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Effect of number of bi-layers on properties of TiN/TiAlN multilayer coatings

Fawad Ali, Beom Su Park and Joon Seop Kwak*

Department of Printed Electronic Engineering, World Class University Program, Sunchon National University, Sunchon, Chonnam 540-742, Korea.

Multilayer coatings TiAlN/TiN were deposited on silicon and SKD61 steel substrates with various numbers of TiN/TiAlN bi-layer. The total thickness of the coatings is 500 nm, with different number of bi-layers. The multilayer microstructure was characterized by X-ray diffraction, atomic force microscope, nano-indentation and scanning electron microscopy. It is observed that as the number of bi-layer increased the RMS roughness of the coatings decreased. Also, with the increase in number of bilayers the wear resistance of the multilayer TiN/TiAlN films increased and the hardness decreased. The low hardness of TiAlN/TiN multi-layers and increase in wear resistance is attributed to diffused interfaces.

Key words: TiN/TiAlN, Multilayer coatings, Hardness, Wear resistance.

Introduction

At present ceramic multi-layer coatings are consider as a promising materials. The properties can be improved by depositing layers of coatings that separately have different properties and adhesion to the substrate. Depositing several layers with various mechanical properties on each other the stress on the surface region and conditions for crack propagation could be controlled. So compared to monolayer coatings, multi-layer coatings have more amazing properties in the number of cases.

In recent years nano-layered multi-layered coatings of transition metal nitrides (TiN, TiAlN) have received considerable interest high adhesion at very low bi-layer thicknesses. Apart from high adhesion, the ceramic multi-layer coatings also exhibit high strength and wear resistance. In addition to high adhesion and strength, the thermal stability of hard coatings with respect to oxidation is very important for wear resistance applications. Therefore, these coatings have great potential as protective coatings on cutting tools and other mechanical components [1]. Recently, several multi-layered coatings have been reported to optimize and/or enhance coating's properties and performance [2, 3]. In detail, there are some reasons which show why it may be advantageous to use multi-layered coatings. For example, for adhesion improvement an interface layers can be used to the substrate and to ensure a smooth transition from coating properties to substrate properties at the coating-substrate boundary. Also, the stress concentration and crack propagation can be reduced by depositing several thin layers with various mechanical properties on each other. Finally, the properties of diverse property layer can be improved by depositing layers of coatings that separately have different kinds of effects on the surface, such as corrosion protection, wear protection, thermal isolation, electrical conductivity, diffusion barrier and adhesion to the substrate. The work by Sudgren *et al*., [4, 5] and Holleck and Schulz [6] has shown that the multilayer coatings have improved properties over single layer coatings. In applications at lower temperatures, the performance of TiN is better than that of TiAlN, for example in the case of slow sliding speed or an interrupted cutting process. This is due to differences in brittleness and the friction coefficients of the two materials [7]. In the present work an attempt is made to compare the adhesion and hardness of multi-layer TiN/TiAlN coatings with that of single-layer TiN and TiAlN coatings. The basic purpose of this work is to improve the adhesion of coatings to the substrate, and to compare the adhesion of multilayer Tin/TiAlN coatings to single layer TiN and TiAlN coatings.

*Corresponding author:
Tel : +82-61-7503559
Fax: +82-61-7505260
E-mail: jskwak@sunchon.ac.kr

Experimental

For multi-layer coatings the substrates were chemically cleaned in an ultrasonic agitator in acetone, methanol and de-ionized water and were dried by blowing nitrogen gas. Subsequently, the substrates were cleaned in situ by Ar+ ion bombardment for 10 min, wherein a DC bias of -100 V was applied to the substrate at an argon pressure of 1.5×10^{-6} Torr. TiAlN films were prepared from reactive sputtering of a Ti and Al targets in Ar+N_2 plasma operated at a pressure of 1.5×10^{-3} Torr. TiN and TiAlN layers were deposited from the reactive sputtering of Ti and Al targets, respectively. The process parameters were first optimized to achieve high hardness for TiN and TiAlN. Multi-layer films with controlled layer thicknesses and repeatability were deposited using power on and off approach. In this system the Al power is switched off for the formation of TiN coatings and power is switched on for the TiAlN layer. For multi-layer coatings the individual layer thickness of the two films was the same. The thickness of all the coatings was approximately 500 nm. Approximately a 100 nm thick Ti interlayer was also incorporated to improve the adhesion of the coatings on the substrate. A substrate bias of −100 V, a substrate temperature of 100 °C and a nitrogen flow rate of 8 sccm were used for all the coatings.

A series of TiAlN/TiN multi-layered thin films were deposited on silicon wafer substrates by a RF/DC reactive magnetron sputtering system. This series included multi-layered coatings with the same thickness ratios of TiAlN : TiN layers (TiAlN : TiN) = 1 : 1 and different bi-layer periods. Multi-layers were deposited by controlling the target power of Al and Ti. Various bi-layer periods were achieved by controlling the holding time of substrates in the plasma stream from Ti and Al target. The deposition time of each coating was controlled to achieve a fixed thickness around 500 nm. The starting nitride layer and the uppermost layer were TiN and TiAlN coatings, respectively, for all specimens. In the case of the TiN/TiAlN multilayer, the individual thickness was varied as a function of the bi-layer number from n = 2 to n = 6, producing bi-layer periods (Λ) from 200 nm to 67 nm.

Results and Discussion

Fig. 1 presents the XRD patterns of TiN/TiAlN multi-layer coatings. The XRD pattern represents a cubic structure where the strongest peaks (111) and (200) correspond to the TiN (111) and (200) planes, indicating a light textured growth along this orientation. The other weak peaks correspond to diffractions of TiN (220), and TiN (311) of the FCC structure. The structure of single-layer TiN and TiAlN coatings are strongly oriented along (111) and (200) respectively. While, all investigated multi-layer coatings were highly textured with a preferential orientation in the (111), (200) and (220) direction with the corresponding 2θ of about 36.5 °, 42.5 ° and 61.4 °, respectively. The intensities of other diffraction peaks such as (311) and (222) were very low, which were often observed in the PVD processes [8, 9]. The titanium atoms of TiN lattice were replaced by aluminum atoms to cause the lattice distortion and the internal stress change in TiAlN, which leads to the XRD peaks of TiN/TiAlN multi-layer coatings overall shift to the right [10]. XRD peaks of (111) and (220) have different relative intensities for the multi-layer coatings with different number of pairs. The randomly oriented multi-layer coatings have higher adhesion to substrate than single layer coatings oriented in a particular direction.

SEM micrographs illustrating the microstructure and surface morphology of the multi-layer TiN/TiAlN coatings with different number of bi-layers are shown in Fig. 2. A porous tapered columnar structure similar to the microstructure of zone 1 of Thornton's [14] structure zone model developed at high number of bi-layers. As the number of bi-layer decreased, the structure became densified, producing a very fine grain structure with features similar to the zone T structure of the Thornton's model. The densified structure can be correlated to the lower bi-layer number. Also the composition changed with changing the number of bi-layers investigated, a densified structure with finer grain size and improved surface morphology developed with low number of bi-layer as shown in Fig. 2.

The RMS roughness measured through AFM decreased from 5.5 nm for single pair TiN/TiAlN to around 4 nm for 4 numbers of pairs, as shown in Fig. 3. Fig. 2 shows higher magnification views of the surface topography of these coatings. The TiN/TiAlN multi-layer films at high number of layers Fig. 2(c-d) shows

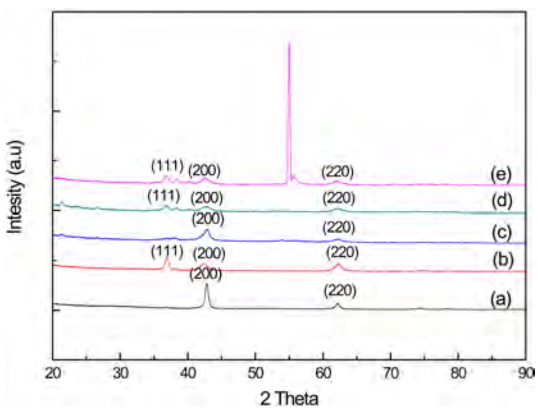

Fig. 1. XRD peaks of single layer and multi-layer coatings (a) TiN, (b) TiAlN (c) TiN/TiAlN 1 pair, (d) TiN/TiAlN 2 pair, (e) TiN/TiAlN 3 pair.

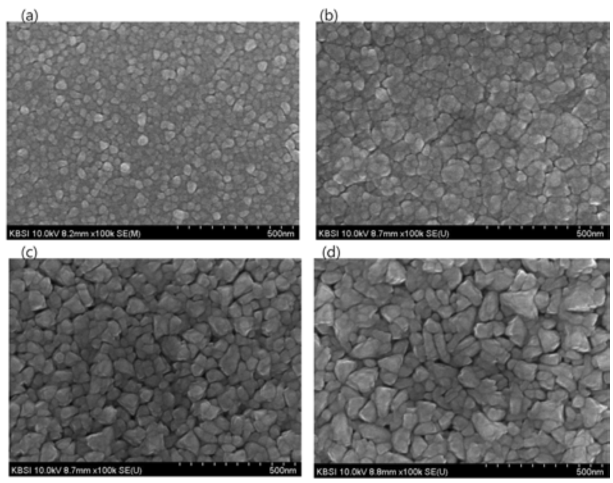

Fig. 2. SEM micrographs of (a) TiN, (b) TiN/TiAlN 1 pair, (c) TiN/TiAlN 2 pair, (d) TiN/TiAlN 3 pair.

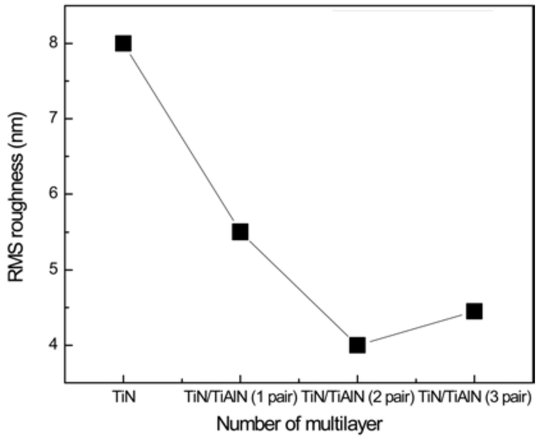

Fig. 3. RMS roughness of single layer TiN, TiAlN, and multi-layer TiN/TiAlN coatings.

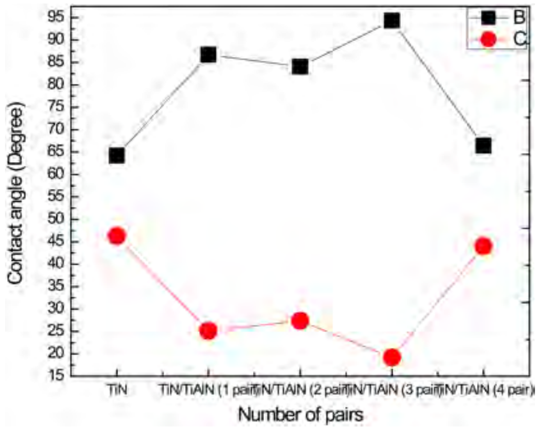

Fig. 4. Contact angle and surface energy of single layer and multi-layer films.

the surface to be faceted, and with large gaps between them. In contrast, at lower modulation wavelength in Fig. 2(a-b) have much smaller rounded ends to the surface structures, with no obvious gaps between the structural units which make up the coating. The total roughness of the coating decreased with increasing the number of bi-layer, as the roughness of TiN is 8 nm and that of TiAlN is 3 nm, so as the number of bi-layer increases the roughness decreased as shown in Fig. 3. With increasing the bilayer number the TiAlN layers increases in the coatings which reduces the overall roughness of the coatings. The results show that the adhesion of the coatings increased with the decrease of surface roughness while the hardness decreased.

To examine the effect of surface roughness on contact angle, the contact angle was measures for films with different number of bi-layers as shown in Fig. 4. The results show that as the number of bi-layer increased the contact angle decreased which is in agreement with surface roughness. This revealed the rougher and more porous nature of the TiN/TiAlN multi-layer films deposited with high number of bi-layers. As the contact angle decreased the surface energy increased, with

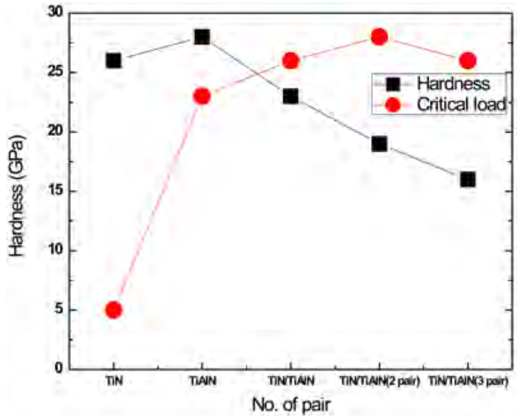

Fig. 5. Hardness and critical load of single and multilayer coatings as a function of number of layers.

increasing number of bi-layer. The decrease of contact angle is in good agreement with RMS roughness.

Fig. 5 shows the hardness and critical load (C_l) of the binary nitride single layers such as monolithic TiN with H = 26 GPa, C_l = 5 GPa, ternary nitride single layers TilAN with H = 28 GPa, C_l = 23 GPa and multilayer coatings depending on the bilayer numbers (n) or bilayer periods (Λ). According to the figures, the properties of the multilayer coatings are strongly affected by the bilayer period, Λ. The hardness and critical load of TiN/TiAlN multilayer coatings ranged from approximately 22 GPa to 16 GPa and 23 GPa to 28 GPa respectively, having found the maximum value for both properties for n = 3, which corresponded to Λ = 67 nm.

The scratch test technique was carried out to characterize coating adherence strength. The adhesion properties of monolithic TiN, TiAlN single layers and TiN/TiAlN multilayer coatings can be characterized by using the upper critical load, which is the load where the first delamination occurred at the edge of the scratch track (adhesion failure) [11]. The critical loads in adhesive failure values for the different coatings are summarized in Fig. 5. In this figure, it is clearly showed the increased adhesion properties of TiN/TiAlN multilayer coatings as a function of the decrease in the bi-layer period (Λ). It was assumed that the adhesion between the substrate and the first layer of the multilayer system remains constant, because the conditioning of samples and the parameters for coating depositions used in this study were the same. Besides, in all cases it was verified that the parameters of the scratch test for all samples were also the same. According to the latter, it was expected that the response to the applied load would only be depending on the coating properties, due to the effect of each layer and the interfaces that conform the entire multilayer system.

From Fig. 5, it was observed that the critical load increased when the bilayer period (Λ) was reduced and the bi-layer number (n) was increased. In this mechanism each interface serves as crack tip deflector, which changes the direction of the initial crack when it penetrates deep into the coating and strengthens the coating systems, moreover, by decreasing the bi-layer period ($\Lambda = tTiN + tTiAlN$) the dislocations that are among the layers found a major impediment to moving, therefore, TiN/TiAlN multilayer will require a higher critical shear stress to move and spread through the whole coating and allow the delaminating of the coating [12, 13].

Conclusion

TiN/TiAlN multilayer coatings were deposited by reactive magnetron sputtering using simultaneous deposition from Al and Ti targets in $N_2 + Ar$ mixture. The X-ray diffraction pattern confirmed the formation of the TiN binary phase in nano-structured multilayer coatings. Tribological properties (adhesion) exhibited an improvement as a function of increase of bi-layer number due to multilayer effect. In general, these multi-layered TiN/TiAlN coatings had higher critical load than single-layered TiN and TiAlN. By nano-indentation, it was found that the hardness of the multi-layers, about 23 GPa, were decreased largely than those of the individual TiN and TiAlN layers with the increase of bi-layer number. The RMS roughness decreased with the increase of bi-layer number. The increase of bi-layer number and decrease of bi-layer period (Λ) in the multilayer coatings allow the improving of critical load.

Acknowledgments

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