The Effect of Copper Content in Sputtered Powder Cathodes on the Characteristics of Vacuum Arc Nanostructured Coatings[1]

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Abstract – This paper presents results of investigation of nanostructured coatings, synthesized by vacuum arc sputtering of composite Ti-Cu system cathodes. The composite cathodes were produced by sintering of powder mixtures containing from 5.5 to 12 at % Cu.

1. Introduction

In recent years nitride coatings, deposited from multicomponent plasma, which includes metal (Ti, Al, Zr etc.), non-metal (Si, B, C) and nitrogen ions have been intensively investigated. Nitride Ti-Si-N, Ti-Cu-N, Ti-Al-N, Ti-Al-Si-N system coatings are of great interest. High hardness of these coatings [1, 2] combines with thermal stability and reduced coefficient of dry friction in contact with steels [3, 4]. The effect of improved properties of nitride coatings with doping of silicon are explained by formation of thin amorphous films on growing TiN crystallite surfaces. The films suppress the column growth and result in a grain size reduction to a few nanometers. Due to nanocrystallite structure coating hardness increases up to twice compared with that of coatings deposited from plasma composed of only titanium and nitrogen ions. The same effect of hardness increase is observed for coatings deposited from plasma including some metal ions (Cu, Ni, Y etc) which are nonreactive with nitrogen.

In the papers [5–7] Ti-Cu-N coatings deposited from multicomponent plasma generated by vacuum arc sputtering of cathodes with different phase and chemical compositions are investigated. Three versions of multicomponent plasma synthesis were used concurrent sputtering of titanium and copper cathodes, sputtering of the mosaic cathode [6] and sputtering of the cathode obtained by sintering of titanium and copper powders. The application of sintered powder cathodes was substantially found to improve the coating characteristics compared with coatings deposited by other methods such as sputtering of the cathodes contained macroscopic regions of pure copper. It was found that during sputtering of the powder cathode with high (30 at.%) copper contents a lot of microdroplets were deposited on the substrates due to reduced melting temperature of cathode material.

The goals of the present work were comparable investigation of vacuum arc coatings deposited by sputtering of sintered powder cathodes with different copper contents and also investigations of microstructure and properties of sputtered cathode material.

2. Experimental technique

Copper (<100 μm) and titanium powders with different dispersion (<45 μm and <160 μm) were used to prepare the powder mixtures. Composite Ti-Cu system cathodes were made by conventional technology of powder metallurgy: preparation of metal powder mixture with given composition, cold pressing and vacuum sintering. Sintered cathode sections were soldered to titanium sections to provide the effective heat-removal. The effect of sintering temperature on the volume variations, microstructure and hardness was investigated by using powder mixture composed of fine titanium powder. Coating synthesis was carried out on special-purpose vacuum ion-plasma setup in arc low-pressure discharges. The main components of the multicomponent plasma generation were an arc evaporator (source of metal plasma from cathode spot) and a gas-discharge plasma source based on non-self-sustained arc discharge [8]. Concurrent operation of both sources in the same range of the gas pressure ($\sim 2^{-3} \cdot 10^{-3}$ Tor) allows to increase the effectiveness and the rate of plasma-chemical reactions during the coating condensation owing to increase of ion gas fraction. The samples made of austenite steel SUS 302 and hard alloy WC-8%Co were used as substrates. Structural investigations were performed by a metallographic mic-

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roscope (MIM-9, Russia), a scanning electron microscope (SEM 515 Philips) and a contact–free profilometer (Micro Measure 3D Station, CSEM Instruments). Thickness of deposited coatings was measured by a calotest method (Calotest, CSEM Instruments). Coating hardness was determined by a microhardness tester (PMT-3, Russia) under normal load of P_n=500; 1000 mN and a nanohardness tester NHT-S-AX-000X under normal load of P_n=50 mN. Adhesion investigations of coating-substrate system were performed by means of scratch test method (Micro-Scratch Tester MST-S-AX-000, CSEM Instruments) with following parameters: indenter radius – 20 μm; increasing load in the range of 0,1–10 N; scratch length – 10 mm; loading rate – 10 N/min.

3. Results and discussion

3.1. Preparation and investigation of powder cathodes

There are difficulties of the preparation of pore-free sintered materials from titanium and copper powder mixture due to complication of equilibrium diagram of binary system (Fig. 1). According to available literature, titanium and copper form 4–6 intermetallic compounds. Four or five of them are stable at room temperature. There are four phases: two solid solutions (based on α-Ti and β-Ti), Ti_2Cu compound and liquid in the investigated range of concentration (up to 20 at.% Cu). In the general case any one of the compounds stable at the sintering temperature can grow in a diffusion zone. However, in accordance with the previous investigations [6] sintered alloys (up to 30 at.% Cu) consist of the only two phases: α-Ti and Ti_2Cu.

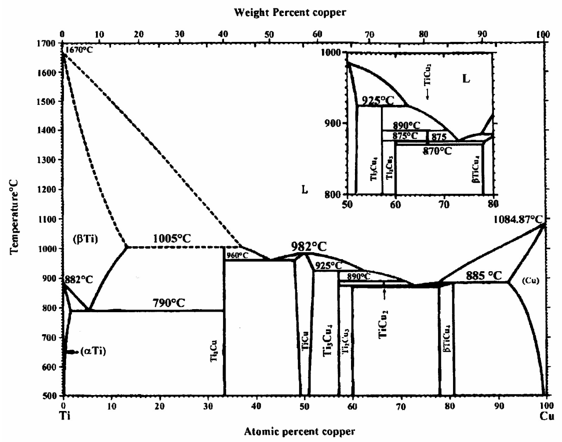

Fig. 1. Equilibrium diagram of Ti-Cu system [9]

Analysis of the volume variations during sintering of powder Ti-Cu mixture reveals the extreme character of shrinkage (Fig. 2) versus copper concentration in the range of 0 – 20 at. %. At the sintering temperature about 950–1100 °C the stable maximum of shrinkage is observed at 5.5 at.% Cu content. On the equilibrium diagram, this composition corresponds to the point of eutectoid decomposition of β-solid solution. Appearance of the shrinkage extremum in two-phase region during solid-phase sintering of double system was reported earlier [10]. Moreover, the maximum and the minimum of the shrinkage were usually observed in the case of eutectoid type system and system with peritectic decomposition correspondingly. There is not a simple and logically relevant explanation of this effect. The monotone reduction of the shrinkage was observed at all investigated sintering temperatures in the range of copper concentration 5.5–20 at. %. The volume effect depends on the sintering temperature for the composition with 30 at. %Cu content. At sintering temperature 950 °C swelling takes place instead of shrinkage, but increase of sintering temperature up to 1000 °C results in the high shrinkage. This fact is explained by decomposition of Ti_2Cu compound and appearance of liquid phase. At the existence of liquid phase the compaction possibility arises under the action of capillary forces with the aid of particle transposition.

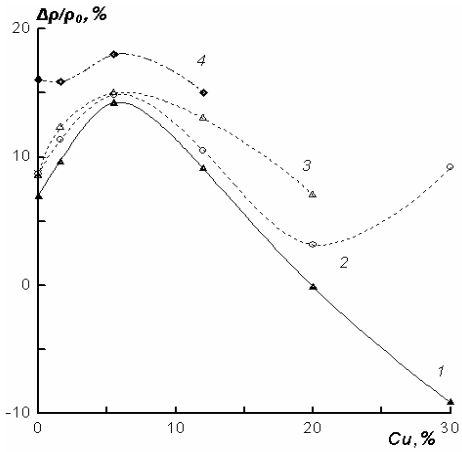

Fig. 2. Volume changes of Ti-Cu compacts sintered at 950 (1); 1000 (2); 1050 (3) and 1100 °C (4) versus copper content

Investigation results of volume changes during sintering (Fig. 2) were used to select the technological regimes of cathode sintering.

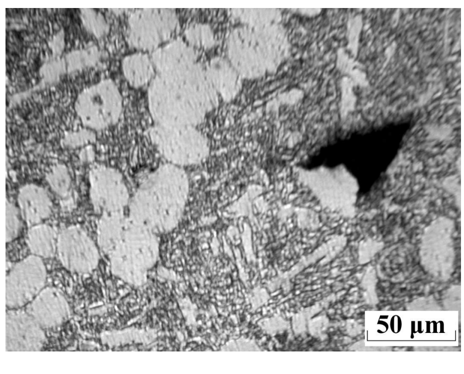

Fig. 3. Microstructure of powder compact Ti-9 %Cu cathode sintered at 1150 °C for 60 min

Typical microstructure of sintered cathode material is illustrated in Fig. 3. It includes circular grains of Ti_2Cu compound with a size of 30–50 μm and eutectoid mixture of Ti_2Cu compound inclusions of different shapes and sizes in the matrix of α-Ti solid solution.

A less expensive coarse Ti powder was used for sintering of the cathodes. Therefore the porosity of the cathode material was higher than that of sintered experimental specimens with a fine titanium powder. In Table 1 data of sintering temperatures TS and some properties of sintered cathode materials for three investigated compositions are listed. There are also presented approximate melting temperature T_L of given cathode compositions as an additional information.

Table 1. Characteristics of the sintered cathodes

Cu content, at.%	T_L	T_S	Residual porosity, %	Hardness HB, MPa
5,5	1350	1150	18,6	915±23
9,0	1150	1150	16,7	988±25
12,0	1050	1050	18,7	990±69

3.2. Coating deposition and investigations of their properties

Coating depositions were carried out using one of the composite Ti-Cu system cathodes: Ti-5.5 %Cu; Ti-9 %Cu; Ti-12 %Cu. Just before coating deposition the specimen surfaces were cleaned by argon ions from oxide films and adsorb gases. Due to ion bombardment, surface layers of samples were activated to provide a high adhesion between the coating and the substrate. During the stage of treatment the substrates were heated up to 300 °C. Prior to the condensation of nitride coating the deposition of sublayer from cathode material in plasma obtained by sputtering of the metal in the cathode spot of arc discharge argon plasma was performed during 5 min. After formation of transition layer with thickness of ~100 nm argon was substituted to reactive gas nitrogen. During the substrate cleaning, activation, sublayer and multicomponent coating formations the process parameters such as U_b, I_d, p were kept constant for all of sputtered composite Ti-Cu cathode. Discharge currents of plasmagenerator and arc evaporator, pressure of employed gas and energies of ions arrived at the substrates were selected via following reasons:

1) Formation processes of coating thickness should predominate over sputtering processes of growing coating;
2) Coating growth rate should be higher than 1 μm/h;
3) Number of microdroplets generated by cathode spot on the cathode surfaces should be minimum at given growth rate of coating;
4) Combination of deposition parameters should provide coating formation with composition close to stoichiometric TiN coating.

During 120 min under given current of arc evaporator (50 A) and bias voltage U~300 V TiN type coating with thickness ~2,5 μm were formed on the substrates (Fig. 4).

By transmission electron microscopy it was found that the coatings deposited by sputtering of the composite Ti-Cu system cathodes had nanocrystalline structure with a grain size in rage of 10–15 nm [7].

Investigations of cross-section fractures by scanning electron microscopy has shown that all coatings with uniform thickness are dense and pore-free.

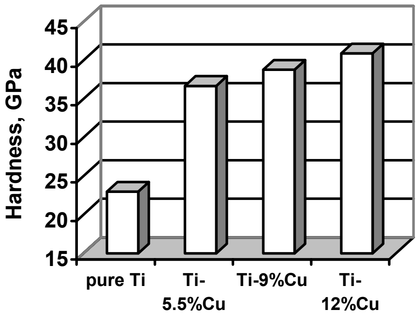

Fig. 4. Coating hardness as a function of Ti-Cu cathode composition

It was observed that increase of copper content in sintered cathode composition used for coating formations results in increase of coating hardness (Fig. 4, 5). It was determined that the maximum hardness (HV=40,881 GPa) belongs to coating deposited by sputtering of Ti-12 %Cu cathode. Reduction of copper content to 9 % results in negligible decrease of coating hardness even to ~38 GPa. Further copper reduction to 5.5 % leads to consequent hardness decrease to ~36 GPa, although that value is higher approximately 10 GPa than that of conventional TiN coatings (~20–25 GPa).

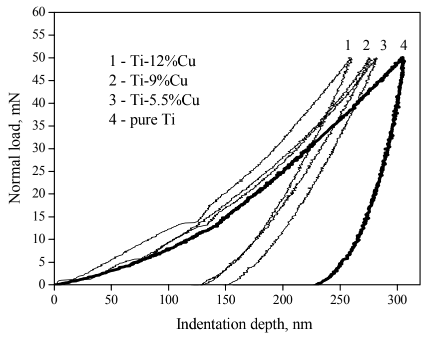

Fig. 5. Nanoindentation load-displacement curves for Ti-Cu-N coatings deposited using 1) Ti-12 %Cu; 2) Ti-9 %Cu; 3) Ti-5.5 %Cu cathode in the arc discharge plasma

It was obtained that doping even negligible copper content assists to sharp increasing of coating hardness. It should be pointed that the use of the cathode with ~30 % copper content [6, 7] results in coating formation with porous structure and relatively low hardness (≤22) approaching to that of conventional TiN coatings.

On loading-unloading curves (Fig. 5) it was observed that all nanostructure coating types possess the same compliance extent ~50 % at their different hardness whereas microstructured TiN type coatings are more plastic (residual deformation 75,5 %). Hence, doping of insignificant copper content into cathode composition affects not only on hardness but on the extent of elastic recovery of deposited coatings.

Investigations of adhesion characteristics have shown that destruction of coating obtained by the sputtering Ti-Cu system cathode took place under approximately equal critical load (Table 2).This is indirect evidence of the same adhesion with substrate for all coatings. The destruction of conventional TiN coating occurred under the same test conditions but under lower critical load. This fact indicates that copper doping into cathode composition affects to structure formation and adhesion properties of coatings.

Table 2. Characteristic critical load values for TiN and Ti-Cu-N coatings

Cathode composition	Normal critical load Lc, N
Ti-12 %Cu	6,015
Ti-9 %Cu	5,300
Ti-5.5 %Cu	5,896
pure Ti	3,550

Special feature of arc discharge deposition is the presence of microdroplets fraction. It is known that microdroplet number and size depend on melting temperature of cathode. Investigations performed by scanning electron and optical microscopies show that difference between microdroplet number on surface of coatings obtained by composite cathodes with different copper content and different melting temperature lies in the range of the error of the measure test.

The analysis of roughness profiles of surfaces for all Ti-Cu-N coatings determined that the average roughness of coatings deposited by sputtering of Ti-9 %Cu and Ti-12 %Cu cathodes is approximately the same and equal R_a~0,07 μm. In case of Ti-5.5%Cu cathode average roughness is insignificantly lower and equal R_a~0,06 μm. This fact can be explained by relatively low discharge current (50 A) close to threshold current of stable arc discharge burning with the use of the titanium cathode (~20 A).

4. Conclusion

1. Sintered powder cathodes Ti-Cu can be used successfully for vacuum arc sputtering of nanostructured coatings with improved properties.
2. Nanostructure Ti-Cu-N coatings can be deposited by arc discharge deposition using composite Ti-Cu system cathodes with different Cu contents;
3. Nanostructure Ti-Cu-N coatings have advantages in mechanical properties and industrial application perspectives over traditional microstructure TiN coatings.

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