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Effect of Cu Content on TiN-Cu Nanocomposite Film Properties: Structural and Hardness Studies

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Abstract

Titanium nitride-Copper (TiN-Cu) nanocomposite films were deposited onto stainless steel substrate using hollow cathode discharge ion plating technique. The influence of Cu content in the range of 2-7 at.% on the microstructure, morphology and mechanical properties of deposited films were investigated. Structural properties of the films were studied by X-ray diffraction pattern. Topography of the deposited films was studied using atomic force microscopy. Film hardness was estimated by a triboscope nanoindentation system. However, X-ray photoelectron spectroscopy analysis was performed to study the surface chemical bonding states. It was found that addition of soft Cu phase above 2 at.% to TiN film drastically decreased the film hardness from 30 to 2.8 Gpa due to lubricant effect of segregated copper particles. X-ray photoelectron spectroscopy results showed that Cu and TiN phases grew separately. In our case,the formation of a solid solution or chemical bonding between Cu and Ti was rejected.

1. Introduction

In the recent years, hard nanocomposite films have attracted much attention for protection of materials and particularly to enhance the life time of cutting tools [1]. They usually represented by nc-MeN/soft symbol in which Cu, Ni, Y, Ag, etc are soft phase and Me indicates metals of Ti,W, Zr, Cr, Mo, Al as a hard phase.

In addition, the mechanical properties of a material basically depend on binding between the atoms and the lower probability of movement of dislocations. A change in the interatomic interaction energy is achieved by chemically mixing different ratios of different atoms, which makes it possible to create a broad range of alloys and compounds with considerably improved properties [2]. TiN thin film has been widely investigated for wear resistant [3]. As reported, the hardness of TiN films could be significantly increased by addition of the copper below 2 at% concentration in the TiN matrix[4]. These nanocomposite films have been widely prepared using the various methods [5-8].

In this study, TiN-Cu nanocomposite films were deposited using the hollow cathode discharge ion plating (HCD-IP) technique. The effects of Cu content ranges between 2-7 at% concentration on the structure and mechanical properties of TiN-Cu nanocomposite films were investigated.

2. Materials and Methods

Titanium nitride-Copper (TiN-Cu) nanocomposite films were deposited onto polished and ultrasonically pre-cleaned AISI316 stainless steel substrate (1×1×0.5 cm^3) using HCD-IP technique under the experimental conditions at 350 °C (Table 1).

Table 1. Deposition conditions of (TiN-Cu) nanocomposite films.

Bias Voltage (V)	Working Pressure (Pa)	Ar /N_2 (Sccm)
-30	7×10^{-2}	25/1

The substrates were immediately inserted into a vacuum chamber for deposition. The materials (titanium and copper granules) were placed in a graphite crucible. Different amounts of Cu granules were loaded in the crucible containing Ti granules. Then they were evaporated by an electron source. The evaporated elements reacted with nitrogen gas in plasma and then deposited as a compound film on the substrates with various Cu contents. After deposition, microstructure of the deposited films was studied by X-ray diffraction analysis (H2E-STOE-Germany, STIDY-MP model). The morphology and topography of the films were examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Film hardness was estimated from the unloading curve using a triboscope nanoindentation system. X-ray photoelectron spectroscopy (XPS) was performed to study the surface chemical bonding states. The Cu content (at.%) of the TiN-Cu nanocomposite films was determined by energy dispersive spectroscopy (EDS).

3. Results and discussion

The copper content of the films is estimated by EDS analysis to be 2.0, 3.3, 5.9 and 7.0 at. % . Fig. 1 shows typical EDS spectrum of the TiN-Cu nanocomposite films with Cu content of 5.9 at.%.

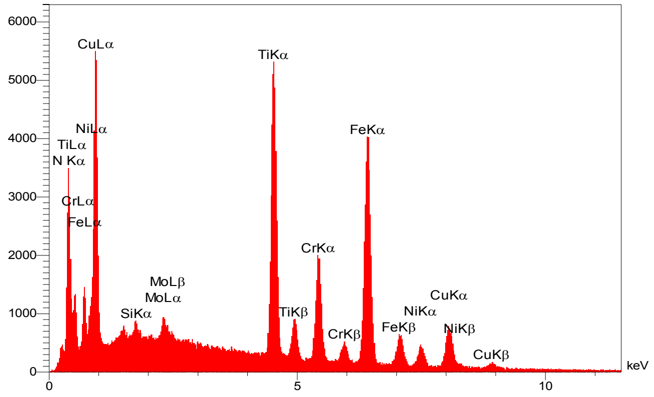

Fig. 1. Typical EDS spectrum of TiN-Cu nanocomposite film with 5.9 at.% Cu content.

It should be noted that the Cr, Ni, Mo and Fe peaks are related to the stainless steel substrate. However, EDS results of all samples are tabulated in Table 2.

Table 2. Composition of TiN-Cu nanocomposite films with different Cu contents.

Sample	Cu Content (at. %)	Ti content (at. %)	N content (at. %)
1	0	22.64	68.85
2	2.00	13.86	68.98
3	3.33	14.14	67.74
4	5.90	10.49	59.33
5	7.00	11.33	61.20

The XRD patterns of the TiN-Cu nanocomposite films with different Cu contents are depicted in Fig.2. All films have diffraction peaks assigned to cubic TiN (B1-NaCl type structure) in addition to the substrate peaks.

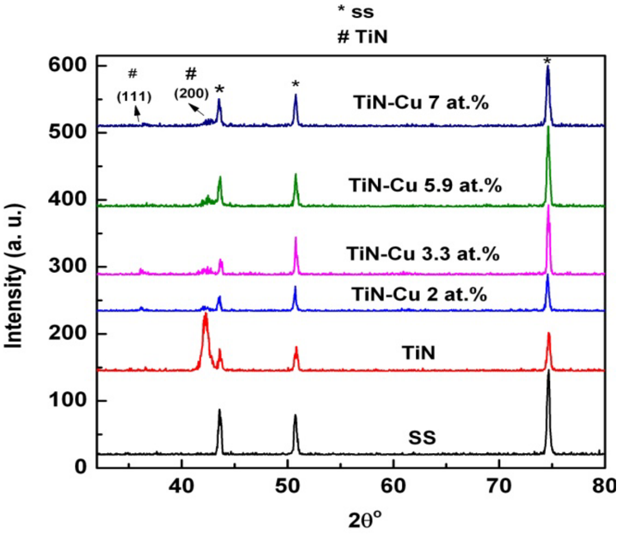

Fig. 2. XRD patterns of TiN-Cu nanocomposite films containing different Cu contents.

The absence of Cu peaks indicates amorphous state or very small crystallite size of the Cu grains.

According to Fig. 2, increasing the Cu content decreases the crystalline character of TiN phase. It should be noted that no shift is seen in the position of the TiN peaks. Substitution of titanium or nitrogen atoms by copper in the TiN lattice is virtually ruled out because i) the interaction between titanium and nitrogen atoms is stronger than the interaction between Ti atoms and copper and ii) the formation of Cu-N bonds is impossible at 350 ^{o}C according to Ref[9-10]. Considering the sufficiently large radius of the copper atom as well as the above explanations, we can conclude that copper acts as an impurity in TiN film grain boundaries.

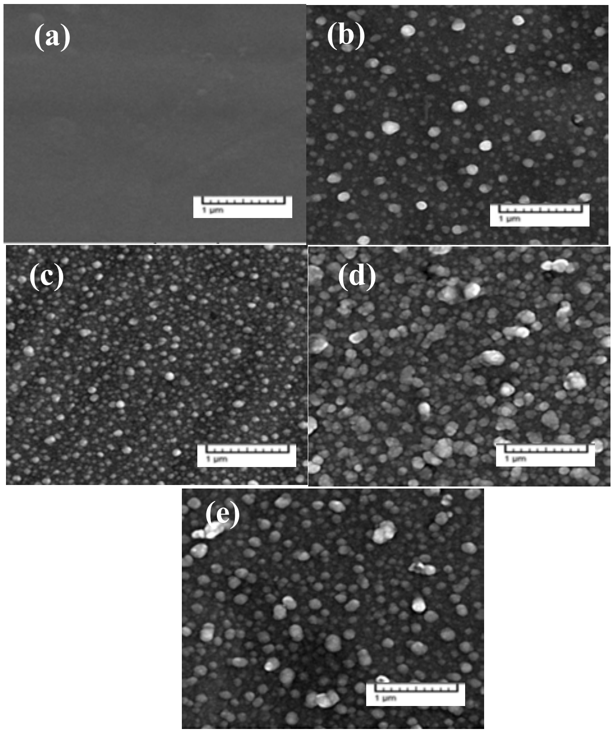

Fig. 3. SEM images of TiN-Cu nanocomposite films containing (a) 0, (b) 2, (c) 3.3, (d) 5.9 and (e) 7 at. % Cu contents

SEM micrographs of the samples with different Cu contents are shown in Fig.3. After addition of Cu, bright protrusions with hillock-like structure are appeared on the film surface. It leads to an increase of the surface roughness. EDS results of two different points of the surface (A and B points as shown in Fig. 4) are summarized in table 3. It is found that the bright grains (point A) contain high Cu concentration.

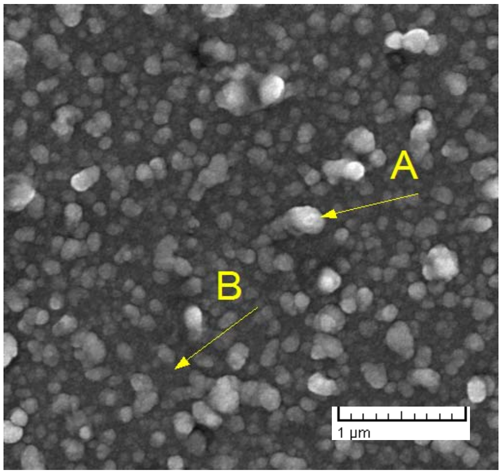

Fig. 4. EDS measurement in two different A and B surface points of the TiN-Cu nanocomposite film containing and5.9 at. % Cu content.

Table 3. EDS results in two different A and B surface points of the TiN-Cu nanocomposite film containing and5.9 at. % Cu content.

Elt		A%
N	**A**	64.46
	B	63.95
Ti	**A**	10.86
	B	10.51
Cr	**A**	2.35
	B	4.13
Fe	**A**	7.20
	B	14.46
Ni	**A**	0.91
	B	1.16
Cu	**A**	14.22
	B	5.80

The average of Cu grain size in different samples is listed in Table 4.

Table 4. Cu grain size estimated by SEM image at different Cu contents

Cu conten (at. %)	Average Grain size (nm)
2	70
3.3	112
5.9	136
7	140

The survey XPS spectrum of TiN-Cu nanocomposite film deposited at -30 V (Fig.5) clearly indicates presence of O 1s, C 1s, N 1s and Ti 2p bands on the surface. Presence of carbon and oxygen bands is related to environmental pollution of the surface. Deconvoluted N 1s, Ti $2p_{1/2}$, Cu $2p_{3/2}$ and Cu $2p_{1/2}$ XPS spectra of TiN-Cu nanocomposite film with 5.9 at.% Cu content are shown in Fig. 6. The N 1s peak (Fig.6a) is deconvoluted to the peaks at 396.3, 397.7 and 400 eV binding energies which are related to TiON, TiN and adsorbed atomic or molecular nitrogen, respectively.

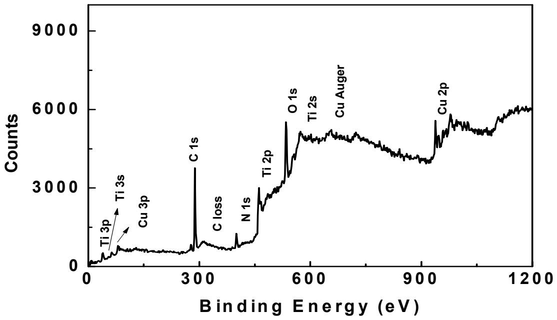

Fig. 5. The survey XPS spectrum of TiN-Cu nanocomposite film with 5.9 at.% Cu content deposited at -30 V

In Fig 6b the deconvoluted peak centered at 461 eV corresponds to Ti $2p_{1/2}$ of stoichiometric TiN [11], 457 eV to TiON [12], 458.4 eV corresponds to Ti $2p_{3/2}$ in TiO_2 compound [13].

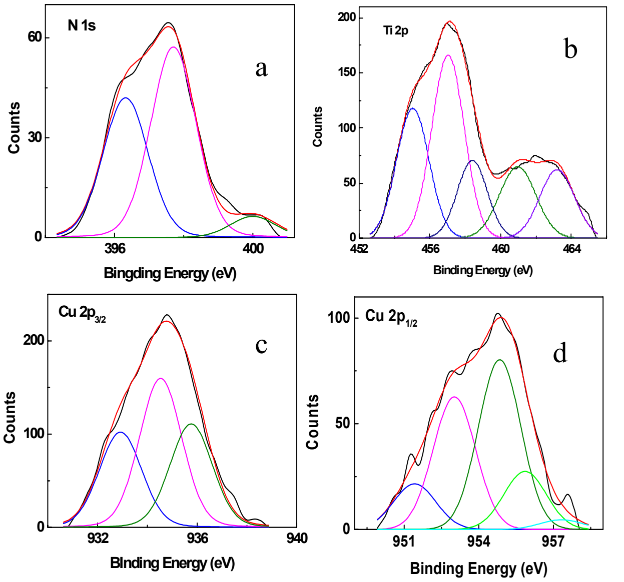

Fig. 6. XPS spectra of TiN-Cu nanocomposite film with 5.9 at.% Cu content d (a) N 1s, (b) Ti 2p and Cu (c) $2p_{3/2}$ and (d) $2p_{1/2}$ orbitals

The peak located at 455 eV belongs to binding energy of Ti $2p_{3/2}$ in re-oxidation process of TiO_2 during conversion to TiO [14]. The peak located at 463.2 eV is assigned to Ti atoms in Ti^{3+} oxidation state [15].

The Cu $2p_{3/2}$ peak (Fig.6c) is deconvoluted to peaks located at 933.2 (Cu^{2+} in CuO compound) [16], 935 (carbon bands in hydroxil groups) and 935.9 eV (Cu^{2+} in Cu-O band)[17].

The Cu $2p_{1/2}$ state (Fig.6d) is also deconvoluted to peaks located at 951.6 (Cu^{+}) [18], 953.3 (CuO) [19] and 955.5 eV (Cu^{2+})[20].

Fig. 7(a) shows the spin-orbit component of Ti $2p_{3/2}$ (samples with 5.9 and 7 at.% Cu contents). The Ti^{3+} peak results from Ti $2p_{3/2}$ peak deconvolution located at 457-458 eV is corresponding to pure TiN. Fig. 7(b) shows Cu 2p spectra at 935 and 955 eV for 5.9 and 7 at. % Cu contents. From this figure, no shift is seen in peak positions indicating the presence of separate metallic Cu and TiN phases on the surface [21].

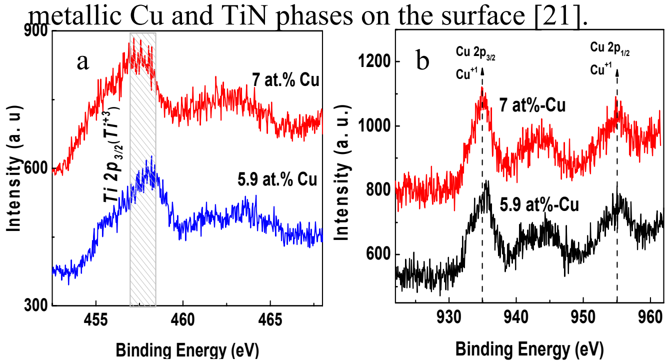

Fig. 7. XPS of TiN- Cu films with 5.9 and 7 at.% Cu contents (a) for Ti 2p and (b) Cu 2p .

As a result, it can be concluded that in our case, the TiN-Cu nanocomposite film are formed. Also, the peak located between two Cu $2p_{3/2}$ and Cu $2p_{1/2}$ as shake up-satellite peak is may be related to TiN K_{α} and Cu^{2+} $2p_{3/2}$ radiations.

According to the literature [5] metallic Cu can be distributed in the grain boundary region around the nitride grains.

Fig.8 shows hardness and elastic modulus as a function of Cu content. The hardness and elastic modulus of pure TiN is about 30 and 290 Gpa, respectively. It can be seen from Fig. 8 that film hardness drastically decreases to ~5 GPa with the increase of Cu content from 2 at.% up to 3.3 at.% and then becomes approximately flat. This result is in direct contradiction to what has been reported in Ref [4] when Cu amounts below 2 at.% were used. The soft Cu metallic phase plays a role of lubricant between the grains of hard phase at these concentrations. AFM image of the TiN film shows a smooth surface with roughness of 5.53 nm. With addition of Cu content surface roughness significantly increases to 46 nm because of metallic Cu growth .

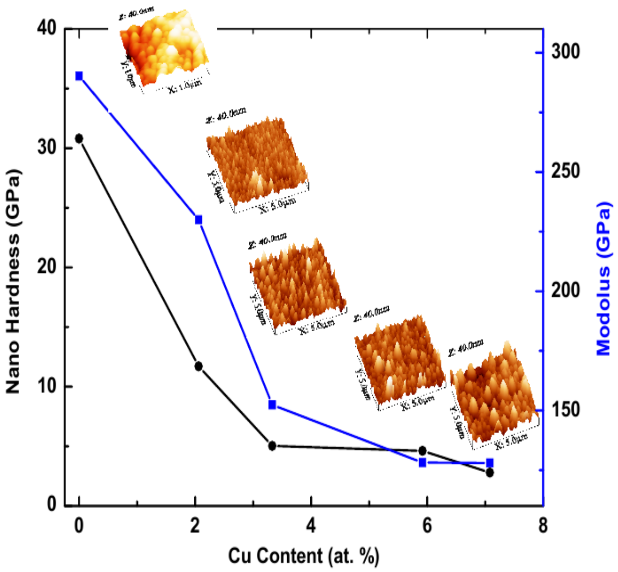

Fig. 8. Hardness,Young modolus and AFM images of TiN-Cu nanocomposite films as a function of Cu content

4. Conclusions

TiN-Cu nanocomposite films were deposited onto stainless steel substrate using hollow cathode discharge ion plating technique. The influence of Cu content in the range of 2-7 at.% on the microstructure and mechanical properties of the deposited films were examined. XPS results showed that Cu atoms were aggregated as metallic Cu in TiN matrix forming TiN-Cu nanocomposite films. Hardness of TiN film significantly decreased from 11.7 to 2.8 GPa with addition of Cu content above the 2 at.% concentration due to lubricant effect of copper particles.

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