한국표면공학회지
J. Korean Inst. Surf. Eng
Vol.54, No.3, 2021.
https://doi.org/10.5695/JKISE.2021.54.3.133
ISSN 1225-8024(Print)
ISSN 2288-8403(Online)

〈연구논문〉

Effect of Negative Substrate Bias Voltage on the Microstructure and Mechanical Properties of Nanostructured Ti-Al-N-O Coatings Prepared by Cathodic Arc Evaporation

Sungbo Heo, Wang Ryeol Kim and In-Wook Park*

Korea Institute of Industrial Technology (KITECH), Yangsan 50623, Republic of Korea

(Received 11 June, 2021 ; revised 22 June, 2021 ; accepted 27 June, 2021)

Abstract

Ternary Ti-X-N coatings, where X = Al, Si, Cr, O, etc., have been widely used for machining tools and cutting tools such as inserts, end-mills, and etc. Ti-Al-N-O coatings were deposited onto silicon wafer and WC-Co substrates by a cathodic arc evaporation (CAE) technique at various negative substrate bias voltages. In this study, the influence of substrate bias voltages during deposition on the microstructure and mechanical properties of Ti-Al-N-O coatings were systematically investigated to optimize the CAE deposition condition. Based on results from various analyses, the Ti-Al-N-O coatings prepared at substrate bias voltage of -80 V in the process exhibited excellent mechanical properties with a higher compressive residual stress. The Ti-Al-N-O (-80 V) coating exhibited the highest hardness around 30 GPa and elastic modulus around 303 GPa. The improvement of mechanical properties with optimized bias voltage of -80 V can be explained with the diminution of macroparticles, film densification and residual stress induced by ion bombardment effect. However, the increasing bias voltage above -80 V caused reduction in film deposition rate in the Ti-Al-N-O coatings due to re-sputtering and ion bombardment phenomenon.

Keywords : Ti-Al-N-O Coatings, Substrate bias voltage, Cathodic arc evaporation, Microstructure

1. Introduction

Ti-Al-N hard coatings have been widely used in various industrial applications such as cutting and forming tools because of their high hardness, good oxidation resistance and significant wear resistance [1-2]. The high oxidation resistance of the Ti-Al-N films is due to the formation of a stable aluminum oxide layer on the film surface when it is exposed to high temperature like in a high speed cutting tool application. [3]Up to now, Ti-Al-N coatings have been synthesized through using several techniques such as cathodic arc evaporation (CAE) [4], direct current magnetron sputtering (DC-MS) [5], and plasma assisted chemical vapor deposition (PACVD) [6].

Among above coating techniques, vacuum cathodic arc evaporation is one of the most widely used for production of hard and wear resistance coatings. Highly ionized plasma produced during cathodic arc discharge enables the production of dense coatings with high

*Corresponding Author: In Wook Park
Korea Institute of Industrial Technology
Tel: +82-55-367-9401, Fax: +82-55-367-9841
E-mail: ipark@kitech.re.kr

deposition rates. Moreover, applying a high negative voltage to the substrate results in the acceleration of ions towards the substrate surface. However, the CAE method has a serious disadvantage of attached macroparticles whose presence deteriorates the tribological properties and corrosion protection ability of the coatings during cutting applications. [7] During the CAE deposition, negative bias voltage is applied to the substrate for enhancement of adatom mobility and ion bombardment effect leading to a modification in the coating's structure, morphology and mechanical properties. [8] The authors have reported a successful depositions for Ti-Si-N, Ti-Al-Si-N, Ti-B-C-N, Cr-Al-N, Cr-Al-Si-N, etc. with various deposition techniques, e.g. magnetron sputtering, plasma chemical vapor depositions, arc ion plating, and hybrid system.[9-10] However, the understanding of the substrate bias effects is necessary for Ti-Al-N coatings by the CAE process for future works.

Therefore, in this study, nanostructured Ti-Al-N-O coatings with different negative substrate bias voltages were investigated in an effort to optimization of a key deposition parameter using a cathodic arc evaporation (CAE) technique, and discussed on the relationship between microstructure and mechanical properties for cutting tool applications.

2. Experimental Details

Ti-Al-N-O coatings were deposited onto silicon wafer and WC-Co (WC 89.5 wt.%, Co 10 wt.%, Others 0.5 wt.%) substrates by a cathodic arc evaporation (CAE) using high purity (99.99 %) $TiAl_2$ and Ti targets with argon-nitrogen reactive gases. Prior to the depositions, the substrates were ultrasonically cleaned in acetone and ethanol for 20 min, respectively, and the glow discharge was cleaned in vacuum chamber using a DC bias voltage of -600 V under Ar atmosphere of 9.3×10^{-1} Pa for 40 min. In order to enhance the adhesion between the coating and substrate, Ti/TiN interlayers (~0.32 μm) was first deposited using pure Ti targets. A typical deposition conditions of the Ti/TiN interlayers and the Ti-Al-N-O coatings is summarized in Table 1.

Table 1. Typical deposition conditions for the Ti-Al-N-O coatings by the cathodic arc evaporation system

Parameters	Interlayers (Ti/TiN)	Ti-Al-N-O layer
Base pressure (Pa)	9.33×10^{-4}	9.33×10^{-4}
Working pressure (Pa)	4.37×10^{-1}	6.67×10^{-1}
Reactive N_2 gas (sccm)	400	400
Substrate temperature (℃)	350	350
Substrate bias voltage (V)	-50	0 to -100
Ti Target current (A)	70	N/A
$TiAl_2$ Target current (A)	N/A	70

X-ray diffactometer (XRD, Rigaku, Ultima4) was adopted to investigate the crystallinity and phase transformation of the Ti-Al-N-O films. To analysis of chemical bonding state and quantification of the elements, X-ray photo-electron spectroscope (XPS, Thermo VG scientific, SIGMA PROBE) was used. Detailed structural information on the coatings was obtained from the high-resolution transmission electron microscopy (HR-TEM) using a field emission transmission electron microscope (FE-TEM, JEOL, JEM-2012F) with a 200 kV acceleration voltage. The surface morphology and surface roughness of the coatings were investigated by atomic force microscopy (3D Profiler, Bruker Ltd., Contour GT-X). Hardness and Elastic modulus were measured by a computer-controlled nano-indentation (Anton Par, NHT^2). With hardness (H) and elastic modulus (E) obtained from the nano-indentaion,

H/E value called ‘elastic strain to failure’ and H^3/E^2 value called ‘resistance of materials against plastic deformation’ were calculated.

3. Results and Discussion

Table 2 shows the deposition rate of Ti-Al-N-O coatings with various substrate bias voltages. The substrate bias voltage exerted a strong influence on the deposition rate of Ti-Al-N-O coatings. It was also observed that the deposition rate of the Ti-Al-N-O coatings gradually decreased from about 16.5 to 10.8 nm/min when the substrate bias was changed from 0 to -100 V. Since the increase of the substrate bias voltage results in large augmented energy of the ions impinging on the growing coating, the decrease of deposition rate with the increase of the substrate bias voltage would be related to re-sputtering phenomenon. [11]

Figure 1 shows the X-ray diffraction patterns of Ti-Al-N-O coatings deposited with various substrate bias voltages. It was revealed that multiple orientations of the crystallized structure, corresponding to TiN (111), (200) and (220) diffraction peaks. The TiN (111) and (200) peak intensities were gradually increased and a peak broadening was observed with increasing in the substrate bias voltage up to -80 V. This broadening was probably resulting from residual stress induced into the coating by ion bombardment [12]. However, TiN (200) peak intensity almost disappeared at higher substrate bias voltage above -100 V. Figure 2 presents the XPS spectra near binding energies of Ti (Figure 2a), Al (Figure 2b), N (Figure 2c), and O (Figure 2d) for the Ti-Al-N-O (-80 V) film. For Ti 2p (Figure 2a), four peaks were observed. The main peaks at 455.4 and 461.2 eV correspond to the TiN compound. The other peaks at 457.4 and 463.3 eV correspond to TiO_2 compound. For the Al 2*p* region (Figure 2b), two peaks were observed. The main peak at 74.2 eV corresponds to the AlN compound. Another weak peak corresponding to Al_2O_3 (75.8 eV) was also observed in the Al 2*p* spectrum. For the N 1*s* region (Figure 2c), the nitrogen binding energy spectrum can be divided into two peaks. The major peak N 1*s* component at about 397.2 eV corresponds to the TiN phase. The minor component at about 399.1 eV corresponds to AlN phase. Finally, the O 1*s* spectrum in Figure 2d confirms the existence of TiO_2 (530.5 eV) and Al_2O_3 (532.4 eV). It is believed that the majority of oxygen is introduced from the arc target preparation, in which powders, especially titanium, could absorb a certain amount of oxygen onto the target surface.

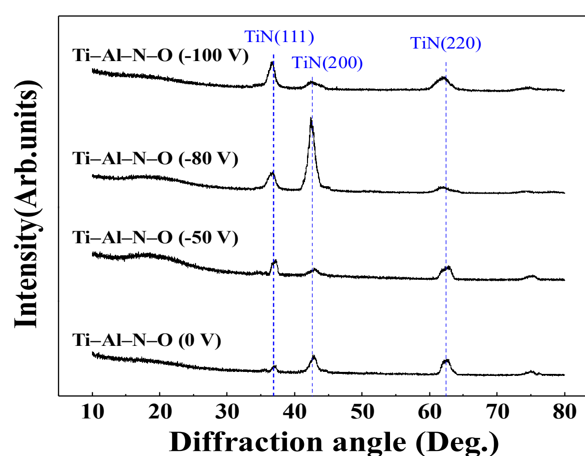

Fig 1. X-ray diffraction patterns of the Ti-Al-N-O coatings at various substrate bias voltages.

Table 2. Summary of mechanical properties of the Ti-Al-N-O coatings with different substrate bias voltages.

Sample ID	Deposition rate (nm/min)	Film compositions (at.%)				Hardness (GPa)	Elastic modulus (GPa)	H/E ratio	H^3/E^2 ratio (GPa)	Residual stress (GPa)	Roughness Ra (nm)
		Ti	Al	N	O						
Ti-Al-N-O (0 V)	16.3	21.2	20.6	52.7	5.5	17.1	219.9	0.078	0.103	-0.51	202.1
Ti-Al-N-O (-50 V)	15.9	22.1	21.4	51.4	5.1	21.7	295.7	0.073	0.117	-0.96	155.4
Ti-Al-N-O (-80 V)	14.7	23.6	22.7	49.2	4.5	28.9	303.3	0.095	0.262	-1.81	56.7
Ti-Al-N-O (-100 V)	12.1	22.8	21.7	50.6	4.9	13.3	192.2	0.069	0.063	-1.12	121.2

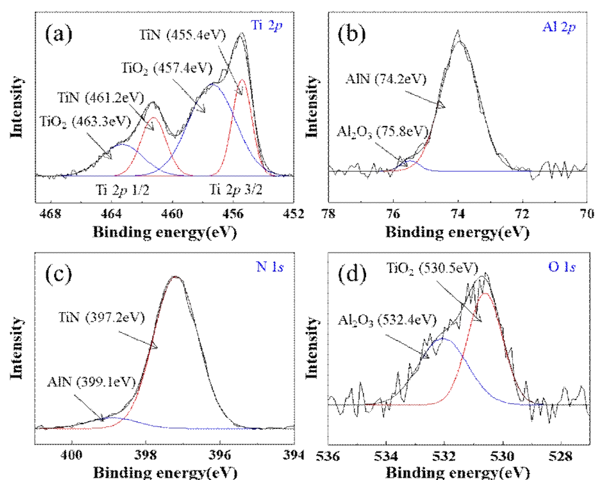

Fig 2. XPS spectra of the Ti-Al-N-O (-80 V) coating for (a) Ti 2*p*, (b) Al 2*p*, (c) N 1*s* and (d) O1*s*.

In order to understand the microstructure of the Ti-Al-N-O film, TEM investigation of the sample deposited at bias voltage of -80 V was performed. Figure 3 shows a bright field TEM image and the corresponding selected area electron diffraction pattern (SADP, Figure 3b) obtained from the Ti-Al-N-O (-80 V) film, which exhibited a fine nano-columnar grain structure. The SADP indicated that the film is poly-crystalline with TiN (111), (200), (220) and (311) phases. Figure 3c shows a high resolution TEM image obtained from the Ti-Al-N-O (-80 V) film and the corresponding inverse fast Fourier transform (IFFT) image (Figure 3d), which clearly show that the Ti-Al-N-O film has the fine nano-columnar structure in which the crystallites exhibited regular and spherical shapes with sizes ranging from 10 to 20 nm in an amorphous TiO_2 or Al_2O_3 matrix. Figure 4 shows the three dimensional surface morphologies with surface roughness of the Ti-Al-N-O (0 V) and Ti-Al-N-O (-80 V) film deposited on the silicon wafer substrate as measured using 3D profiler. The surface roughness of the Ti-Al-N-O (0 V) coating with no bias voltage (Figure 4a) was found to be very rough (R_a, 202.1 nm) than that (R_a, 56.7 nm) of Ti-Al-N-O (-80 V) film. This should be attributed to macroparticles due to a little porous film owing to no ion bombardment effect. However, at the substrate bias voltage of -80 V (Figure 4b), the number of macroparticles significantly decreased when the bias voltage increased. Generally, ion velocity is higher than macroparticle velocity. [13] The highly increased kinetic energy of ion by applying the substrate bias voltage might accelerate the ionization of macroparticles before reaching to substrate. Therefore, increasing of the bias voltage up to -80 V also caused the diminution of macroparticles and the smoothing of surface morphology due to densification of coatings by ion bombardment effect.

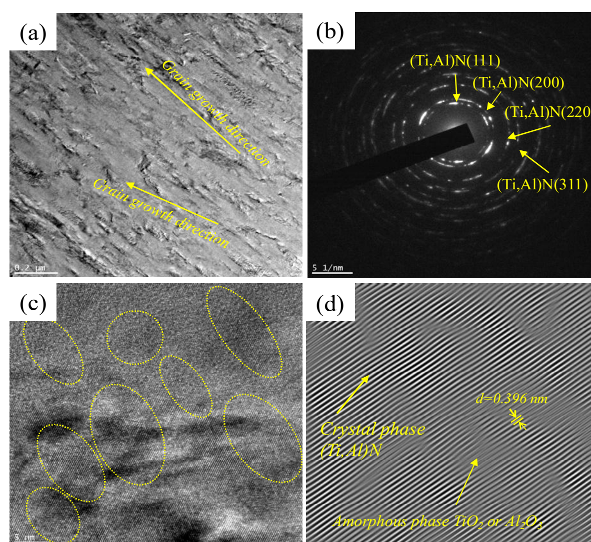

Fig 3. HR-TEM image from (a) A bright filed TEM image, (b) the corresponding selected area electron diffraction pattern (SADP), (c) a high resolution TEM image and (d) inverse fast Fourier transform image for the Ti-Al-N-O (-80 V) coating.

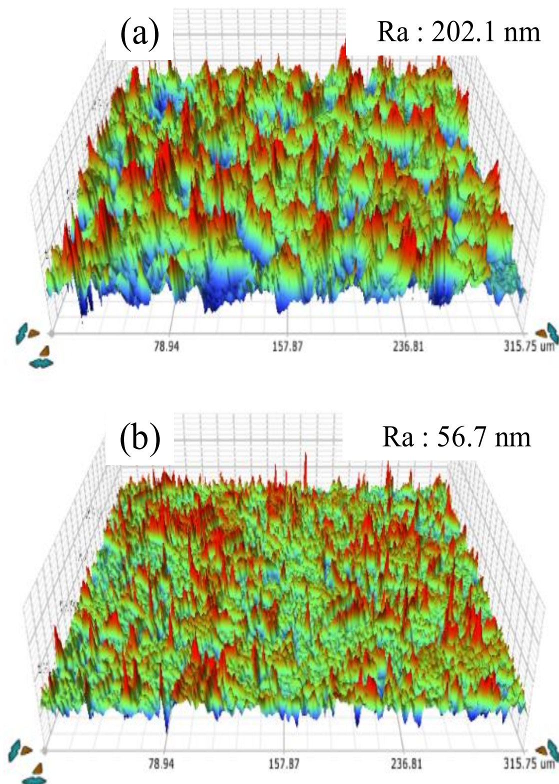

Fig 4. Surface morphology with average roughness of the (a) Ti-Al-N-O (0 V) and the (b) Ti-Al-N-O (-80 V) coating.

Figure 5 shows the hardness and elastic modulus of Ti-Al-N-O coatings as a function of substrate bias voltage. The hardness and elastic modulus gradually increased with increase in the substrate bias voltage, and reached the maximum value of ~30 and ~303 GPa, respectively, at the substrate bias voltage of -80 V. The hardness and elastic modulus values, however, suddenly decreased with further increase of the substrate bias voltage above -80 V. The increases of hardness and elastic modulus with increase of the substrate bias voltage up to -80 V could be explained by the diminution of macroparticles. Because the macroparticles were relatively soft metal Ti or TiAl droplets, their incorporation into Ti-Al-N-O coatings would result in the reduction of hardness. Furthermore, the residual stress, as summarized in Table 2, induced by ion bombardment effect would cause the increase of hardness.

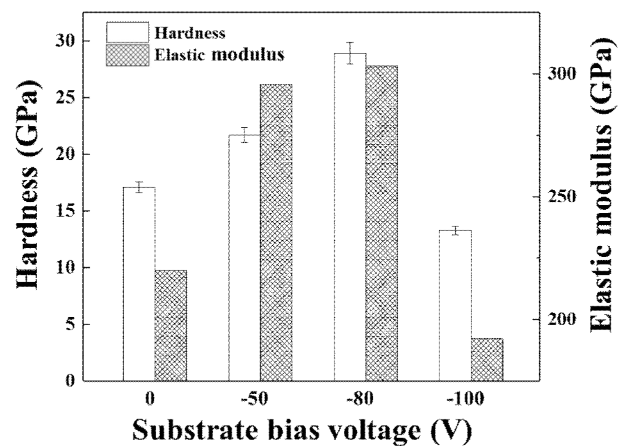

Fig 5. Hardness and elastic modulus of the Ti-Al-N-O coatings as a function of negative substrate bias voltage.

Based on results from relationships between microstructural analyses and mechanical properties, it can be concluded that negative substrate bias voltage as a key parameter during a cathodic arc evaporation process leads to considerable changes in microstructure and mechanical properties of the Ti-Al-N-O coatings.

4. Conclusions

Ti-Al-N-O coatings were deposited onto silicon wafer and WC-Co substrates by a cathodic arc evaporation (CAE) technique at various negative substrate bias voltages. With increase in substrate bias voltage up to -80 V during Ti-Al-N-O coating process resulted in the significant diminution of macroparticles and smoothening of surface morphology. The hardness and elastic modulus values were also significantly increased, and showed the highest values of ~30 and ~303 GPa, respectively, at a bias voltage of -80 V. The improvement of mechanical properties with optimized bias voltage of -80 V can be explained with the diminution of macroparticles, film densification and residual stress induced by the ion bombardment effect. However, the increasing

bias voltage above -80 V caused reduction in film deposition rate in the Ti-Al-N-O coatings due to re-sputtering and ion bombardment phenomenon.

Acknowledgment

This work was supported by the Technology Innovation Program (no. 20003058, Development of Hydrogen Gas Charging system for decreasing by half of FCEV Bus charging time and increasing two times of Hydrogen gas Tube Trailer transport capacity) funded by the Ministry of Trade, Industry and Energy (MOTIE, Korea).

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