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A study on the microstructure and property development of d.c. magnetron co-sputtered ternary titanium aluminium nitride coatings

Part II *Effect of magnetron discharge power*

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Advanced ternary (Ti,Al)N coatings were produced by reactive magnetron co-sputtering technique with separate titanium and aluminium targets at a 30° magnetron configuration. The aluminium magnetron discharge power was adjusted from 0 to 6.0 W/cm^2 to investigate the effect of magnetron discharge power on the microstructure and property development of the coatings. It was found that increasing the aluminium magnetron discharge power caused the deposition rate and the aluminium content to increase, and the grain size and surface roughness of the coatings to decrease substantially. Tighter packing of the grain columns occurred and the microstructure changed from a porous zone 1 to a densified zone T structure, resulting in a continuous increase of the coating hardness. The major texture component of the coatings changed from the (111) to (200) orientations. The (101) orientations of the AlN structure also developed. It was found that the microstructure and hardness enhancement of the coatings was associated with an increased formation of the TiAlN and AlN phases and a densified, fine grain structure at higher magnetron discharge powers.

1. Introduction

The magnetron discharge power is an important parameter in sputter deposition that determines the sputtering yields and consequently the rate of deposition of the coatings. Recent research on the effect of magnetron discharge power has been concentrated on binary nitrides. Information about the effects of magnetron discharge power on ternary nitrides is very limited. Perry *et al.* [1, 2] have investigated the effect of sputter target power on the properties of TiN films produced by reactive sputtering. The results showed that the discharge power had imposed significant effect on the deposition rate and the lattice parameters of the coatings. As the magnetron discharge power increased, both the deposition rate and lattice parameter on the TiN film increased. Sproul *et al.* [3] also reported that the target power had significant effect on the hardness and crystallographic orientation of TiN coatings prepared by reactive sputtering. At low magnetron discharge powers, the coating was relatively soft with a low hardness. As the discharge power increased the hardness increased rapidly. Orientations of the coatings also changed from a very strong (111) orientation at low discharge powers to random orientations at mid to high target powers. Hohl *et al.* [4] have examined the residual stress, morphology and mechanical properties of TiN as a function of discharge power. It was found that the stress and hardness of the films increased with increasing discharge power. Examination of the film morphology revealed that increasing the target power caused a continuous development from a coarse to a fine grain structure.

On ternary nitride coatings, Gredic and Zlatanovic [5] have investigated the effect of magnetron discharge power levels on the plasma deposition of TiAlN coatings with a composite magnetron target. It was found that increasing the magnetron discharge power caused an increase in deposition rate, hardness and bias current. The ratio of metal to nitrogen and the flux of substrate bombarding particles were found to increase as well. It was also reported that the density of the columnar coating structure and the size of the columns increased with increasing discharge power. The results were attributed to an increased sputtering rate of the target material and an increase in the flux of substrate bombarding particles. In the present study, the ternary titanium aluminium nitride coatings were produced using separate titanium and aluminium magnetron targets at a 30° magnetron configuration. The magnetron discharge power of the aluminium target was adjusted as a controlling deposition parameter. This paper reports the microstructure and property development of the coatings under different magnetron discharge powers.

2. Experimental

The reactive magnetron co-sputtering technique, with separate titanium and aluminium targets, was used to produce the titanium aluminium nitride coatings in the present study. (Ti,Al)N coatings were deposited with two slightly unbalanced, independently controlled magnetrons at a 30° magnetron arrangement. The target to substrate distance was set at 110 mm. The (Ti,Al)N coatings were deposited on glass slides 75 mm (length) × 25 mm (width) × 1.5 mm (thickness), which were thoroughly cleaned with ethanol and dried before being placed in the vacuum chamber.

The system used for coating was a Varian 3120 deposition unit equipped with Pirrani gauges and Tylan mass flow controllers to monitor the pressures and flow rates of nitrogen and argon gas respectively. Before sputtering, the chamber was evacuated to a pressure below 2×10^{-6} Torr. Once a high vacuum of at least 2×10^{-6} Torr was reached, the sample holder was heated and maintained at a predetermined temperature of 240°C. The targets were then sputter cleaned with argon for 10 minutes while the substrate were shielded by shutters over the magnetrons. Then a thin intermediate layer of titanium followed by a titanium aluminium layer were each deposited for 5 minutes respectively on the substrate with a constant bias set at negative 100 volts. After the titanium and titanium-aluminium interlayer films were deposited, reactive gas of high purity nitrogen was injected through an Alltech gas purifier filter into the deposition chamber to form titanium aluminium nitride. The coatings were deposited at a constant nitrogen pressure of 0.4 mTorr, which corresponded to gas flow rates of 10 standard cubic centimeters (sccm). The argon pressure was maintained constant at 2.4 mTorr during the deposition process. The titanium magnetron current was set at a constant level of 0.6 A, which corresponds to a discharge power of 9.0 W/cm^2. The aluminium magnetron discharge power was adjusted as a process variable from 0 to 6.0 W/cm^2. After completing a deposition for 60 minutes, 1.5 to 2.0 μm thick coatings developed on the substrate. The coating thickness was determined using a Tencor Alphastep profilometer.

A number of characterisation techniques including scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffractometry (XRD) were used to study the microstructure and morphology of the coatings. The microstructure of the coatings was examined using a JEOL 6300F field emission SEM operated at an accelerating voltage of 8 kV. Composition of the coatings was determined using energy dispersive X-ray spectroscopy (EDS) at 8 kV and the $\Phi(\rho Z)$ quantitative analysis software. Aluminium and titanium standards of high purity (99.99%) were used in the EDS analysis to determine the contents of aluminium and titanium of the coatings and the nitrogen content was calculated as a difference of the element contents. Hardness of the coatings was measured at 2 and 10 g loads using a LECO M400-H1 microhardness tester with a Vickers indentor. The phase development and other crystallographic properties of the coatings were examined by XRD technique using a Siemens D5000 diffractometer with Cu K_α radiation at small scattering angles. AFM analysis was performed on a Park Scientific Instrument Autoprobe using ultralever tips. Region and line scans were conducted to determine the surface roughness and other topographical features of the coatings.

3. Results
3.1. Deposition rate

The deposition rates of (Ti,Al)N coatings produced at different aluminium magnetron discharge powers are shown in Fig. 1. The results showed a significant increase of the deposition rate with increasing aluminium magnetron discharge power. As the magnetron discharge power increased from 0 to 6.0 Watts/cm^2, the deposition rate of the coatings increased from 15 nm/min to 24 nm/min.

3.2. Chemical composition

An increase of the aluminium magnetron discharge power affected the chemical composition of the coatings. It was found that as the aluminium magnetron discharge power increased from 0 to 6.0 Watts/cm^2, the titanium content of the coatings decreased from 50 at.% to 31 at.%, the aluminium content increased from 0 at.% to 26 at.%, and the nitrogen content decreased from 50 at.% but then remained around 41 at.%, Fig. 2. The appearance of the coatings changed from gold to a blue-grey colour with increasing aluminium content.

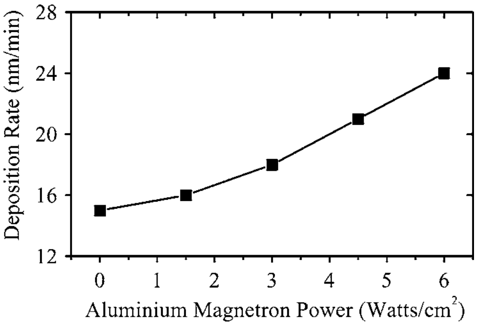


Figure 1 Effect of aluminium magnetron discharge power on the deposition rate of the coatings.

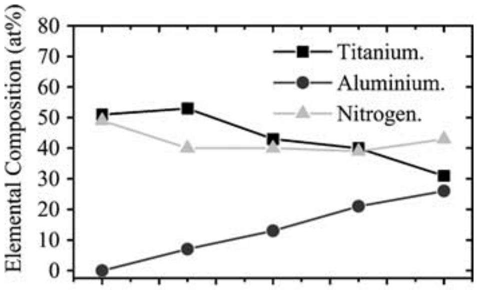
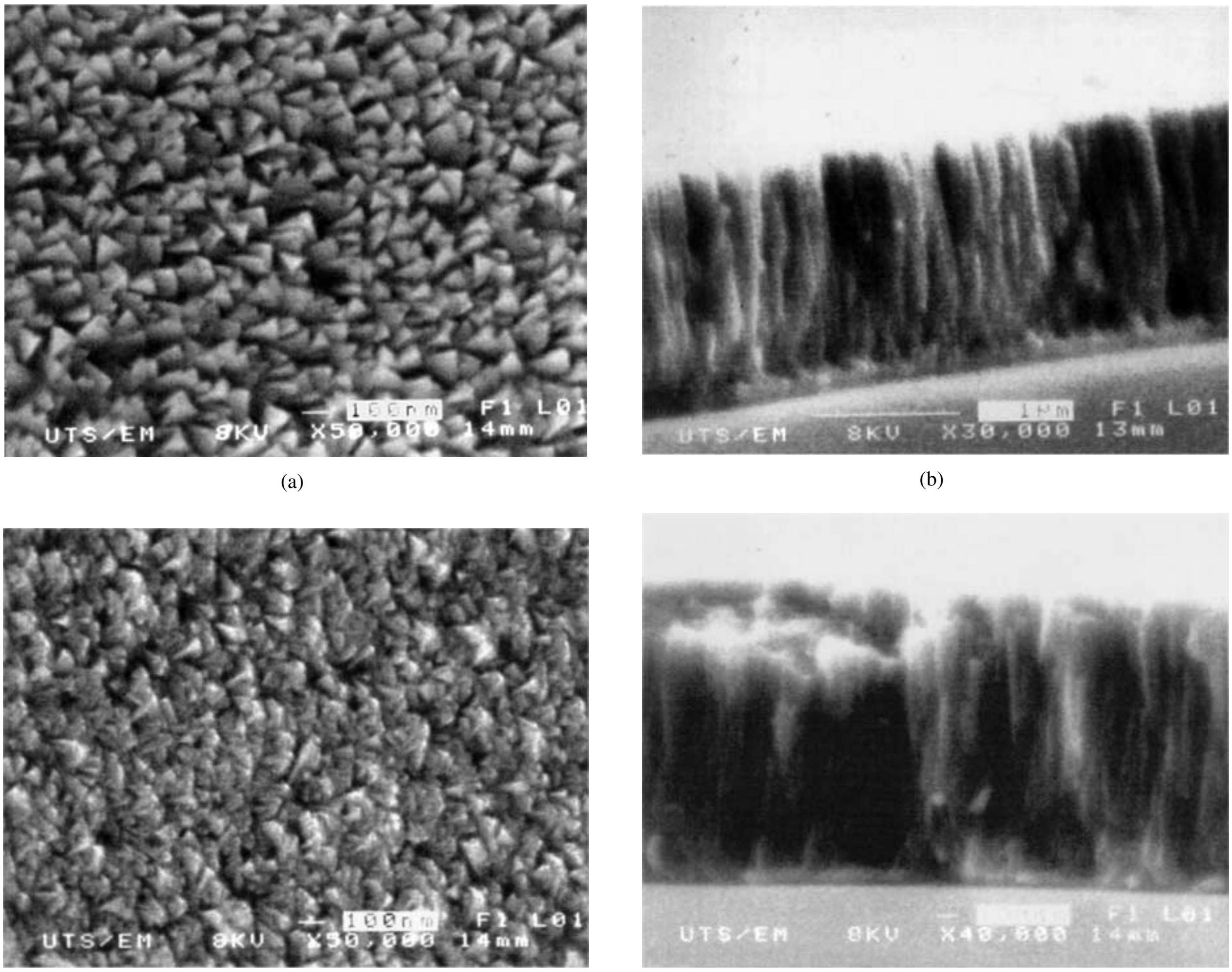


Figure 2 Effect of aluminium magnetron discharge power on the chemical composition of the coatings.



(a) (b) (c) (d)

Figure 3 Effect of aluminium magnetron power on (Ti,Al)N microstructure: (a) SEM micrograph of (Ti,Al)N produced at 1.5 Watts/cm^2, (b) SEM micrograph of cross-section of (Ti,Al)N produced at 1.5 Watts/cm^2, (c) SEM micrograph of (Ti,Al)N produced at 6.0 Watts/cm^2, (d) SEM micrograph of cross-section of (Ti,Al)N produced at 6.0 Watts/cm^2.

3.3. Microstructure and surface morphology

SEM micrographs, which illustrate the microstructure and surface morphology of the (Ti,Al)N coatings deposited at different aluminium magnetron discharge powers, are shown in Fig. 3. Very fine grain nanostructures developed and became evident with increasing aluminium magnetron discharge power. When the aluminium magnetron discharge power was reduced to zero, where only TiN formed, a domed and rounded columnar structure with similar features of the zone 1 structure of the Thornton's model [6] developed. As the magnetron discharge power increased to 1.5 Watts/cm^2 a zone 1 faceted structure was formed, Fig. 3a and b. A further increase in aluminium magnetron discharge power caused tighter packing of the grain columns with features similar to the zone T microstructure of the Thornton's model [6], Fig. 3c and d.

Scan measurements of the AFM analysis across the "troughs" of the grain structure confirmed that the average columnar diameter of the coatings, decreased substantially from 200 nm to 90 nm as the aluminium magnetron discharge power increased from 0 to 6.0 Watts/cm^2, Fig. 4a. Refinement of grain structure was most effective as the aluminium discharge power increased from zero to 1.5 Watts/cm^2. AFM region analysis also showed significant morphological changes on the coatings with increasing aluminium discharge power. It was found that as the aluminium magnetron discharge power increased from 0 to 6.0 Watts/cm^2, the rms roughness decreased from 6.5 nm to 3.2 nm and the average roughness decreased from 5.3 nm to 2.6 nm, Fig. 4b. The mean height of the grain structure decreased from 23 nm to 12.3 nm and the median height decreased from 24 nm to 12.6 nm, Fig. 4c. The line scan measurements showed similar morphological changes with increasing aluminium discharge magnetron power.

3.4. Microhardness

The microhardness of the (Ti,Al)N coatings, measured with 2g and 10g loads respectively, is shown in Fig. 5. The microhardness measured at a 2g load was found to increase from 1500 HV to 2000 HV as the aluminium magnetron discharge power increased from 0 to 6.0 Watts/cm^2. The microhardness, measured at a 10g load, followed similar development and increased from 700 HV to 1300 HV with increasing aluminium magnetron discharge power.

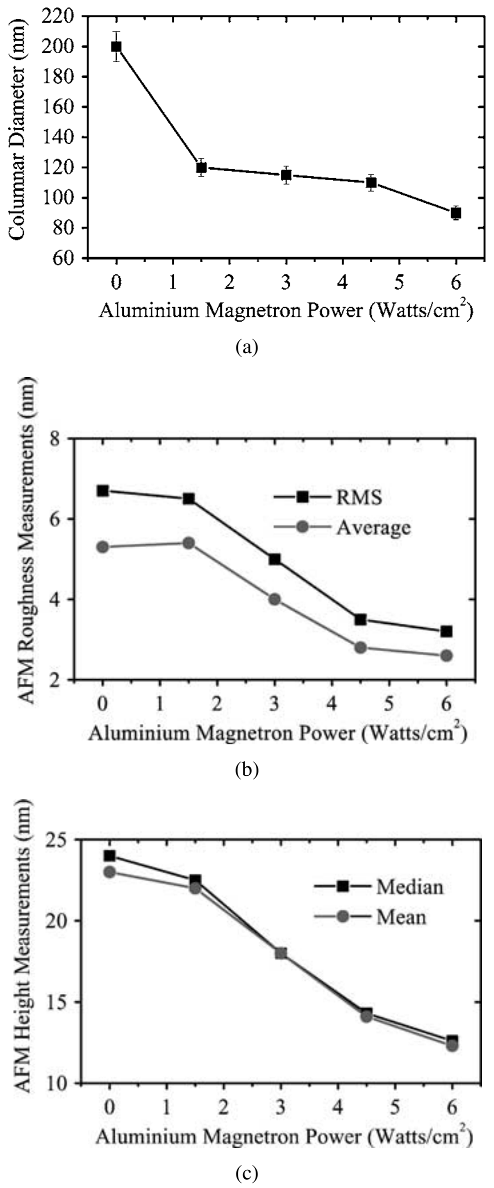


Figure 4 Effect of aluminium magnetron discharge power on the (a) columnar diameter, (b) RMS and average roughness and (c) mean and median height of the coatings.

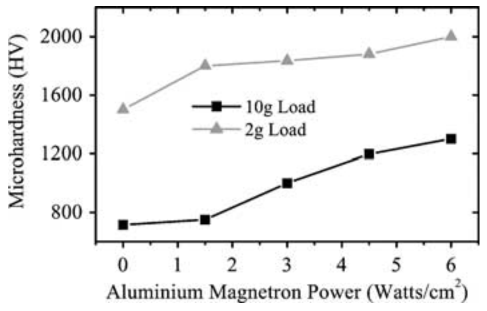


Figure 5 Effect of aluminium magnetron discharge power on the microhardness of the coatings.

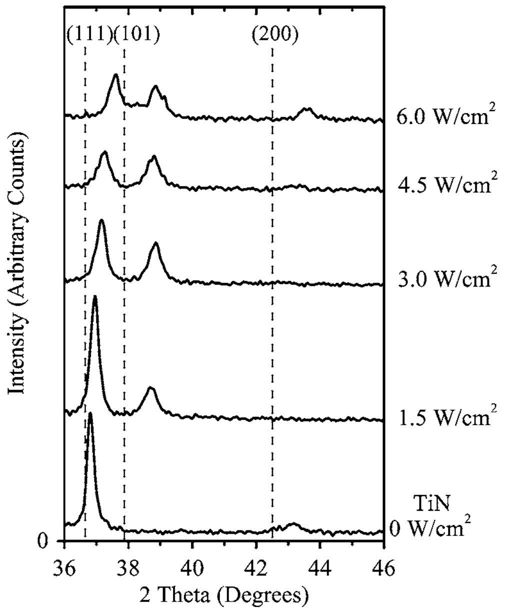


Figure 6 XRD patterns measured on coatings produced at different aluminium magnetron discharge powers. The dashed lines shown represent the standard 2θ positions for the (111) and (200) reflections of the cubic TiN structure and the (101) reflection of the hexagonal AlN structure. The same intensity scale is used for each XRD pattern.

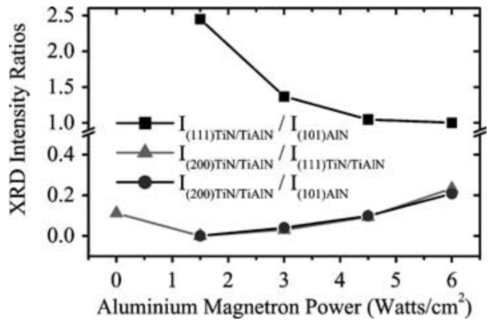


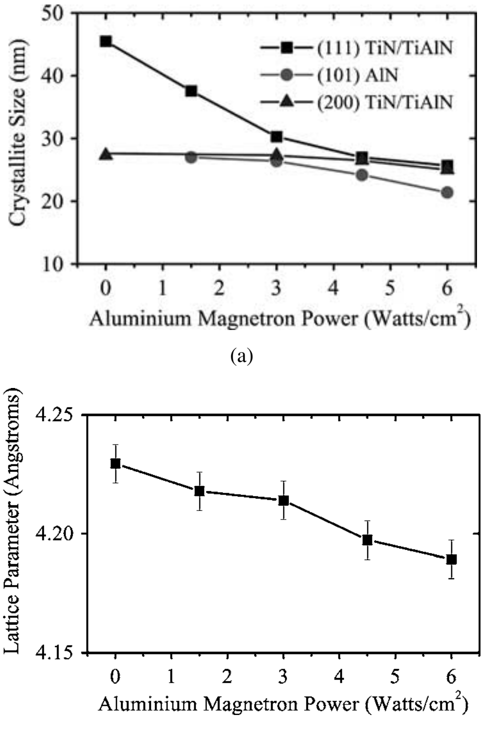
Figure 7 XRD intensity ratios measured on coatings produced at different aluminium magnetron discharge powers.

3.5. Phase development and crystallographic properties

XRD patterns of the (Ti,Al)N coatings deposited at different aluminium magnetron discharge powers are shown in Fig. 6. The standard 2θ positions for the (111) and (200) reflections of the cubic TiN structure and the (101) reflection of the hexagonal AlN structure are also included in Fig. 6 for comparison purposes. The calculated integrated intensity ratios for the peak reflections and other important lattice parameters are presented in Figs 7 and 8.

The XRD analyses of the coatings showed a continuous shift of the peak positions from the standard 2θ values with increasing aluminium magnetron discharge power, Fig. 6. As the aluminium magnetron discharge power increased from 0 to 6.0 Watts/cm^2, the 2θ values for the (111) reflection of the TiN/TiAlN structure shifted from 36.803° to 37.459°, suggesting an increased formation of the TiAlN structure with a reduced lattice parameter. Similar shift of the 2θ values for the (200) reflections of the TiN/TiAlN from 43.130° to 43.452° was evident as well. A small shift of the 2θ values for the (101) reflections of the AlN structure was also observed. As the aluminium magnetron discharge power increased from 1.5 to 6.0 Watts/cm^2, the 2θ values for the AlN (101) reflection increased from 38.682° to 38.905°.

Integrated intensity ratios for the major peaks of the (200) and (111) reflections of the TiN/TiAlN cubic structure and the (101) reflection of the hexagonal



(a)

(b)

Figure 8 Effect of aluminium magnetron discharge power on (a) crystallite size and (b) lattice parameter of the coatings.

AlN structure are shown in Fig. 7. It was found that at low aluminium magnetron discharge powers, the (200) reflection from the TiN/TiAlN structure was of very low intensities. As the aluminium magnetron discharge power increased above 4.5 Watts/cm^2, a stronger development of the (200) reflection became evident. On the other hand, the (111) components of the TiN/TiAlN structure was continuously weakened with increasing aluminium discharge power. With changes in the peak intensities, the intensity ratio of the $I_{(200)\mathrm{TiN/TiAlN}}/I_{(111)\mathrm{TiN/TiAlN}}$ first decreased from 0.12 to zero and then increased to a value above 0.24, the ratio of $I_{(200)\mathrm{TiN/TiAlN}}/I_{(101)\mathrm{AlN}}$ increased continuously but the ratio of $I_{(111)\mathrm{TiN/TiAlN})}/I_{(101)\mathrm{AlN}}$ decreased significantly as the aluminium discharge power was increased.

The results for the calculated crystallite size and the lattice parameters of the coatings are shown in Fig. 8. It was found that as the aluminium discharge power increased from 0 to 6.0 Watts/cm^2, the crystallite size calculated for the main peak reflections decreased. The change was most significant for the TiN/TiAlN (111) component, Fig. 8a. On the other hand, the lattice parameter of the coating structure decreased from 4.230 Å to 4.189 Å, Fig. 8b.

4. Discussion

In magnetron co-sputter deposition using separate titanium and aluminium targets, the aluminium magnetron power can be set to zero and consequently TiN is produced. The results showed that when producing TiN, a columnar structure with large grain size and voids developed, Fig. 3. Increasing the aluminium magnetron power from 0 to 6.0 Watts/cm^2, causes the deposition rate to increase, which is associated with a higher yield of aluminium atoms from the target. Consequently, the amount of aluminium within the (Ti,Al)N film is expected to increase with increasing aluminium magnetron discharge power, and changes in microstructure and properties of the coatings will occur.

Experimental results of the present study confirmed that as the aluminium magnetron power increased, the major (111) and (200) peak reflections showed a continuous shift from the standard positions of the TiN structure to higher 2θ values. The results indicated that unlike the effect of nitrogen deposition pressure, an enhanced formation of (TiAl)N structure and replacement of titanium atoms by aluminium atoms in the TiN lattice continuously occurred. The lattice parameter and crystallite size of the coating structure was also observed to decrease constantly with increasing aluminium magnetron power, that is in consistence with the formation of a smaller sized (Ti,Al)N unit cell structure. SEM EDS measurements also showed a substantial increase in the aluminium content of the coatings. As the aluminium discharge power increased, the aluminium content of the coatings increased from 7 at.% at 1.5 Watts/cm^2 to 26 at.% at 6.0 Watts/cm^2 of aluminium discharge power.

With an increased formation of the (Ti,Al)N phase, changes in microstructure, morphology and properties of the coatings were evident. A summary of the structural and property development of the coatings is illustrated in Fig. 9. The incorporation of aluminium atoms into the TiN structure generally caused the grain size, surface roughness and grain height of the coatings to decrease. At zero aluminium magnetron discharge power, a round columnar TiN structure with features of the zone 1 structure of the Thornton's model developed. As the aluminium discharge power increased, the coating structure was densified. When the aluminium magnetron power was

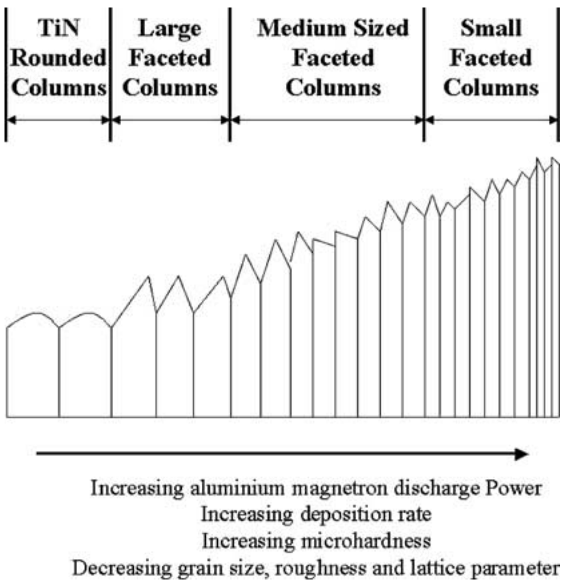


Figure 9 A two dimensional schematic structure zone model showing the effect of aluminium magnetron power on the microstructure and property development of (Ti,Al)N coatings deposited with a 30° magnetron configuration.

increased to 6.0 Watts/cm^2, a densified coating typical of the zone T structure of the Thornton's model with a much finer grain size and a mixture of rounded and faceted columns formed. For the texture development of the coatings, the (111) texture components decreased with the increasing aluminium discharge power in association with the re-emergence of the (200) orientations and an increased formation of the (Ti,Al)N phase and a densely packed structure. On the other hand, (101) orientations of the AlN structure became established, suggesting an increased formation of the AlN phase at higher aluminium discharge powers.

The formation of the (Ti,Al)N phase and the densified structure had improved the strength of the coatings. The hardness of the (Ti,Al)N coatings was found to continuously increase with increasing aluminium content. The hardness measured with a 2g load increased from 1500 HV in the TiN coatings produced at zero aluminium discharge power to 2000 HV in those produced at 6.0 Watts/cm^2, with a $\sim$30% increase in hardness. Increasing the aluminium target discharge power therefore raised the sputter yield of aluminium atoms and promoting the formation of (Ti,Al)N phase with a continuous increase of the hardness. As the aluminium discharge power increased, the coating structure was densified with a much smoother surface and a finer grain size. It is understood that when the depositing atoms arrive the substrate surface, two phenomena, namely statistical roughening and self-shadowing, may affect the microstructure and morphology development of the coatings [7]. The observed structural improvement is believed to be attributed to a high density of depositing atoms arriving at the substrate with increased magnetron discharge power, thus filling the voids and creating a higher nucleation rate in the coatings. According to the results obtained in the present study, an aluminium discharge power between 4.5 to 6.0 W/cm^2 has been identified for producing magnetron co-sputtered (TiAl)N coatings with optimum structure and hardness.

5. Conclusions

The effect of magnetron discharge power on the microstructure and property development of ternary (Ti,Al)N coatings produced by reactive magnetron co-sputtering technique was investigated. It was found that increasing the aluminium magnetron discharge power caused the deposition rate and the aluminium content to increase and the grain size and surface roughness of the coatings to decrease substantially. Tighter packing of the grain columns occurred and the microstructure changed from a porous zone 1 to a densified zone T structure, resulting in a continuous increase of the coating hardness. The texture of the coatings also changed from the (111) to (200) orientations. It is believed that the microstructure and property enhancement of the coatings with increasing magnetron discharge power is attributed to the significantly higher number and greater energy of the depositing atoms taking part in the growth of the coatings, which lead to an increased formation of the TiAlN and AlN phases and a very fine grained, densified structure of the coatings.

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