

The effect of metal composition on the structure and properties of Ti-Cu-N superhard nanocomposite coatings

Hyun S. Myung, Hyuk M. Lee, Jeon G. Han

*Center for Advanced Plasma Surface Technology(CAPST),
Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu,
Suwon 400-746 Korea
E-mail : mhs0106@hanmail.net*

Abstract

Ti-Cu-N nanocomposite films deposited by arc ion plating and magnetron sputter hybrid system with various copper contents. The microstructure and mechanical properties of Ti-Cu-N superhard nanocomposite films depend on the Cu concentration. In X-ray diffraction (XRD) analysis, intensity of TiN (111) and TiN (220) peak decreased and peak broadness increased with increasing the copper contents and Cu peak was not detected. The grain size of films decreased with increasing at%Cu and Transmission Electron Microscopy (TEM) analysis also showed that Ti-Cu-N film containing 1.5at%Cu was composed of very fine ($< 10\text{nm}$) nanocrystalline grains.

The maximum hardness of Ti-Cu-N (1.5at%Cu) film reached to 45GPa and friction coefficient was measured 0.3.

1. Introduction

In recent years, the search for new superhard coatings is increasing considerably. Superhard coating means coating whose Vickers hardness exceeds 40Gpa. These new coatings can be classified into superlattice with alternating nano-layers of compatible materials such as TiN/WC, TiAlN/WC, TiN/NbN, TiN/TiB₂ and TiN/AlN etc.¹⁻⁵⁾ and nanocomposite (nc-) which is formed isolated nanocrystals in a thin amorphous matrix.⁶⁻¹¹⁾ Superlattice coatings are nanometer-scale multi-layers composed of two different alternating layers with a superlattice period λ , i.e. the bilayer thickness of two materials, ranging from 5 to 10nm and their properties are determined by the

superlattice period. The hardness H of these coatings varied from low values of about 20GPa to very high values, achieving up to 35~50GPa. However the maximum hardness of the superlattice coating is very strongly dependent on the superlattice period. The strong dependence of H on λ may cause large variations in the coating hardness H when deposited in industrial machines because it is difficult to ensure the same thickness of all superlattice layers on all coated objects, particularly when they have a complex shape. Similar variations in H can also be caused by the interdiffusion of elements in neighboring layers at high service temperatures. These problems can be avoided if the superlattice coating is replaced with a single-layer nanocomposite coating.⁶⁾

Two-phase nanocomposite coatings can be divided into two groups. One is nc-MeN/hard phase nanocomposite such as a-Si₃N₄ and a-TiB₂ etc. and the other is nc-MeN/soft phase such as Cu, Ni, Y and Ag etc.^{6, 7)} Here nc- and a- denote the nanocrystalline and amorphous phase, respectively, and Me = Ti, W, Zr, Cr, Mo, Al, etc., are elements forming hard nitrides.

In this study, using the arc ion plating and unbalanced magnetron sputtering method, we deposited nanocomposite films of Ti-Cu-N which composed of one hard and one soft phase, and investigated the relationship of their microstructure, film hardness and amount of Cu dopant.

The results confirmed that the hardness of TiN could be significantly improved by addition of the soft metal copper, provided that an appropriate amount was selected.

This paper reports the preparation, microstructure and mechanical properties of Ti-Cu-N nanocomposite films.

2. Experimental details

The films were synthesized using the cathodic arc ion plating and unbalanced magnetron sputtering hybrid method. The experimental conditions are listed in Table 1. The source materials were Ti and Cu, and were simultaneously evaporated and sputtered in nitrogen atmosphere.

The thickness of the coatings was kept to 1.5 μ m. Si(100) wafer and D2 steel substrates were used to characterize microstructure and mechanical properties, respectively. They were cleaned in acetone using the ultrasonic cleaning method.

Cu contents in the film were analyzed using EDS. XRD analysis was performed to evaluate the crystal structure and compounds formation behavior. The microstructures of the Ti-Cu-N nanocomposite films were observed using XTEM, and their crystal structures were analyzed in detail using electron diffraction patterns. Investigation of the microhardness was performed using a commercial nano-indentation instrument, Nano-indenter II developed by MTS instrument Co. With this instrument, the continuous stiffness method (CSM) which is applying a vibration of 45 Hz during the indentation process is possible. CSM enables us to measure the continuous microhardness of the film from initial depth of indentation to the final maximum depth of indentation. For each test indentations were produced in line at a constant interval of 30 μ m. The indenter tip was then moved to a new location and the process was repeated automatically until 10 measurements were made on a given specimen. Continuous loading-unloading indentations up to a load of 30mN were made. The wear tests were performed by the ball-on-disc test method using Al₂O₃ ball at normal loads of 6N.

Table 1. Deposition conditions for TiN and Ti-Cu-N coatings

Conditions	Substrate bias (V)	Ar partial pressure (torr)	Cu target power density (W/cm ²)	Treatment time (min.)
Ti ion precleaning	-700	3×10^{-3}	-	2
Ti interlayer coating	-200	3×10^{-3}	-	5
TiN buffer layer coating	-200	3×10^{-3}	-	5
TiN & Ti-Cu-N coating	-150	3×10^{-3}	0 ~ 7.2	60

3. Result and discussion

3.1 Chemical compositions and microhardness of Ti-Cu-N nanocomposite coatings

The correlation between Cu content and Cu target power density is shown in Fig. 1. The copper concentration increases with increasing the Cu magnetron target power density.

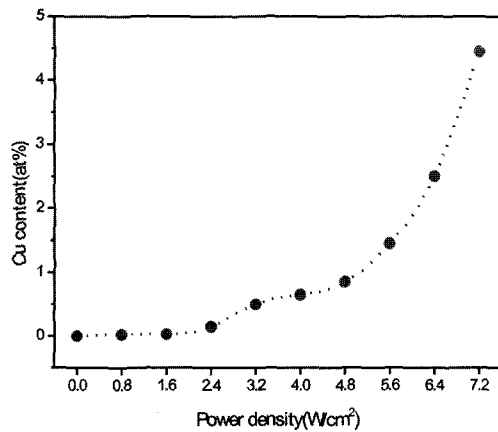


Fig. 1 Cu content of Ti-Cu-N as a function of Cu power density.

Fig. 2 shows the film hardness as a function of the copper content. The zero point represents the pure TiN. The microhardness increased slightly

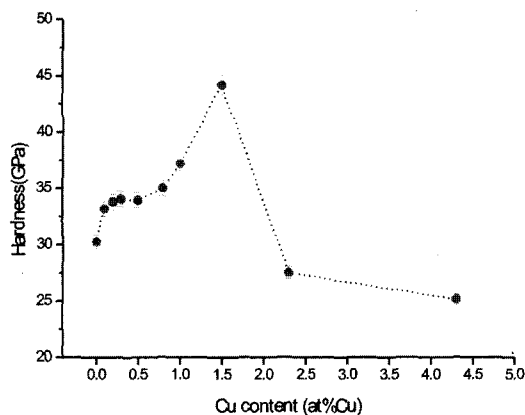


Fig. 2 Hardness of Ti-Cu-N films as a function of the Cu content.

with an increase the copper content up to about 1.0at%Cu. However, when the copper contents reach 1.5at%Cu, the microhardness of Ti-Cu-N film dramatically increases to approximately 45 GPa. This value is approximately 1.5 times higher than that of the TiN film. Out of this range, the hardness quickly dropped to much lower values with increasing copper content. This is similar to the results obtained by Musil et al. on Zr-Cu-N nanocomposites where the maximum hardness corresponds to the low Cu content of 1 ~ 2at%.¹⁰

The microhardness of Ti-Cu-N films with copper content ranging from 1.2 to 1.8 atomic percent is presented in Fig. 3. Ti-Cu-N film of 1.5at%Cu shows likewise maximum hardness value of about 45GPa. This should be considered as apparent hardness enhancement owing to addition of copper.

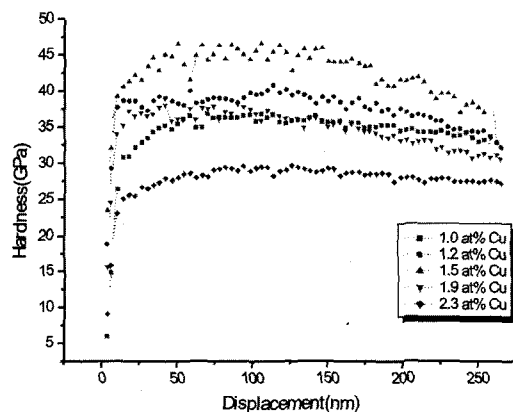


Fig. 3 Nanoindentation hardness of Ti-Cu-N films with various Cu content.

3.2 Structures of Ti-Cu-N films

Fig. 4 illustrates the XRD patterns of the deposited films. In the case of pure TiN, the film showed strong (111) orientation and the (220) peak was detectable. However TiN (220) peak disappeared and Cu(111) peak detected with in-

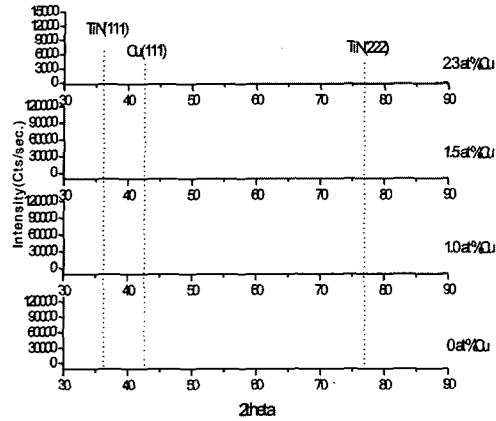


Fig. 4 The XRD patterns for TiN and Ti-Cu-N films

creasing copper content. Therefore, the film hardness was dramatically decreased over 1.5at% copper because soft Cu is easy to deform under external penetration.

Intensity of TiN(111) and TiN(220) peak decreases and peak broadness increases with increasing copper concentration. In this result, addition of copper is accompanied by reduction of grain size. Accordingly our XRD experiments show that Ti-Cu-N films with 1.5at%Cu can be supposed to exhibit nanocomposite phase with such a large hardness up to 45GPa.

3. 3 TEM observation

A cross sectional TEM micrographs of various TiN and Ti-Cu-N films are shown in Fig. 5. The crystal orientations of the TiN and Ti-Cu-N films are (111), (200), (220) and (222) orientations and TiN film without copper content is columnar structure, which consist of columnar grain of 25 ~ 30nm wide in the lateral direction. However it is clear that column propagation was interrupted by addition of copper and electron diffraction patterns were changed from spot pattern to ring pattern by increasing copper dopant.

Microstructure observations using HR-TEM were carried out for the Ti-Cu-N coatings with Cu content of 1.5at%. TEM bright field images with the selected area electron diffraction (SAED) patterns are presented in Fig. 6. The formation of nanocrystal composite is confirmed by the fine ring pattern of electron diffraction pattern and the nanocrystalline nature of the grains is revealed with a dispersion of grain sized between 8 and 10nm. From this results, it is suggested that the suppression of grain growth is associated with large induced strain in one of the biphasic can generate the superhard nanocrystalline composite by mixing process of mutual immiscible material.

3. 4 Wear test

Ti-Cu-N film with 1.5at%Cu showed low friction coefficient of about 0.3 after testing using the tribotester of ball-on-disc type against Al_2O_3 ball under no lubricant condition at atmosphere. However the TiN film represented abrupt increase in the friction coefficient as shown in Fig. 6. This abrupt behavior was attributed to failures of TiN film, creating microcracks across track in wear scar, as shown in Fig. 6.

4. Conclusions

1) Ti-Cu-N films showed high hardness as copper was added and the maximum hardness of 45GPa was obtained for Ti-Cu-N film synthesized at the 1.5at%Cu content. However, out of this range, the hardness quickly dropped to much lower values with increasing copper content.

2) TiN film showed strong (111) orientation and the (220) peak was detectable and TiN(220)

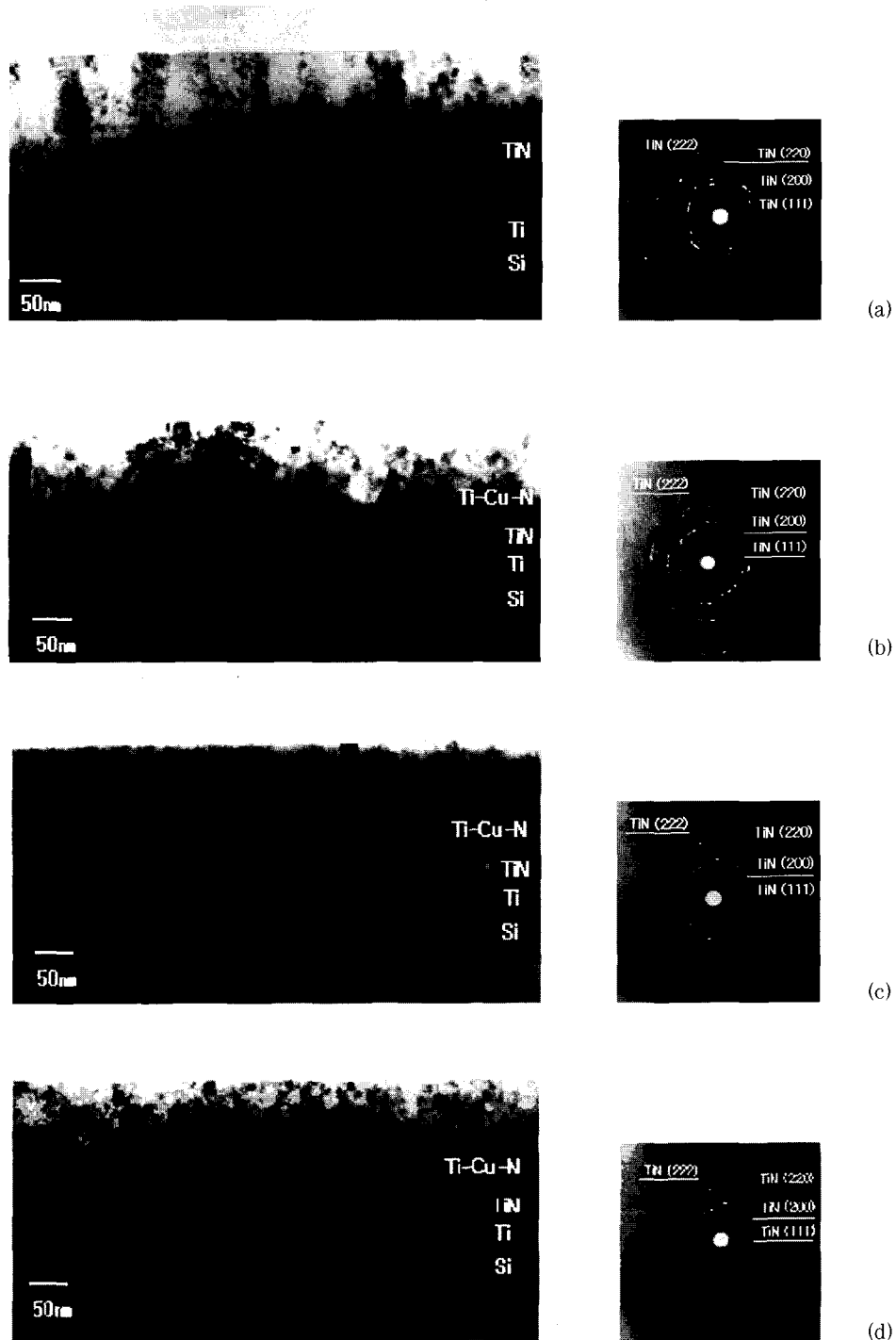


Fig. 5 A cross sectional TEM micrographs and electron diffraction patterns of various TiN and Ti-Cu-N films (a) 0 at%Cu (b) 1.0 at%Cu (c) 1.5 at%Cu (d) 2.3 at%Cu

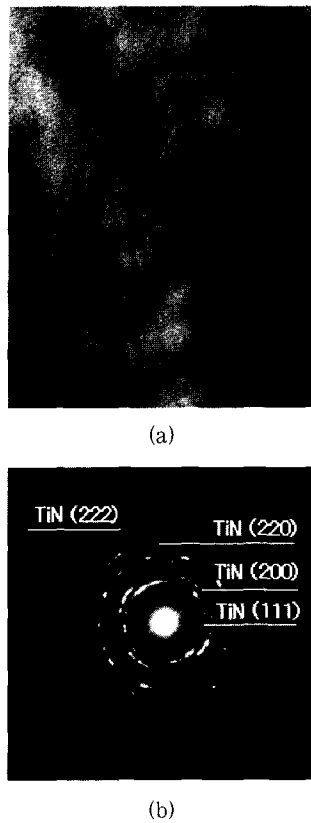


Fig. 6 HR-TEM micrograph of Ti-Cu-N(1.5 at%Cu) nanocomposite film bright field image (a) TED pattern (b)

peak disappeared and Cu(111) peak detected with increasing copper content. Intensity of TiN (111) and TiN(220) peak decreases and peak broadness increases with increasing copper concentration.

3) TiN film was columnar structure and column propagation was interrupted by addition of copper.

4) Grain size of Ti-Cu-N nanocomposite film with 1.5at%Cu was measured about 10nm.

5) Friction coefficient of Ti-Cu-N nanocomposite film with 1.5at%Cu was decreased to about 0.3

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