The Mechanisms of Nanocrystal Nitride Films Deposition by Arc Spattering of Composite Cathodes. II. Structure, Phase Content and Mechanical Properties of Coating[1]

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Abstract – For research into phase content, structure and mechanical properties of a film deposited by electro-arc plasma assisting spattering of composite cathodes T-30%Cu and Ti-12%Cu in nitrogen medium the following methods were used: metallography, scanning and transmission diffraction electron microscopy, microhardness analysis. It has been revealed that regardless of substrate material the titanium nitride film of nanocrystal structure with average crystallite size of –10 nm is deposited. Microhardness of the film considerably depends on cuprum content in cathode and when spattering Ti-12%Cu target microhardness could reach its maximum level (~ 50 GPa). The barrier effect is considered one of the reasons of a film nanocrystal structure. This effect is caused by cuprum and impurity atoms (oxygen, carbon) location on the surface of growing titanium nitride crystallites section.

1. Introduction

Present paper describes the results of experiments aimed at identifying the rules of structure formation as well as formation of phase and elemental composition, identifying the mechanical properties of titanium nitride films (containing cuprum atoms and without them) deposited on the hard substrate using the methods of vacuum electro-arc coating of composite Ti–Cu cathodes with nitrogen plasma assisting.

2. Materials and Research Methods

The films deposited by electro-arc plasma assisting cathode spattering in nitrogen medium were used as a material of the research. The film was deposited in plasma of arc discharge with heated cathode. The compositional multicomponent Ti-30%Cu and Ti-12%Cu cathodes made from metal powders were spattered. Before coating the substrate surface (hard alloy WC-8%Co and stainless steels (SS) type SUS304 was polished mechanically and applying electrolytic method, organic impurities were removed in ultrasonic bath. Cathodes were spattered in ionized nitrogen medium. Deposited films were analyzed using methods of optical, scanning and diffraction electron microscopy of thin foil, secondary ion mass-spectrometry. Mechanical properties of the film were tested by measuring microhardness.

3. Research Results and Discussion

Mechanical properties testings has revealed that nitride film deposited by both cathodes spattering has super high microhardness about 52–55 GPa. For comparison, the microhardness of nitride film deposited by titanium cathode spattering comes to 23–25 GPa.

Morphology of a film deposited on hard alloy was analyzed applying methods of optical of scanning electron microscopy. The surface of the deposited film and structure of its transverse section were tested.

Structure and morphology of the film surface were analyzed applying the method of scanning electron microscopy (Fig. 1). It has been determined that despite the cuprum concentration in cathode (12 and 30%) and despite the substrate position in regard to direction of plasma flow dissemination (whether substrate is placed in parallel with or at right angle to the plasma flow), the continuous film is formed which contains some amount of drop fractions.

Drops quantity considerably depends on cuprum content in cathode and on substrate position in regard to direction of plasma flow dissemination. Drops quantity on the surface of a film deposited by Ti–12%Cu cathode spattering is considerably less than on the surface of a film deposited by Ti–30%Cu cathode spattering (Fig. 1). At the same time in the last case the film has gradient structure, i.e. the layer adherent to the substrate surface is uniform but the more remote film layers are less uniform, and the top layer is of

[1] The work was supported in part by Siberian Branch of Russian Academy of Sciences under Integration project No. 7 for 2003–2005 years period and by CRDF in the framework of BRHE program (project No. 016-02) Research-education center “Physics and Chemistry of high-energy system”.

high-porous structure due to drop particles (Figs. 1,c,d and 2,a). If compare surface images presented in Fig. 1,a,b it becomes evident that films deposited on substrate which is located in parallel with direction of plasma flow dissemination contains less number of drop particles while the drops size is less than of "front" coatings.

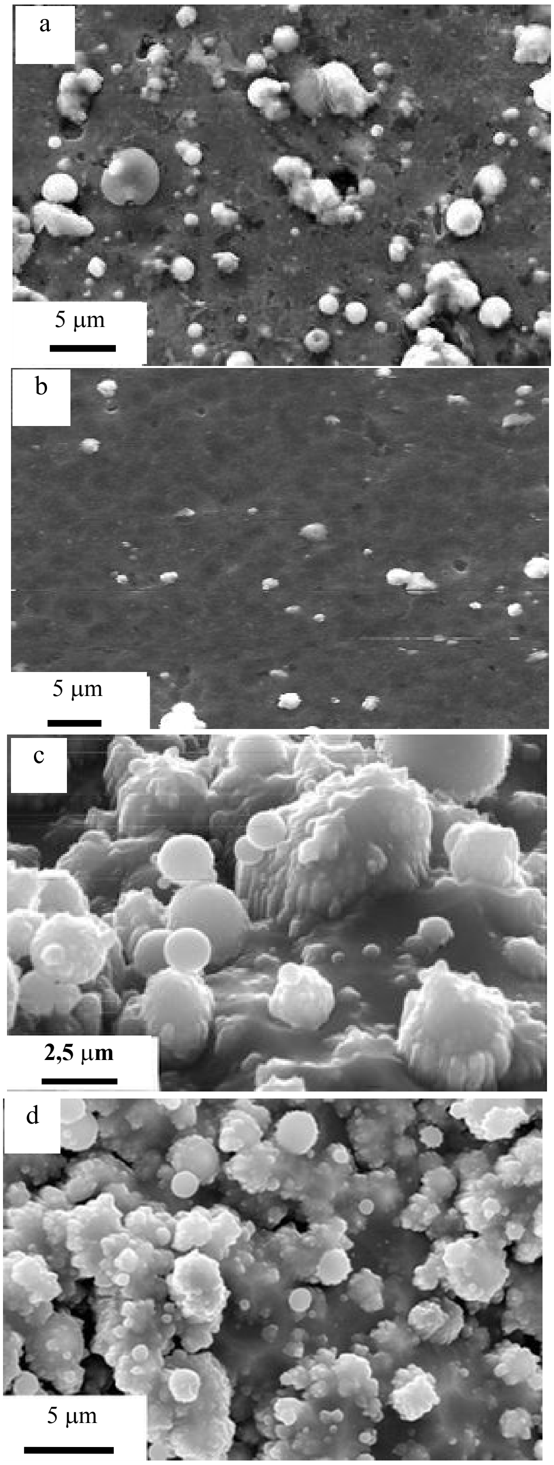

Fig. 1. SEM image of Ti–Cu–N film surface; a, c – substrate is placed at right angel to, b, d – in parallel with plasma flow. Cathode Ti-12%Cu (a, b) and Ti-30%Cu (c, d)

Film surface analysis has showed the complex structure of a film. Micro photos in Fig. 2 demonstrate that the film consists of round shape crystallites which size varies from 50 up to 100 nm. Diffraction electron microscopy analysis has revealed that crystallites have the substructure of nanometer range.

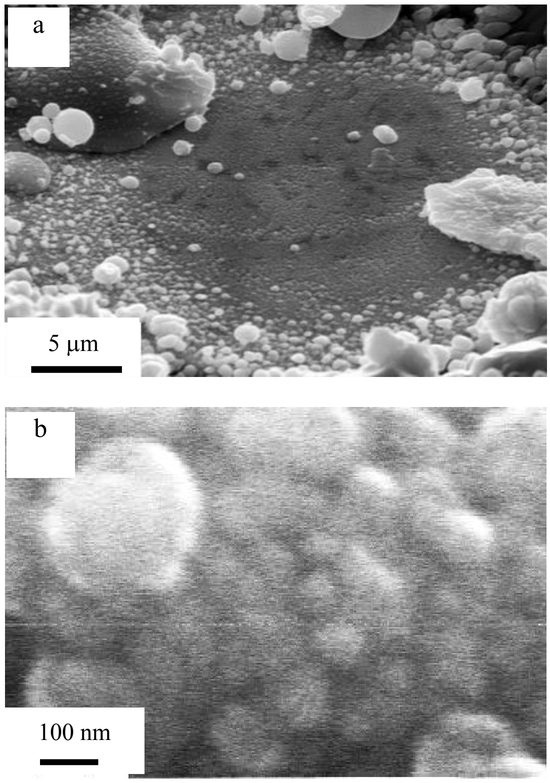

Fig. 2. SEM image of Ti–Cu–N film surface. Cathode Ti-30%Cu

Film thickness and its structure were analyzed at to break down. Chips were prepared by brittle failure of a substrate with deposited film. It has been determined that thickness of a film deposited on the substrate placed in parallel with the direction of plasma flow dissemination is approximately three times less than thickness of a film deposited on a "front" substrate (Fig. 3). At the same time the films formed when spattering cathode made from Ti-30%Cu alloy have more evident substructure (Fig. 4).

Intercrystallite substructure and phase content of a film were analyzed by methods of diffraction electron microscopy of thin foils. It has been revealed that when spattering composite Ti–Cu cathodes on the substrate made from stainless steel type 304 and hard alloy WC-8%Co the deposited film obtains nanocrystal structure with crystallites of 10–15 nm. The typical electron microscope image of such film is shown in Fig. 5. In some cases the growth texture is of columnar structure. But in this case, the columnar structure has nanocrystal structure. Micro diffraction analysis and the consequent indicating of diffractions pattern has showed that the film is made from titanium nitride of TiN composition.

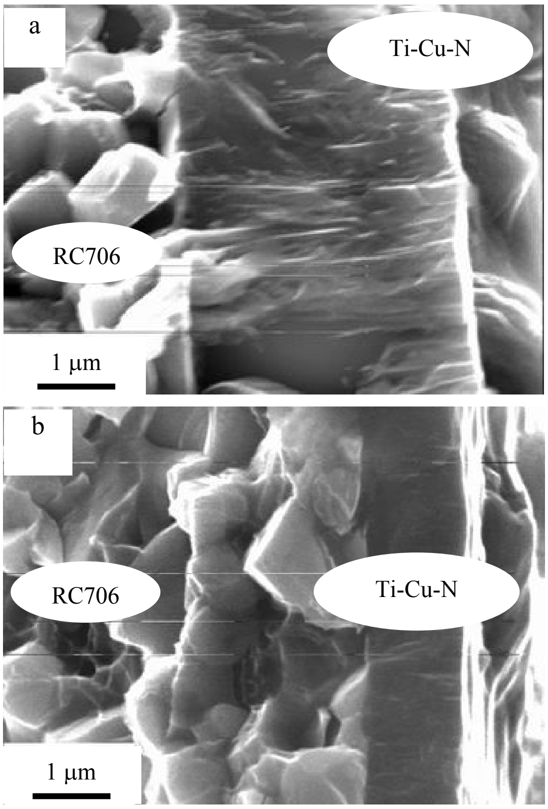

Fig. 3. SEM image of WC-8%Co hard allow chip section with Ti-Cu-N film; a – substrate is placed at the right angel to, b – in parallel with plasma flow. Cathode Ti-12%Cu

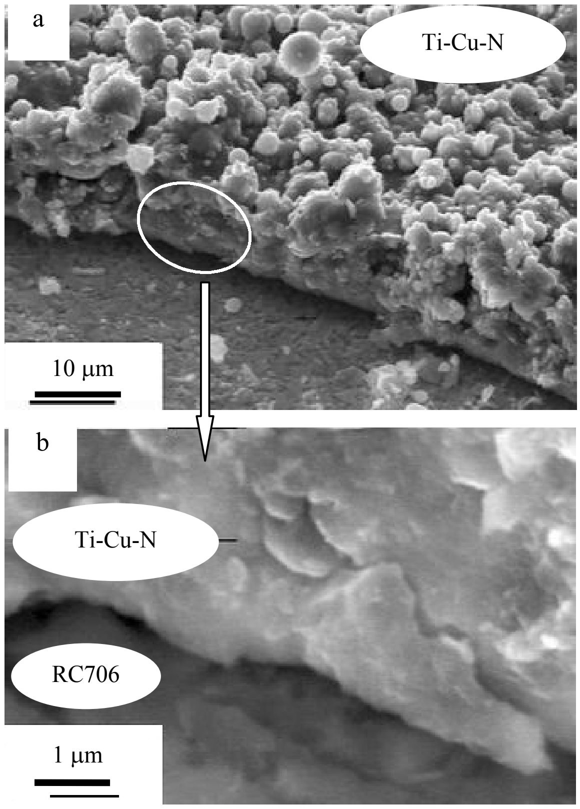

Fig. 4. SEM of Ti–Cu–N film on hard alloy, a – substrate is placed at the right angel to, b – in parallel with plasma flow. Cathode Ti-30%Cu

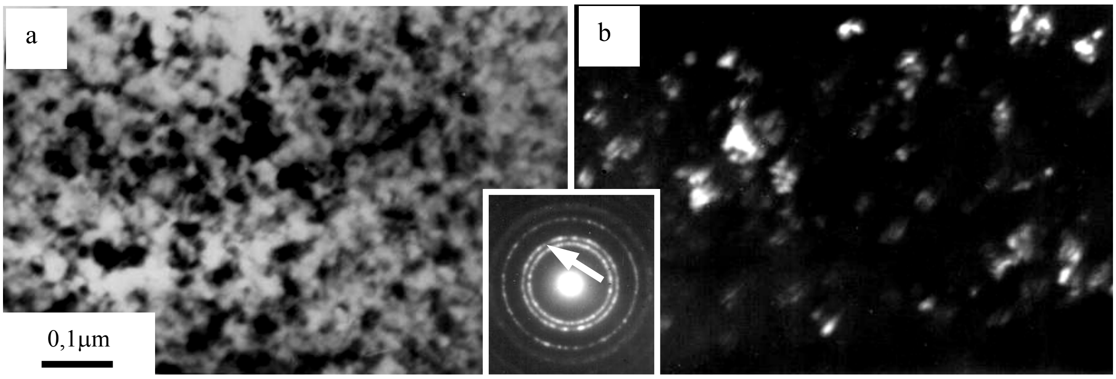

Fig. 5. Transmission electron microscopy image of film structure deposited on stainless steel type 304 by Ti-30% Cu cathode spattering; a – white field; b – dark field obtained in reflex of (111) TiN type; diffractions pattern (arrow marks dark field reflex)

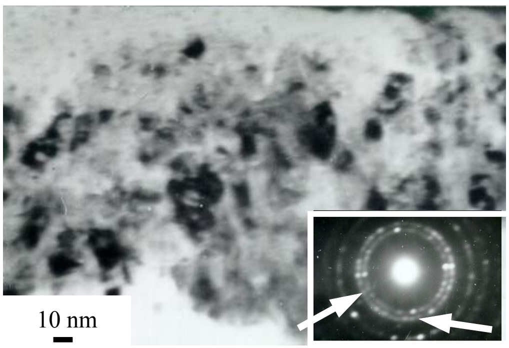

Fig. 6. Transmission electron microscopy image of the film structure after 6 months aging at indoor temperature. Ti-30%Cu cathode is used. diffractions pattern (arrow marks <111> cuprum reflexes)

Using the method of electron microscopy cuprum has not been found as crystallites able to cause revealing of their own reflexes on diffractions pattern. Coatings aging at indoor temperature for 6 months leads to complication of diffractions pattern such as cuprum reflex (Fig. 6). It means that newly deposited film contains cuprum in amorphous state presumably along the titanium nitride crystallite boundary. Such cuprum deposition could be one of the most significant mechanisms of the inhibition of crystallite growth that causes nanostructure state of a film.

Films aging causes cuprum crystallization that is reflected at diffractions pattern images. diffractions pattern (Fig. 6) analysis has revealed that image reflects not only diffraction fringes of titanium nitride lattice but also separate drops of cuprum reflexes. These results have proved the statement that cuprum at the time of film deposition is in amorphous state and most likely forms thin films.

3. Conclusion

Research made applying methods of optical, scanning and diffraction electron microscopy has lead to the following conclusion:

– composite Ti–Cu cathode spattering in ionized nitrogen medium allows forming multilevel nanocrystal coating based on titanium nitride of TiN composition;

– film thickness and quantity of drop fractions in other equal conditions are increased while changing Ti-12%Cu cathode to Ti-30%Cu cathode, and while changing horizontal position to frontal position;

– one of the mechanisms of forming nanocrystal structure of a film is to replace cuprum atoms at the front of growing titanium nitride crystallites and with consequent forming of amorphous layers. Amorphous layers are an effective barrier at the stage of coagulation of titanium nitride crystallites.

References

[1] G.A. Pribitkov, E.N. Korostelyeva, S.G. Psahjye et al., "The mechanisms of nanocrystal nitride films deposition by arc spattering of compositional cathodes. I. Structure, phase content and mechanical properties of a film", presented at *13th Symposium on High Current Electronics*, Tomsk, Russia, 2004.