

HIGH TEMPERATURE BEHAVIOUR OF MAGNETRON SPUTTERED NANOCRYSTALLINE TITANIUM ALUMINIUM NITRIDE COATINGS

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ABSTRACT

This paper is to study the thermal stability of nanocrystalline ternary nitride coatings at elevated temperatures. Nanocrystalline titanium aluminium nitride coatings were produced by reactive magnetron co-sputtering on glass substrates and AISI H13 tool steel substrates with nitrogen pressures of 0.4 and 0.65 mTorr (0.053 and 0.086 Pa) respectively. Heat treatment was applied to the coatings at temperatures up to 1000°C. It was found that an unexpected grain refinement occurred in the coatings deposited at 0.4 mTorr nitrogen pressure after the heat treatment. A stronger development of TiN/TiAlN (200) component was also evident at temperatures above 800°C. With a finer and densified grain structure, the hardness of the coatings increased substantially from ~1700 to 2300 HV.

Keywords: TiAlN coatings, thin films, Ternary nitride coatings, magnetron sputtering.

1. INTRODUCTION

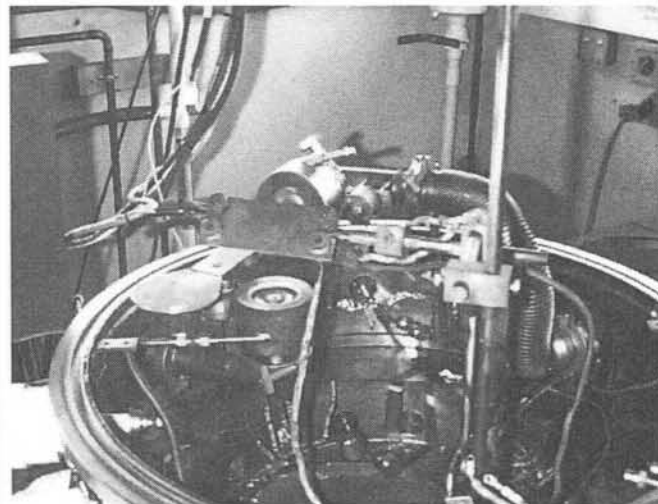
Development of advanced ternary nitride coatings for engineering applications has attracted significant industrial interest in the last 20 years. In a comparative study of (Ti,Al)N and TiN coatings, Munz and co-workers [1,2] reported that the (Ti,Al)N hard coatings are of higher oxidation resistance than TiN. It was found that severe oxidation occurred at 500°C for TiN but did not occur on (Ti,Al)N until the temperature reached 750°C. Since then substantial research activities have been conducted in the development of various complex ternary nitride coatings [3-11]. Despite these extensive studies, information about the thermal stability of these coating structures at high temperatures and their associated properties is still rather limited. More recently, Wuhrer and Yeung [12,13] have conducted a detailed study on the development of nanostructured ternary nitride coatings. It was found that with a nanograin structure, the coatings were of much higher hardness than those of the coarser grain size. However, at an elevated temperature, grain growth may occur and lead to an increase of the grain size and a reduction in the coating hardness. It is therefore of our interest to investigate the structural stability of these nanostructured ternary nitride coatings at elevated temperatures. The structural evolution of titanium aluminium ternary nitrides was studied after annealing at temperatures up to 1000°C. The hardness of the coatings was examined and compared.

2. EXPERIMENTAL PROCEDURE

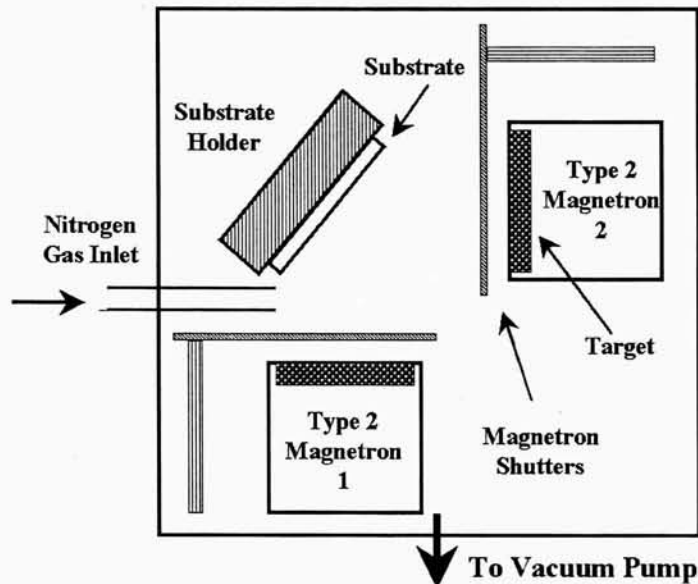
Reactive magnetron co-sputtering, with separate titanium and aluminium sputter targets, was used to produce titanium aluminium ternary nitride coatings on glass substrates and AISI H13 tool steel substrates. The H13 steel substrates were heat treated at 1050°C for 20 minutes followed by water quench. Post-quench tempering was then applied at 500°C for 1 hour followed by air cooling. The average hardness of the tempered steel was measured to be 540HV. The steel substrates were then polished to 1 µm surface finish and carefully cleaned with ethanol before placing in the deposition chamber. The coatings for thermal stability study were deposited on AISI H13 steel substrates at nitrogen pressures of 0.4 and 0.65 mTorr (0.053 and 0.086 Pa) respectively in a Varian 3120 deposition unit using two unbalanced, independently controlled magnetrons (Figure 1). The discharge powers of the titanium and aluminium magnetrons were set at 9.0 and 6.0 W/cm² respectively. The substrate was maintained at a predetermined temperature of 240°C. In the deposition process, the targets were first sputter cleaned with argon at a pressure of 2.4 mTorr for 10 minutes, followed by the deposition of an interlayer of titanium of ~60 nm and an interlayer of titanium aluminium of ~120 nm. A constant d.c. bias of negative 100 volts was set between the targets and the substrate. Reactive gas of high purity (99.99%) nitrogen was injected through an Alltech gas purifier filter into the deposition chamber to form the ternary nitrides. The coatings were deposited for 60 minutes to a thickness of 1.5 – 2.5 µm.

High temperature annealing of the coatings was conducted in the vacuum chamber of a Siemens D5000 diffractometer. Phase development and crystallographic properties of the coatings at 20, 200, 300, 500, 700, 800, 900 and 1000°C were determined by X-ray diffraction (XRD) technique with $\text{CuK}\alpha$ radiation.

The microstructure and the morphology of the coatings prior to and after the heat treatment were examined using scanning electron microscopy (SEM) in a JEOL 6300F field emission scanning electron microscope and atomic force microscopy (AFM) in a Park Scientific Instrument Autoprobe. The microhardness of the coatings was measured with a 10g load.



a.



b.

Figure 1: a) Internal view of Varian deposition chamber and b) schematic of deposition configuration with a 90° magnetron arrangement.

3. RESULTS

3.1 Effect of nitrogen pressure on microstructure

The microstructures of the coatings produced on glass substrates, as a function of nitrogen deposition pressure, are shown in Figure 2. It was found that as

the nitrogen deposition pressure increased, the grain size of the (Ti,Al)N coatings generally increased with higher surface roughness. Examination of the cross sections of the films indicated the coatings consisted of a columnar grain structure, Figure 2.

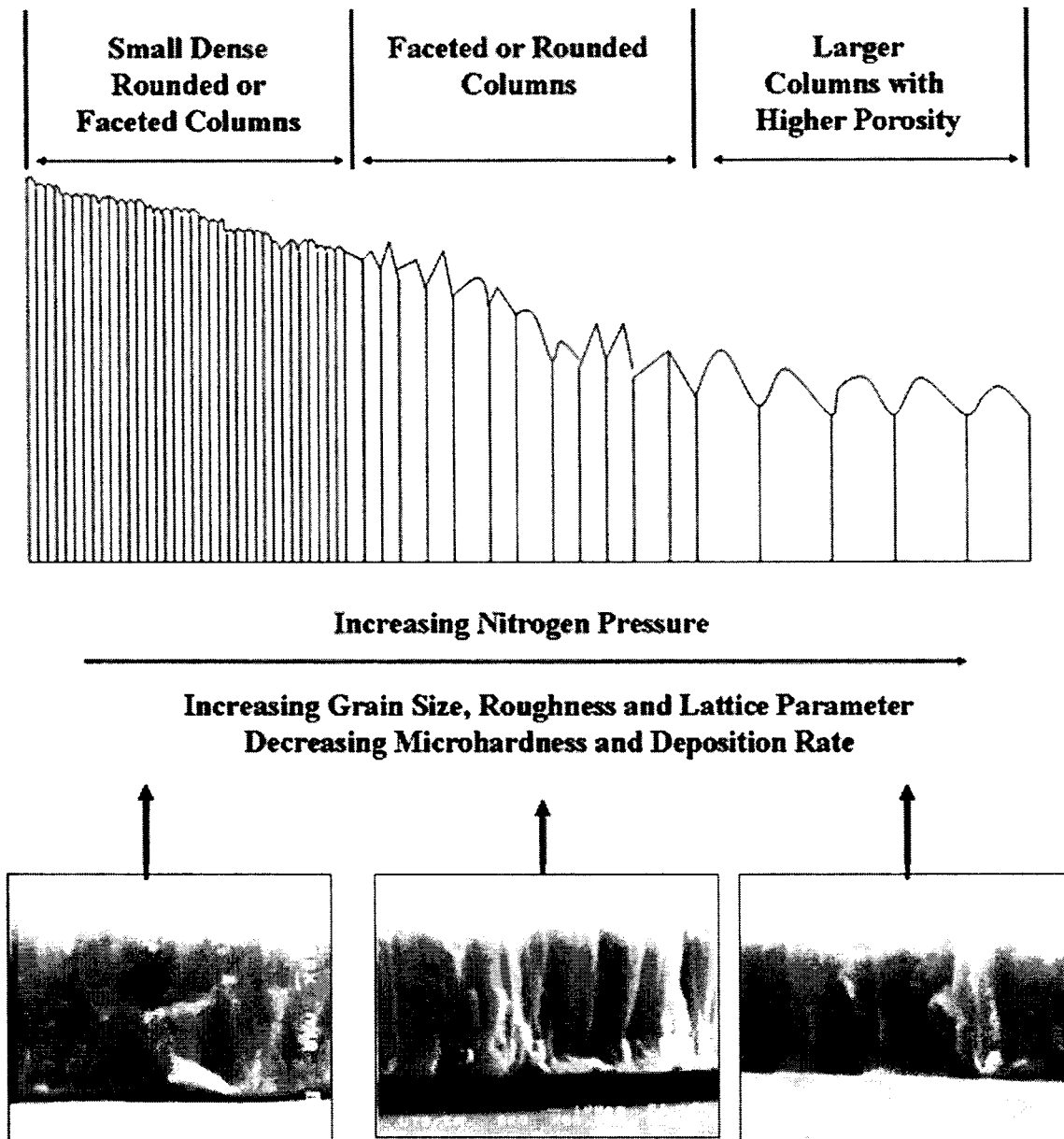


Figure 2: A schematic diagram of a two dimensional structure zone model showing the effect of nitrogen pressure on the morphology and properties of (Ti,Al)N coatings produced with a 90° magnetron configuration.

3.2 Effect of heat treatment on microstructure

The microstructures of the coatings deposited on the H13 steel substrates prior to and after the heat treatment are shown in Figure 3. At a nitrogen deposition pressure of 0.4 mTorr, the coatings exhibited a round, fine grain columnar structure, Figure 3a. As the nitrogen deposition pressure increased to 0.65 mTorr, significant structural changes occurred and

a coarser, faceted grain structure was established, Figure 3b. After heat treatment at a high temperature, densification of the coating structure was evident as observed in SEM micrographs. With the heat treatment at 1000°C, a densified structure developed in both samples, Figures 3c and 3d. However densification of the coating structure was much more significant in the sample deposited at 0.4 mTorr nitrogen pressure with smaller grain size observed.

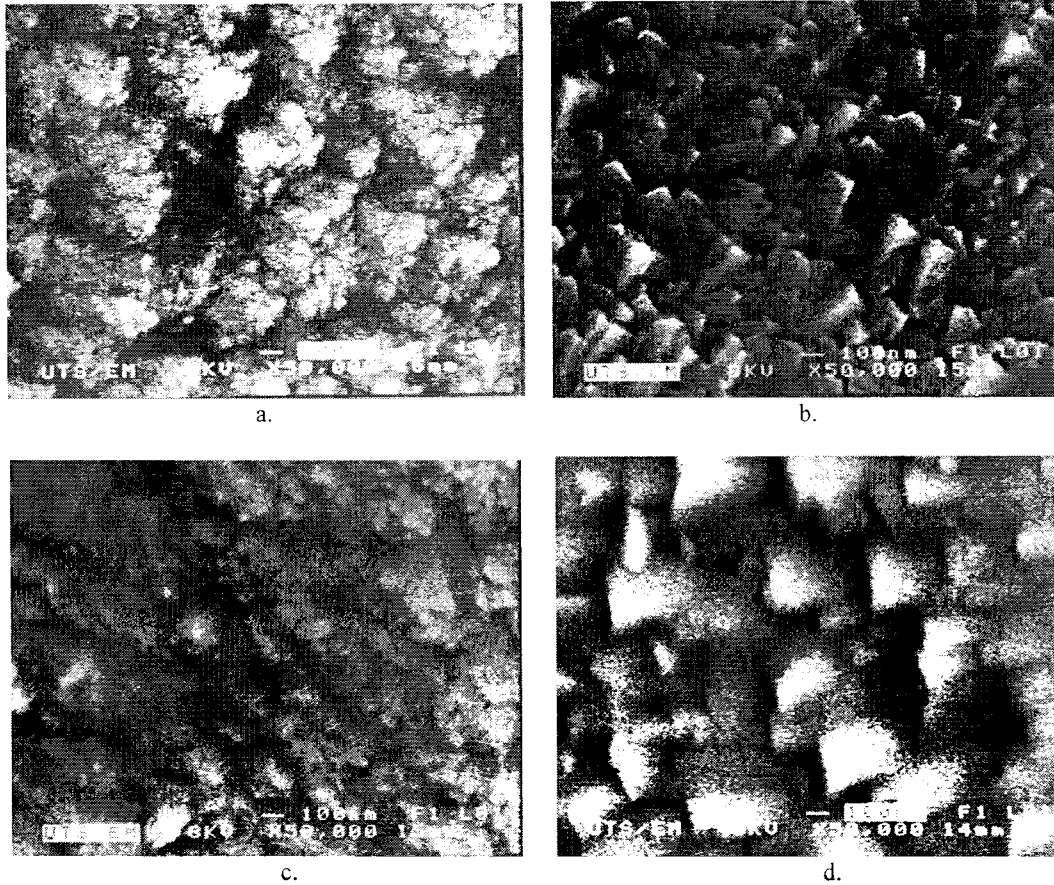


Figure 3: SEM micrographs of (Ti,Al)N coatings prior to and after high temperature heat treatments a) 0.4 mTorr nitrogen pressure, as-deposited, b) 0.65 mTorr nitrogen pressure, as-deposited, c) 0.4 mTorr nitrogen pressure, heat treated and d) 0.65 mTorr nitrogen pressure, heat treated.

3.3 Phase development and crystallographic properties

Analysis of the XRD results measured on the coatings showed that two major crystal structures, namely TiAlN (B1 NaCl cubic structure) and AlN (hexagonal close packed structure) were contained in the coatings (Figure 4). It is noted that the cubic TiAlN B1 NaCl structure has the same bravis lattice (crystal structure) of the cubic TiN structure. However, with replacement of titanium atoms by the smaller sized aluminium atoms, the lattice parameter of the structure decreases, resulting in a shift of the peaks of the XRD reflections

to higher 2θ values. The structure is referred to as the TiN/TiAlN structure in the present study. According to the JCPDS-ICDD data base the TiN structure (JCPDS 38-1420) has peaks at 2θ values of 36.66° for the (111) reflection and 42.60° for the (200) reflection. The hexagonal aluminium nitride structure has a strong (101) peak at 37.92° (JCPDS 25-1133). The 2θ positions of the peak reflections of the coatings for the various nitrogen pressures on the glass substrates are shown in Figure 4 and those for the coatings on the steel substrates are given in Table 1.

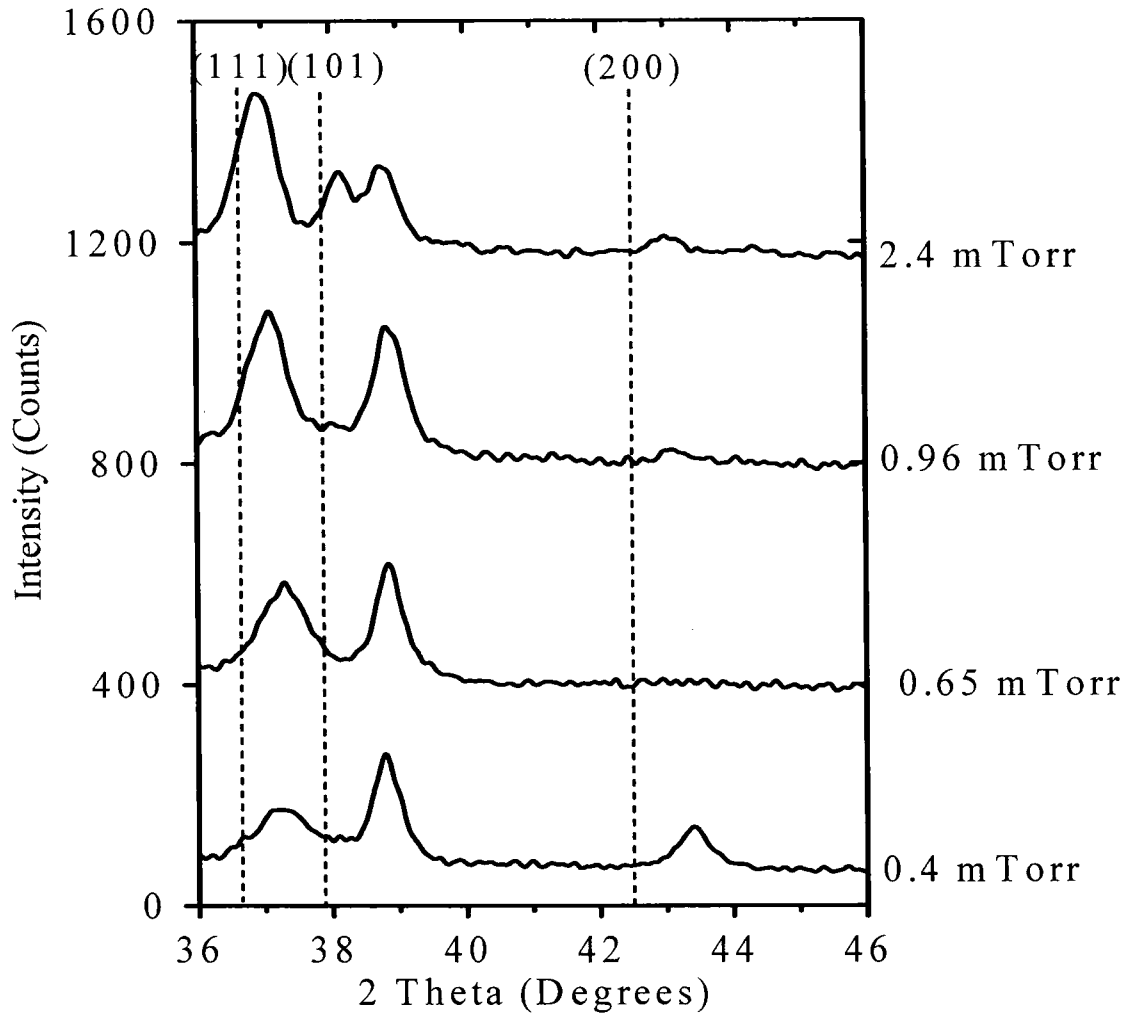


Figure 4: X-ray diffraction patterns measured on as-deposited samples (glass substrates) produced at different nitrogen pressures with a 90° magnetron configuration. The dashed lines shown represent the standard 2θ positions for the (111) and (200) reflections of the cubic TiN structure and the (101) reflection of the hexagonal AlN structure.

Table 1: 2θ positions for major peak reflections of the coatings (steel substrates) deposited at a 90° magnetron geometry.

Nitrogen Pressure (mTorr)	As-deposited		Heat-treated (to 1000°C)	
	0.4	0.65	0.4	0.65
TiN/TiAlN (111)	37.277	37.261	37.150	37.110
AlN (101)	38.812	38.834	38.250	38.200
TiN/TiAlN (200)	43.402	43.141	43.201	43.000

As the nitrogen pressure increased, it was found that the peak positions of the as-deposited coatings generally shifted back to smaller 2θ values, suggesting that the replacement of titanium atoms by aluminium atoms became less effective at higher nitrogen pressures. The peak reflections for the heat treated samples were also observed to shift to lower 2θ values instead, possibly due to the combined effects of stress

relief and refinement and densification of the coating structures occurred in the heat treatment process.

The XRD integrated intensities at different temperatures were determined for the coatings on the H13 steel substrates. Typical results are shown in Figure 5. It was found that as the temperature increased from room temperature (20°C) to 700°C , the intensity

ratio I_{200}/I_{111} for the TiN/TiAlN structure remained constant, but started to increase at temperatures above 700°C (Figure 5a). On the other hand, the intensity ratio between the (200) reflection of the cubic

TiN/TiAlN structure and the (101) reflection of the hexagonal AlN structure decreased significantly, indicating that a strong formation of the AlN (101) component with increasing temperature (Figure 5b).

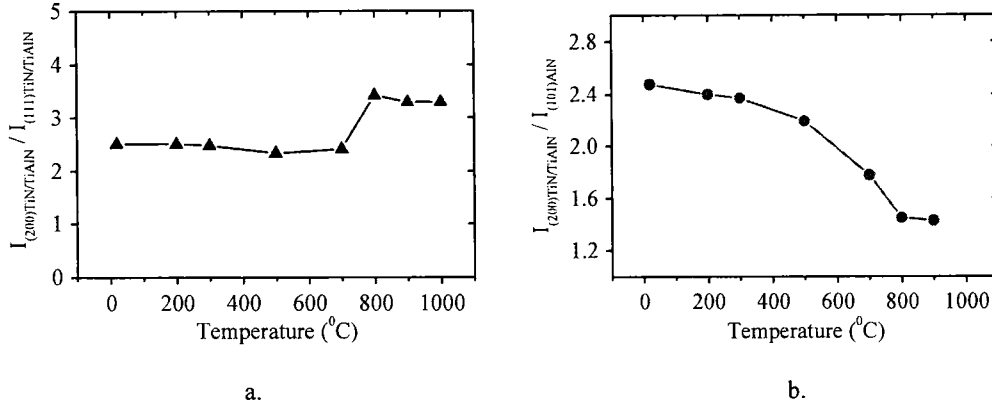


Figure 5: XRD intensity ratios of (a) $I_{(200)TiN/TiAlN} / I_{(111)TiN/TiAlN}$ and (b) $I_{(200)TiN/TiAlN} / I_{(101)AlN}$ determined on coatings produced at 0.4 mTorr nitrogen pressure on steel substrate with a 90° magnetron configuration as a function of increasing heat treatment temperature.

3.4 Surface morphology and grain size

AFM region and line scan measurements across the grain structure were performed on the coatings. The results provide quantitative information on the surface morphology and grain diameter of the coatings and are summarised in Table 2. It was found that after the heat treatment, the average surface roughness and the mean height of the grain structure (measured with reference to the ‘troughs’ of the columnar grains) increased substantially. For the coatings deposited at 0.4 mTorr, the average surface roughness increased from 5.3 nm to 11.2 nm and the mean grain height of the coating structure increased from 20 nm to 39.3 nm. For the coatings deposited at 0.65 mTorr, the average surface roughness increased from 5 nm to 18.8 nm and the mean grain height of the coating structure increased from 20.7 nm to 77.6 nm. On the other hand, a grain refinement (grain size reduction) of the coating

structure was achieved after the heat treatment for the 0.4 mTorr nitrogen pressure sample. The average diameter of the grain columns decreased 130 nm to 90 nm. For the coatings deposited at 0.65 mTorr, the average grain diameter however increased from 168 nm to 220 nm.

3.5 Microhardness

The microhardness of the coatings, measured at a load of 10 g, is given in Table 2. The results showed that after the heat treatment, the mean hardness of the coatings increased from 1688 HV to 2329 HV for the 0.4 mTorr sample, which represents a 38% increase in hardness. The sample produced at 0.65 mTorr only had a slight 5% change in hardness from 1173 HV to 1228 HV.

Table 2: Comparison of grain diameter, surface roughness and hardness of the titanium ternary nitride coatings prior to and after heat treatments.

Nitrogen Pressure (mTorr)	As-deposited		Heat-treated (to 1000°C)	
	0.4	0.65	0.4	0.65
Average Roughness (nm)	5.3	5.0	11.2	18.8
Mean Grain Height (nm)	20.0	20.7	39.3	77.6
Grain Diameter (nm)	130	168	90	220
Hardness (HV)	1688	1173	2329	1228

4. DISCUSSION

The microstructural evolution and properties of titanium aluminium nitride coatings deposited with a 90° magnetron configuration at different nitrogen pressures and under different heat treatments were examined in this study. At low nitrogen pressures below 0.4 mTorr, a fine grain structure developed in the coatings. As the nitrogen pressure increased to 0.65 mTorr, a transition of the microstructure occurred, leading to an decrease in the mechanical properties of the coatings. Analyses of the x-ray diffraction results also reflected that the replacement of titanium atoms by aluminium atoms in the coatings became less effective with increasing nitrogen pressure. It is believed that two major factors, namely increased scattering of the depositing atoms at higher deposition pressures and the formation energy of the nitride compounds, may play an important role in this regard. During transport of the sputtered atoms towards the substrate, collision of the atoms with the reactive gas will occur. With increasing nitrogen pressure, scattering of the depositing atoms by the high density of the reactive nitrogen gas molecules will substantially increase.

An increase of the nitrogen pressure exerts significant influence on the microstructure, morphology and other properties of the coatings. As the nitrogen pressure increases, two effects may be involved. Firstly, the nitrogen pressure affects the formation of different nitride compounds and this in turn determines the structure and properties of the coatings. Secondly, scattering of the depositing species in the gas atmosphere influences their energy and angular distribution arriving at the substrate surface. As the reactive gas pressure increases, the mean free path for sputtered atoms decreases. The sputtered atoms are more heavily scattered and arrive at the surface of the substrates with reduced energy. Consequently, the nucleation rate and the adatom mobility in the coatings are reduced. Recent works by the authors [9,12,13] have shown that improved coating microstructures and properties could be achieved by preparing the coatings at lower nitrogen pressures. Through the use of lower nitrogen pressures, with a substantial increase in the deposition rate, refinement of grain size and densification of the coating microstructures occurred, the coating hardness was significantly increased.

In the present study, an optimum coating development has been identified at a nitrogen deposition pressure of 0.4 mTorr. At this deposition pressure, a densified columnar structure with nanograin size of ~100 nm formed in the coatings. It has been further observed that with a post-deposition heat treatment, the microstructure and the hardness of the coatings could be further improved. It was found that after the heat treatment, the grain size of the coating deposited at 0.4 mTorr decreased from 130 nm to 90 nm, and the hardness of the coating substantially increased from 1688 HV to 2329 HV. On the other hand, the coating

deposited at 0.65 mTorr nitrogen pressure increased from 168 nm to 220 nm and the coating hardness increased slightly from 1173 HV to 1228 HV. The results showed different behaviour between the coatings deposited at the two nitrogen pressures. It is believed that these differences are possibly due to the variations of the amounts of energies created and stored in the coatings at the different nitrogen deposition pressures, resulting in various phase developments and refinement and densification of the coating structures. Further investigation is currently being undertaken. Another interesting observation is the changes in the XRD results occurring at around 700-800 °C. It has been reported by Munz [1] that the (Ti,Al)N coatings started to oxidise at 750 °C. The observed changes in the XRD results are possibly associated with some oxidation of the coatings at these temperatures. Formation of oxynitrides may explain an increase of hardness with grain growth in the coatings deposited at 0.65 mTorr nitrogen pressure. Current work is also being conducted to investigate the critical heat treatment of the (Ti,Al)N thin films below these temperatures.

5. CONCLUSION

Thermal stability of nanocrystalline ternary nitride coatings at elevated temperatures was examined. It was found that an unexpected grain refinement occurred in the coatings deposited at a nitrogen pressure of 0.4 mTorr after the heat treatment. A stronger development of TiN/TiAlN (200) component was also evident at temperatures above 800°C. With a finer and densified grain structure, the hardness of the coatings increased substantially from ~1700 to 2300 HV.

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