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AN EMPIRICAL ANALYSIS OF NITROGEN PRESSURE EFFECT ON GRAIN SIZE DEVELOPMENT OF NANOSTRUCTURED TERNARY NITRIDE COATINGS

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ABSTRACT
An empirical relationship between the grain diameter of ternary nitride coatings and the nitrogen deposition pressure was formulated in the present study. A linear relationship was established between the reciprocals of the square roots of the grain diameter of the coatings and the nitrogen deposition pressure. It was further confirmed that the equation parameter, m_d of the empirical relationship was linearly proportional to the primary sputter yield of the coating materials. With defined discharge conditions and sputter characteristics of the target materials, the values of m_d for different coatings can be calculated and the grain size of the coating structure at different nitrogen deposition pressures can be determined.

1. INTRODUCTION

Development of complex ternary nitride coatings has attracted significant industrial interest in recent years. The coatings are reported to possess improved properties over the conventional binary nitride coatings [1-12]. In reactive magnetron co-sputter deposition of ternary nitrides, nitrogen deposition pressure is one of the main controlling parameters of the deposition process. As the nitrogen pressure varies, the deposition rate and composition of the coatings change, which in turn affect the phase development and microstructure of the coatings. In a review of the sputtering process, Smith [13] has further suggested that the microstructure development of the coatings is primarily governed by the deposition rate and the energy of the depositing atoms arriving at the substrate. The deposition rate and energy of the depositing atoms determine the nucleation and grain growth of the microstructure. Despite extensive studies have been conducted on the microstructures and properties of the sputtered coatings, a quantitative model of the nitrogen pressure effect on the microstructural development of the ternary nitride coatings is still lacking. In the present analysis, by incorporating the experimental results obtained from recent studies of (Ti,Al)N, (Ti,V)N and (Cr,V)N thin films [11,12], simulation for an empirical relationship between the grain diameter of the coatings and the nitrogen pressure is attempted. The study aims to investigate if an empirical relationship exists between the grain size of the coatings and the nitrogen deposition pressure, an important deposition parameter of the process, and if it exists, to determine the relationship. With an established relationship, a control of the grain size of the coatings will become possible under specified deposition conditions.

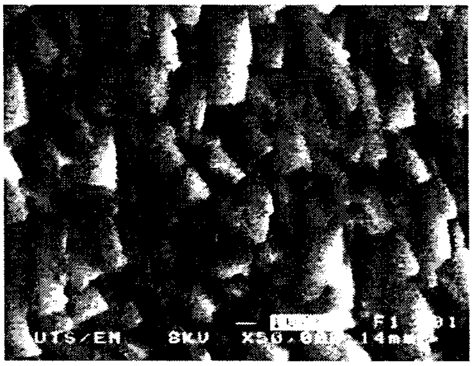
2. EXPERIMENTAL PROCEDURES

Reactive magnetron co-sputtering, with separate magnetron targets, was used to produce titanium aluminium nitride, titanium vanadium nitride and chromium aluminium nitride coatings at various nitrogen deposition pressures. The coatings were deposited with two unbalanced, independently controlled magnetrons at a target-substrate working distance of 65 mm and at an angle of 45° to the substrate. A constant d.c. bias of negative 100 volts was applied between the substrate and the targets. The substrate holder was heated and maintained at a temperature of 240°C for formation of densified coatings [11]. 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. Pirrani gauges and Tylan mass flow controllers were used to monitor the pressure and flow rate of reactive gas through the deposition process. The coatings were deposited to a thickness of 1.5 – 2.0 μm at nitrogen pressures varying from 0.2 – 2.4 mTorr (0.027 – 0.32 Pa). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to examine the microstructure and morphology of the coatings. The microstructure of the coatings was examined using a JEOL 6300F field emission SEM. AFM analysis was performed using a Park Scientific Instrument Autoprobe with an ultralever tip to determine the grain diameter of the coatings.

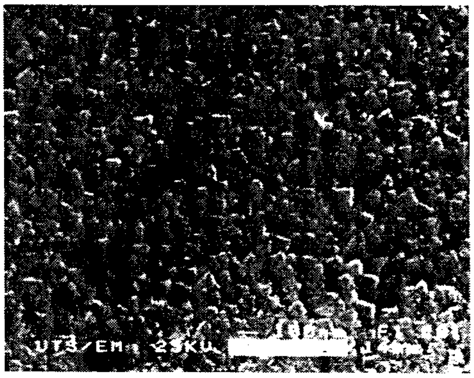
3. EMPIRICAL ANALYSIS OF EXPERIMENTAL RESULTS

3.1 Microstructural Evolution
An increase of nitrogen deposition pressure imposed a significant effect on the microstructural development

of the coatings. At low nitrogen pressures, a nanograin structure with grain size in the regime of 100-150 nm generally developed. Typical structures of the (Ti,V)N, (Ti,Al)N and (Cr,Al)N coatings deposited at a low nitrogen pressure are shown in Figure 1 (a)-(c).



(a)



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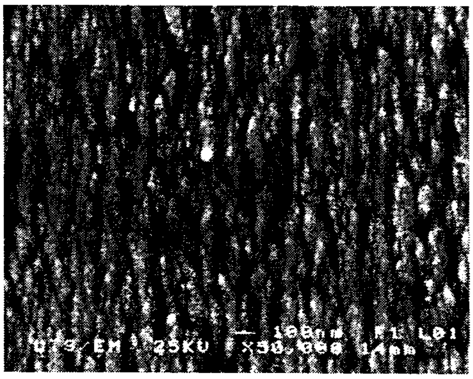
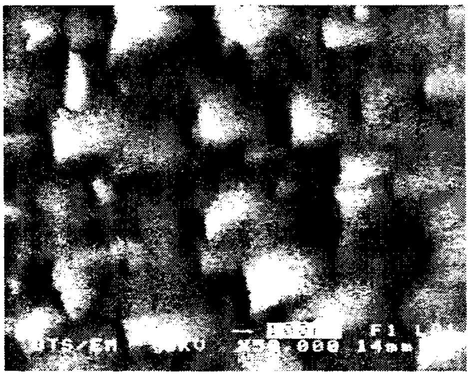


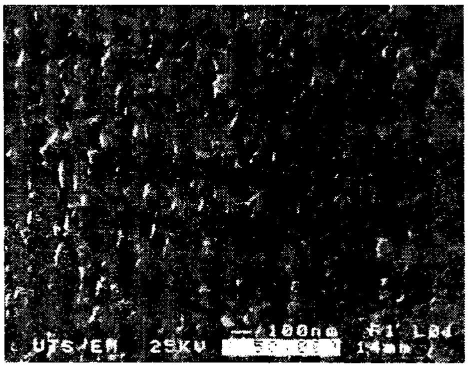
(c)

Figure 1: Scanning electron micrographs of (a) (Ti,V)N, (b) (Ti,Al)N and (c) (Cr,Al)N coatings deposited at 0.4 mTorr nitrogen pressure.

As the nitrogen deposition pressure increased to higher values, the grain size of the coating structure significantly increased, typical structures are shown in Figure 2 (a)-(c). Examination on the cross-sections of the samples showed the coatings consisted of a columnar grain structure, Figure 3.



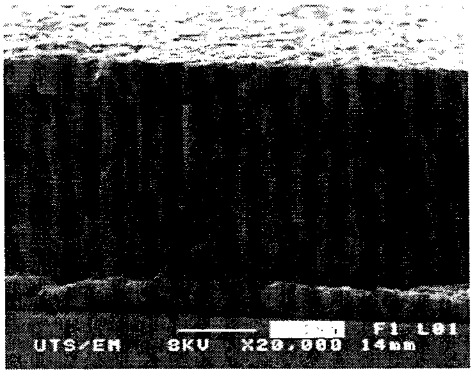
(a)



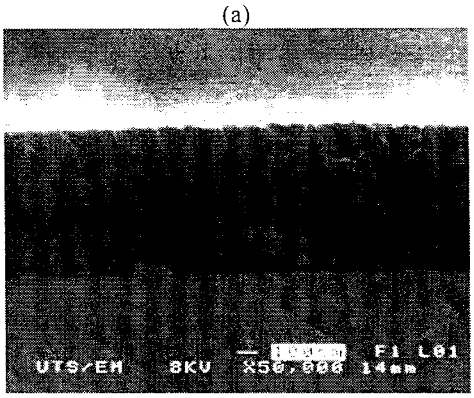
(b)

(c)

Figure 2: Scanning electron micrographs of (a) (Ti,V)N (b) (Ti,Al)N and (c) (Cr,Al)N coatings deposited at 0.65 mTorr nitrogen pressure.



(a)



(b)

(c)

Figure 3: Scanning electron micrographs showing the columnar grain structure of (a) (Ti,V)N, (b) (Ti,Al)N and (c) (Cr,Al)N deposited at 0.65 mTorr nitrogen pressure.

3.2 Grain Size Relationship

AFM analysis was performed to determine the grain diameter of the coatings. Experimental results of the grain size development of the coatings with increasing nitrogen pressure are shown in Figure 4. A consistent relationship was observed between the nitrogen deposition pressure and the grain diameter of the three ternary nitride coatings under investigation. As the nitrogen pressure increased from 0.4 to 2.4 mTorr, the grain diameter of the (Ti,Al)N coatings increased from 90 to 180 nm and that of (Cr,Al)N increased from 100 to 300 nm. On the other hand, as the nitrogen pressure increased from 0.2 to 0.96 mTorr, the grain diameter of the (Ti,V)N coatings increased from 150 to 350 nm.

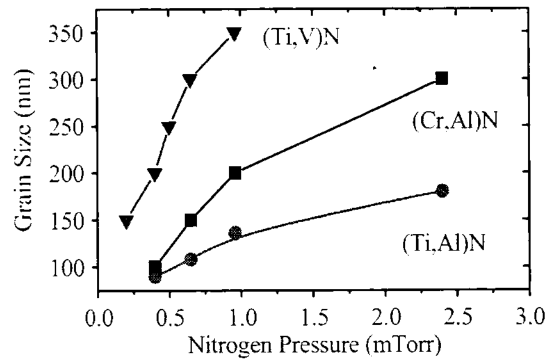


Figure 4: Variation of grain diameter of the (Ti,V)N, (Ti,Al)N and (Cr,Al)N coatings with nitrogen deposition pressure.

Using the results of Figure 4, the data was re-plotted with the reciprocals of the square roots of grain size and nitrogen pressure as shown in Figure 5. A linear relationship, which reflects the grain size development of the coatings as a function of the nitrogen pressure, is successfully established for all the three ternary nitrides.

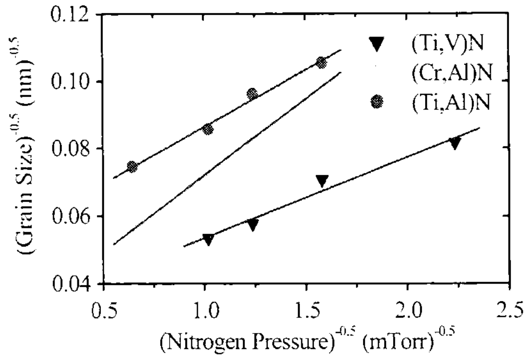


Figure 5: Graph of reciprocal of square root of grain diameter versus reciprocal of square root of nitrogen pressure for the (Ti,V)N, (Ti,Al)N and (Cr,Al)N coatings.

The relationship between the grain size and the nitrogen deposition pressure can be described with the following relationship:

$$\frac{1}{\sqrt{d}} = \frac{m_d}{\sqrt{P_N}} + \frac{1}{\sqrt{d_o}} \qquad (1)$$

where:

m_d = equation constant (reflecting the rate of grain size change w.r.t. nitrogen pressure) ($nm^{-0.5}$ $mTorr^{0.5}$).

d = grain size (nm) of the coating.

d_o = grain size (nm) of the coating at a large nitrogen pressure.

P_N = nitrogen pressure (mTorr).

The values of m_d and d_o for the three ternary coatings are shown in Table 1.

Table 1: Sputter characteristics and equation constants of the ternary nitride coatings.

Constants	(Ti,V)N	(Ti,Al)N	(Cr,Al)N
Magnetron Discharge Power ($Watts/cm^2$)	9 for Ti 6 for V	9 for Ti 6 for Al	9 for Cr 6 for Al
Metal Sputtering Yield (atoms/ion)	0.51 for Ti 0.65 for V	0.51 for Ti 1.05 for Al	1.18 for Cr 1.05 for Al
m_d ($mm^{-0.5}.mTorr^{0.5}$)	23.78	33.78	45.28
d_o (mm)	0.00113	0.000362	0.00140
J_{MP} ($cm^{-2}.s^{-1}$)	$3.323X10^{16}$	$4.262X10^{16}$	$6.622X10^{16}$

3.2 Justification of m_d

In equation (1), m_d defines the rate of grain diameter change of the coatings with respect to the nitrogen deposition pressure. It is understood that as the nitrogen pressure increases, nitriding of the target materials and scattering of the atoms may become significant, and the number and energies of the depositing atoms arriving at the substrate will be greatly reduced [11,12]. As a result, the rate of nucleation will decrease and a coarse grain structure develops. m_d can therefore be interpreted as a term associated with the number and energies of the depositing atoms arriving at the substrate, and acts as the nitrogen pressure dependence upon the change of the grain size of the coatings. In the present analysis, with the same substrate bias voltage and target-substrate working distance, the controlling factor remained on the deposition rate of the three different coatings at a specified nitrogen pressure is the discharge power of the metallic targets. The discharge power of the individual target changes the sputter yield and the deposition flux of the metallic element, which in turn affect the number and energies of the depositing atoms.

In co-sputter deposition of ternary nitrides, the primary sputter yield (J_{MP}) from the two separate magnetron targets (M1 and M2) can be determined using by the following relationship [14]:

$$J_{MP} = (S_M J_{Ar+})_{M1} + (S_M J_{Ar+})_{M2} \quad (2)$$

where:
J_{Ar+} = ion current density at the target ionised by argon ($A.cm^{-2}$).
S_M = sputtering yield of the metal (atoms/ion)

The ion current density at the target (J_{Ar+}) is dependent upon the magnetron power and is generally determined by the following expression:

$$J_{Ar+} = \frac{i_T}{A_T e(1+\gamma)} \quad (3)$$

where:
A_T = area of target (cm^2)
e = elementary charge of an electron = 1.602×10^{-19} C
γ = secondary electron yield = 0.1
i_T = magnetron current (Amps)

The values of J_{MP} of the target materials used in this study are determined and shown in Table 1. The relationship of m_d against J_{MP} is shown in Figure 6. A linear relationship is reasonably established between m_d and J_{MP}, suggesting that m_d can be estimated in relation to the primary sputter yield of the target materials.

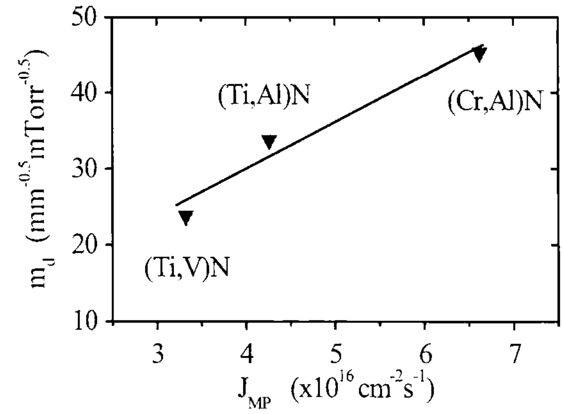


Figure 6: Graph of m_d versus J_{MP} of the (Ti,V)N, (Ti,Al)N and (Cr,Al)N coatings.

4. DISCUSSION

Reactive magnetron co-sputter deposition of ternary nitrides is a complex process in which the process parameters such as nitrogen pressure, sputtering power and magnetron configuration all play a crucial role in determining the microstructure of the coatings [11,12]. The present study aims to investigate if an empirical relationship exists between the grain size of the ternary coatings and one of the important process variables, namely the nitrogen deposition pressure, and if it exists, to determine the relationship. The relationship is expected to make an important contribution in predicting the grain size of the coatings at specified nitrogen deposition pressures. Development of a desired coating structure then becomes possible under design deposition conditions. The results of the current study show that a linear relationship exists between the reciprocals of the square roots of grain size and nitrogen pressure. It is further confirmed that a linear relationship can be reasonably established between the equation parameter, m_d and the primary sputter yield of the target materials. m_d is an important parameter in the grain size – nitrogen pressure relationship as it controls the rate of the grain size development with increasing nitrogen pressure. This implies that the values of m_d can be determined using the material data available in the literature. Once the discharge conditions and the sputter yields of the target materials are known, the values of m_d for different coatings can be calculated and the grain sizes of the coatings at different nitrogen deposition pressures can be worked out, which will provide valuable information for industrial production of these high-valued ternary nitride coatings.

5. CONCLUSIONS

An empirical relationship between the grain size of ternary nitride coatings and the nitrogen deposition pressure was formulated in the present study. A linear relationship was established between the reciprocals of the square roots of the grain size of the coatings and the nitrogen deposition pressure. It was further confirmed that the equation parameter, m_d of the empirical relationship was linearly proportional to the primary sputter yield of the coating materials. With defined discharge conditions and sputter characteristics of the target materials, the values of m_d for different coatings can be calculated and the grain sizes of the coatings at different nitrogen deposition pressures can be determined.

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EDITORIAL

The papers included in this volume of Materials Forum are based on the presentations delivered at the "3rd International Conference on Advanced Materials Processing (ICAMP3)" that was held between 29 November and 1 December 2004 in Melbourne. This conference covers most aspects of advanced materials and the processes by which they are produced. Particular emphasis is placed on lightweight alloys (magnesium, aluminium and low-cost titanium), nanostructured materials and composites, powder metallurgy, thermomechanical processing, surface engineering, processing-microstructure-property relationships, advanced ceramics, biomaterials, energy and fuel cells. All invited and contributed papers were subject to the usual independent peer review process. We would like to take this opportunity to sincerely thank the reviewers who carefully reviewed each manuscript and provided the authors with constructive criticism. The publication of these papers would not be possible without their help.

Jian-Feng Nie
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Preface >

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