely reason of the high arc erosion is a low melting temperature of Ti+30% at.Cu cathode. All investigated coatings contain the titanium nitride as a dominant phase. All (except one porous, drop type)TiN coatings have <111> texture. A lattice spacing varies from 0.4282 to 0.4283 nm. This values and <111> texture are consistent with the reported data for thin film TiN coatings. The porous, drop type coating is not textured and TiN lattice spacing ($a = 0.4245$ nm.) differs from those of thin solid film coatings.**

## 1. Introduction

Multicomponent nitride plasma deposited coating have been investigating intensively for last 10 years, once the ultrahigh hardness of the coatings has been revealed. The data on the mechanical and physical properties of the coatings one can find in the reviews [1, 2]. The structural researches of the multicomponent coatings have shown, that a grain size in the growing nitride film usually does not exceed some tens nanometers. In accordance with the conventional classification, the coatings may be referred to the nanostructure materials. The peculiarity of the superhard multicomponent nitride coatings is a heterogeneity. In most cases a structure of the superhard thin films constitutes a mixture of two or more nanostructure phases. Some of them may be amorphous. The greatest microhardness ($H_\mu > 50$ GPa) have nanocomposite films TiN/BN, TiN/TiB, TiN/TiB$_2$, TiN/Si$_3$N$_4$. A record microhardness (105GPa) has a nanocomposite film, consisting of the TiN nanocristals (3–4 nm in size) enclosed in amorphous Si$_3$N$_4$ phase [1]. By now there is a considerable advance in understanding of the causes of retaining of nanocomposite structure and superhardness of the nanocomposite thin films at the elevated temperatures. The reason is that a tendency to structure coarsening in the nanocomposites is depressed by low energy of the nanocristal – amorphous phase interfaces. The structure stability of nanocomposite thin films increases as nanocristal size decreases.

A common used deposition method of nanocomposite coatings is a plasma chemical deposition (CVD-chemical vacuum deposition). However the CVD technology has a number of disadvantages limiting a wide scale use: high corrosivity and toxicity of gaseous halogenides used at the synthesis, a presence of a carbon impurity in the synthesis products. Among alternative (PVD – physical vacuum deposition) methods a most often used is a magnetron sputtering one [3–5]. The multicomponent cathodes for magnetron sputtering are produced by alloying [6, 7], by (SHS –selfpropagating high-temperature synthesis) method [9] or by sintering [10]. Often used are so-called mosaic cathodes, produced by imbedding of metal insertions into a cathode, made of the other metal [8]. Independently of a cathode type superhard nanocomposite coatings were deposited by magnetron sputtering of many double and some triple metal systems [2, 3, 6–8]. However, alongside with the basic advantage of the magnetron method (dropless sputtering), there are some essential shortages: a rather high gas pressure for discharge maintenance, narrow allowable ranges

for a gas pressure and a current. Because of high gas pressure an energy of the particles deposited on substrate surface is low. As a result magnetron sputtered coatings are more porous, and an adhesion to the substrate is insufficient.

A method of plasma assisted vacuum arc sputtering [11] does not have above-listed shortages, and allows to enhance coating properties. The plasma assisted vacuum arc sputtering method has been applied to get Ti–Cu nanocomposite coating with an initial microhardness 40–50 GPa by concurrent arc sputtering of titanium and copper cathodes. Because of unstable structure of the coatings [12] a microhardness is halved during a month. Vacuum arc sputtering method was used for deposition of sulphide, carbonitride and complex nitride coatings [10, 13]. This report offers the results of investigation of the coatings deposited at vacuum arc sputtering of the composite cathodes Ti–Cu–Al and Ti–Cu.

## 2. Experimental Procedure

Multicomponent Ti–Cu–Al and Ti–Cu cathodes were fabricated of the metal powders. Mosaic type cathodes with Cu and Cu–Al alloy insertions, imbedded into Ti cathode, and Ti cathode too were used for comparison. Hard alloy substrates (BK8 trade mark) were located at 30 cm distance from cathode front surface. Substrate surface was mounted transversally ($\perp$) or parallel ($\parallel$) to plasma flow from the sputtered cathode. For nitrogen plasma generation were used PINK plasma generator [11]. The PINK generator keeps plasma concentration in working area at the $10^9$–$10^{10}$ cm$^{-3}$ level. Phase composition and lattice spacing of the sputtered cathodes and of the coatings deposited were determined by X-ray diffractometer (DRON-UM1, Russia). Microhardness of the coatings was measured by microhardness indentor (PMT-3, Russia) at 50 g and 100 g loading. For microstructure investigation were used metallographic (MIM 9, Russia) and scanning electron (SEM 515 Philips) microscopes.

## 3. Results and Discussion

In Table 1 is represented microhardness of deposited coatings, measured at hard metal substrate. The coatings were deposited by sputtering of mosaic type cathodes. Results in Table 1 displays, that copper and aluminium, being added to titanium cathode, raise coatings microhardness greatly. The record microhardness of the coatings was achieved at sputtering of Ti–Cu mosaic type cathode.

Table 1. Microhardness of the coatings, deposited by sputtering of mosaic type cathodes

| Cathodes chemical composition | $H_\mu$, GPa |
|---|---|
| Ti (standart) | 23 |
| Ti + (Al + 5,47 % at. Cu) | 33–35 |
| Ti + (Al + 50 % at. Cu) | 45 |
| Ti + (100% Cu) | 52–53 |

However vacuum arc sputtering technologies using two cathodes or mosaic type cathodes have a lot of disadvantages. Using of two or more cathodes needs more complicated equipment and necessity to adjust sputtering process variables separately for every cathode. If mosaic type cathode is used, plasma elemental composition is out of control, owing to different rates of arc erosion of the mosaic type cathode components. The other reason of the plasma composition instability is an influence of different electrical ant magnetic properties of metal components of the mosaic type cathodes. Heterogeneity of electrical and magnetic properties on the cathode surface influences on arc spot movement. Instability of the elemental plasma composition results in an instability of the composition and properties of the deposited coating. In order the rate of arc erosion was constant it is necessary, that the arc discharge spot on the cathode exceeded the dimensions of structural components of the multicomponent composite cathode. If a mean phase and the chemical composition at the whole cathode is identical, one can expect also invariable in time an elemental composition of the plasma too. As a result the composition and properties of the deposited coating are expected to be constant throughout the coating. On these reasons, and also taking into account the hardness data (table 1), for further sputtering experiments were used the cathodes having made of titanium and copper powder mixtures with 30 and 12% at Cu.

The microstructure of powder cathodes is shown in Fig. 1. The cathodes phase composition and some properties are represented in Tab. 2. CuTi$_2$ is a dominant phase in Ti + 30%Cu cathode. A volume content of the rest phases ($\alpha$-Ti and TiCu) is less then 18%. Ti + 12%Cu cathode contains CuTi$_2$ и $\alpha$-Ti with nearly equal volume content. Grains of different phases in cathodes structure are 5–30 times less in size, then a size of the arc spot, estimated to be about 100 μm. The residual porosity of the cathodes material is rather modest.

Table 2. Phase composition and some properties of powder cathodes

| Characteristics | Chemical composition, at.% | |
|---|---|---|
| | Ti + 30%Cu | Ti + 12%Cu |
| Density, g/cm$^3$ | 5.4 | 4.2 |
| Porosity, % (pores size, μm) | 12.6 ± 2% (30 ± 6) | 7.2 ± 4.2 % (49.3 ± 26) |
| Phase composition | CuTi$_2$ (dominant) | CuTi$_2$ и $\alpha$-Ti (dominants) |
| Grain size, μm | 7–13 | 3–20 |
| Hardness, HB | 195 ± 6 | 176 ± 9 |

The rates of arc erosion of the titanium cathode ($3.9 \cdot 10^{-5}$ g/C) and Ti + 12%Cu cathode ($4.2 \cdot 10^{-5}$ g/C) differ little, while the erosion rate of the Ti + 30%Cu cathode twice as more ($8.2 \cdot 10^{-5}$ g/C), than of the titanium cathode. The cause of the extreme erosion of the

Ti + 30%Cu cathode is its lower melting point, and a consequence – an enhanced contents of a drop phase in the coating, especially when the substrate is mounted transversally to plasma flow. In this case the coating surface is covered with drops, the compact coating is lacking (Fig. 2,a). At cathode Ti + 12%Cu sputtering a view and thickness $h$ of che coating depend on the substrate orientation too (Fig. 2,b,2c). This coatings achieved a hardness about 50 GPa.
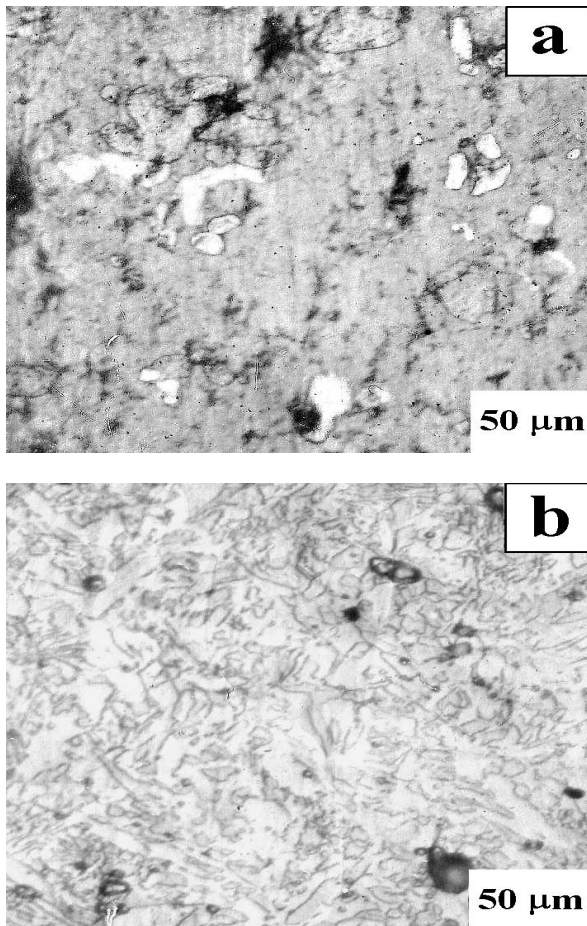




Fig. 1. Microstructure of powder cathodes: a – Ti+30%Cu; b – Ti+12%Cu

According to X-ray investigation results (Tabl. 3) titanium nitride is a dominant phase in all deposited coatings. All the coatings, except one of them (produced by Ti+30%Cu powder cathode sputtering at ⊥ substrate orientation) show strong <111> texture. TiN lattice spacing of the coatings is within the range 0.4268–0.4287 nm. This values as well <111> texture are typical for thin-film TiN coatings, deposited by arc sputtering of titanium or titanium alloys cathodes. TiN lattice spacing of drop type coating (Fig. 2,a) is less, than those for the rest coatings and corresponds to standart value of bulk titanium nitride. WC (and in some patterns Co) X-ray reflections are substrate relative. According to X-ray results three of the investi-

gated coatings contain a cooper or Cu(Ti) solid solution as a phase. The coatings, containing cooper base phase are of poor quality. The coatings deposited at the sputtering of macroscopic size cooper areas (Cu cathode or mosaic type Ti + Cu cathode) exhibit a tendency to degradation [12]. Sputtering of powder cooper rich cathode gave the porous, drop type coating.
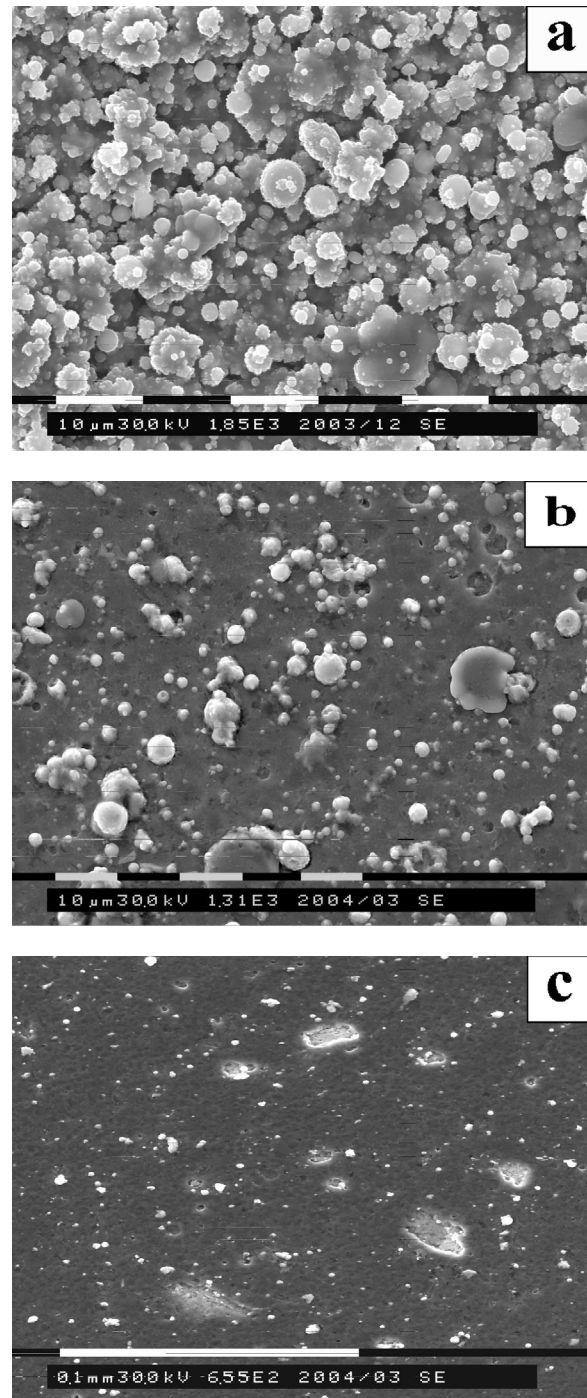






Fig. 2. Scanning electron micrigraphs of the coating surfaces depending on cathode composition and substrate orientation: a – Ti+30%Cu, (⊥); b – Ti+12% Cu, (⊥), $h = 3.7$ μm; c – Ti+12%Cu, (∥), $h = 1.2$ μm

It is believed that the X-ray reflections of cooper base phase originated from drops core, not having been reacted with nitrogen reactive gas. It is obviously, that the drop type coating (Fig. 2,a) is unserviceable for tools. In spite of dense coating at (∥)-oriented substrate, deposited from sputtered Ti+30%Cu powder cathode, there is no purpose of using of Ti+30%Cu powder cathode because of the anomalous arc erosion.

Table 3. X-ray investigation results of the coatings

| Cathodes type (substrate orientation) | Phase composition | | | |
|---|---|---|---|---|
| | TiN:$a$, nm, <texture> | WC | Co | Cu |
| Ti (standart), (⊥) | $a = 0.4280$, <111> | + | − | − |
| Ti+Cu mosaic type, (∥) | $a = 0.4268$, <111> | + | + | + |
| Two cathodes: Ti, Cu, | $a = 0.4283$, <111> | + | + | + |
| Ti+30%Cu, powdered, (⊥) | $a = 0.4245$, − | + | − | + |
| Ti+30%Cu, powdered, (∥) | $a = 0.4282$, <111>. | + | + | − |
| Ti+12%Cu, powdered, (∥) | $a = 0.4287$, <111> | + | + | − |
| Ti+12%Cu, powdered, (⊥) | $a = 0.4280$, <111> | + | − | − |

## 4. Conclusions

It is shown on the example of the titanium – copper system, that by arc sputtering in nitrogen of a composite cathode of the proper chemical composition and structure one can deposit a coating with a microhardness about 50 GPa. Microstructure, phase composition and hardness of deposited coating depend greatly on the cathode chemical composition and structure. To ensure gomogeneous, stable structure and high hardness of the deposited coating a sputtered composite cathode must answer next requirements:

– disperse structure with the size of structural elements about ten times less than that of the arc cathode spot;

– minimal content of low-melting point phases, resulting in an increased drop formation.

**References**

[1] Veprek Stan, J. Vac. Sci. Technol. A. **17**, No. 5, 2401 (1999).

[2] J. Musil, Surf. and coat. technol. **125**, 322 (2000).

[3] J. Musil, J. Vlcek, *in: Proc. of 5$^{th}$ conf. on modification of materials with particle beams and plasma flows,* 2000, pp. 393–398.

[4] J. Musil, J. Vlcek, Surf. and coat. technol. **112,** 162 (1999).

[5] S.A. Shirjaev, M.V. Atamanov, M.I. Guseva, Yu.V. Martinenko, A.V. Mitin, V.S. Mitin, Phizika i khimiya obrabotki materialov, No. 3, 33 (2002).

[6] J. Musil, H. Hruby, Thin solid films (April), 47 (1999).

[7] J. Musil, J. Vlcek, Thin solid films (April), 104 (2000).

[8] S.A. Shirjaev, M.V. Atamanov, M.I. Guseva, Yu.V. Martinenko, A.V. Mitin, V.S. Mitin, P.G. Moskovkin, *Perspektivnie materiali,* No. 3, 67 (2002).

[9] D.B. Shtansky, E.A. Levashov, V.I. Kosianin, N.B. Diakova, I.V. Liasotsky, *Phizika metallovi metallovedenie* **80,** No 5, 120 (1995)

[10] V.M. Savostikov, S.M. Sergeev, A.N. Tabachenков, *in: Proc. of 6$^{th}$ conference on modification of materials with particl beems and plasma flows.* 2002, pp. 606–609.

[11] Yu.H. Akhmadeev, S.V. Grigoriev, N.N. Koval., P.M. Schanin, Laser and Particle Beems **21**, No. 2, 249 (2003).

[12] A.D. Korotaev, A.N. Tyumentsev, Yu.P. Pinzhin, S.V. Ovchinnikov, N.N. Koval, I.M. Goncharenko, *in: Book of Abstracts of the Intern. Workshop "Mesomechanics: Fundamentals and Applications"* (MESO'2003) and the 7$^{th}$ Intern. Conf. "*Comp.-Aided Design of Advanced Materials and Technologies"* (CADAMT'2003), 2003, pp. 101–102.

[13] A.I. Ryabchikov, N.N. Koval, I.B. Stepanov, I.M. Goncharenko, I.A. Sivin, I.A. Ryabchikov, I.A. Shulepov, "Formation of wear-resistant TiN and TiAl coatings using DC filtered vacuum arc plasma", Presented at *7th International Conference on Modification of Materials with Particle Beams and Plasma Flows*, Tomsk, Russia, 2004.