Science of Sintering, **38** (2006) 211-221

DOI: 10.2298/SOS0603211Y

UDK 548.734.3: 539.216

A Nanoindentation Study of Magnetron Co-Sputtered Nanocrystalline Ternary Nitride Coatings

W. Y. Yeung[1*)], S. N. Dub[2], R. Wuhrer[3], Yu. V Milman[4]

[1]Department of Chemistry, Materials and Forensic Sciences, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia.

[2] Institute for Superhard Materials of the National Academy of Sciences of Ukraine, 2, Avtozavodskaya Str., 04074, Ukraine.

[3] Microstructural Analysis Unit, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia.

[4] Institute of Materials Science Problems of the National Academy of Sciences of Ukraine, 3 Krzhizhanovsky Str., 03142, Ukraine.

Abstract:

Nanoindentation testing was used to determine the hardness, elastic modulus and plasticity parameter of three newly developed ternary nitride coatings with nano-sized grains. With decreasing nitrogen deposition pressure, grain diameter of the coatings decreases that leads to both higher nanohardness and elastic modulus with conservation of satisfactory values of plasticity characteristic.

Keywords: *Nanocrystalline Materials, Thin Films, Sputtering, Nanoindentation.*

1. Introduction

Development of complex ternary nitride coatings has attracted significant research and industrial interest in the last 15 years [1]. It has been reported that with additional elements, the oxidation resistance of the coatings is greatly improved at elevated temperatures [1-3]. Since then several research groups have investigated the microstructure and properties of sputtered (Ti,Al)N and (Cr,Al)N coatings [4-14]. In these studies, effects of some important deposition parameters such as nitrogen deposition pressure, target discharge power, substrate bias voltage and substrate temperature on structural evolution of the coatings have been extensively examined. More recently, Wuhrer and Yeung [15] conducted a comparative study of co-sputtered (Ti,Al)N and (Cr,Al)N coatings produced under the same deposition conditions. It was found that the intrinsic properties of the coating elements might play an important role in the magnetron sputter process and resulted in different coating structures and properties, and the (Cr,Al)N coatings showed a great potential for advanced engineering applications. Despite these extensive studies on the development of sputtered coatings, information about their mechanical properties such as the elastic modulus and plasticity characteristic is still very limited. The present study aims to investigate and compare the mechanical properties of these newly developed ternary nitride coatings using the

*) Corresponding author: Wing.Yeung@uts.edu.au

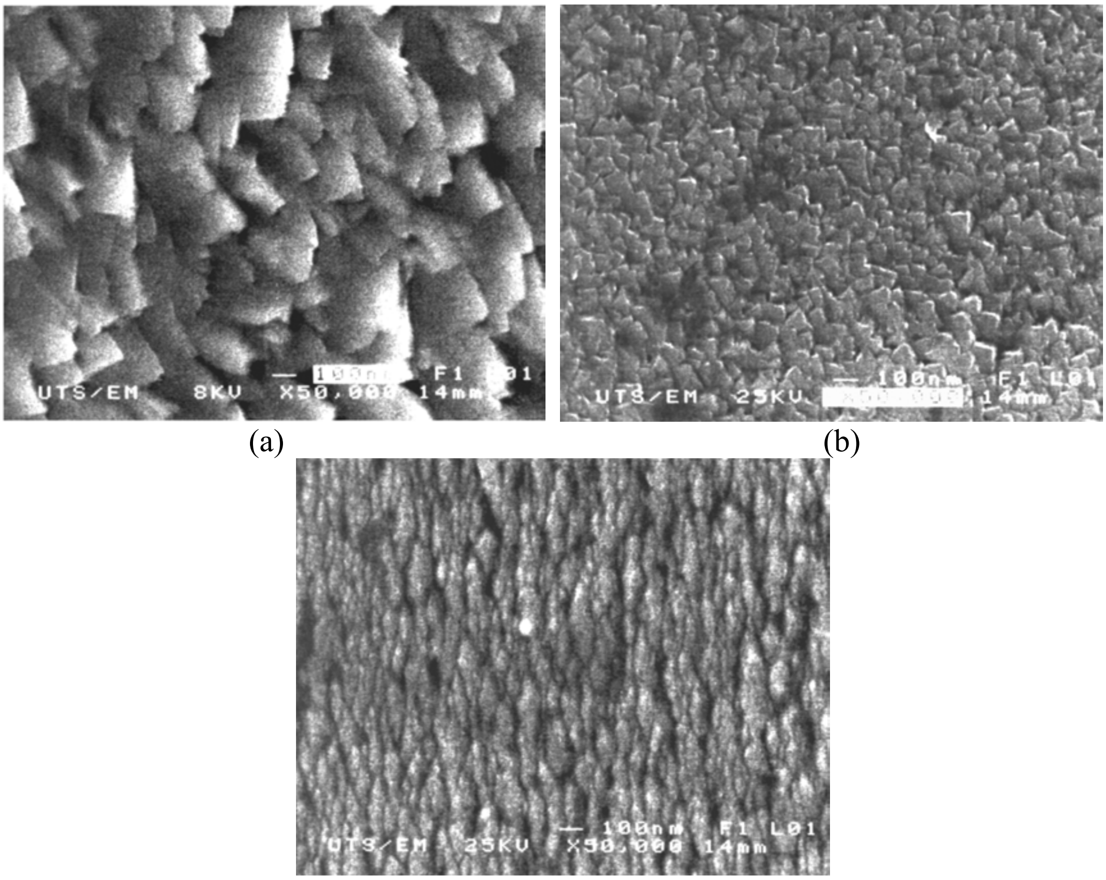
nanoindentation technique. Several models [16-18] have been developed for calculation of hardness (H) and elastic modulus (E) of the materials for nanoindentation testing, but the most used method for determination of nanohardness and elastic modulus was elaborated by Oliver and Pharr [16]. On the other hand, in their studies of high hardness materials and quasicrystals, Milman and co-workers [19-24] developed an analysis of a material's plasticity characteristics and mechanical properties through indentation measurements. This method was applied for analysis of ceramic coatings as well [23,24]. In these analyses, the method of local loading with an indenter is regarded as the method of micromechanical testing which gives hardness, a complex of mechanical characteristics of flow stress, elastic modulus as well as plasticity of the materials. An investigation using the nanoindentation technique is performed in the present study to determine the mechanical properties of ternary nitride coatings. In addition to (Ti,Al)N and (Cr,Al)N, a new coating of (Ti,V)N has also been studied to provide more generalised results for the analysis. The study aims to generate some important information currently not available for these valuable ternary nitride coatings.

2. Experimental Procedure

Reactive magnetron co-sputtering, with separate titanium and vanadium sputter targets, titanium and aluminium sputter targets, and chromium and aluminium sputter targets, was used to produce the titanium vanadium, titanium aluminium and chromium aluminium ternary nitride coatings at nitrogen deposition pressures of 0.40 and 0.96 mTorr (0.053 and 0.128 Pa). The coatings were deposited in a Varian 3120 deposition unit with two unbalanced, independently controlled magnetrons with a target-substrate working distance (W.D.) of 65 mm. The discharge powers of titanium, chromium, vanadium and aluminium magnetrons were set at 9.0, 9.0, 6.0 and 6.0 W/cm^2 respectively. 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 or chromium of ~60 nm and an interlayer of titanium vanadium, titanium aluminium, or chromium aluminium of ~120 nm on a glass substrate. A constant d.c. bias of negative 100 volts was then 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 to a thickness of 1.5 – 2.0 microns. The microstructure and the morphology of the coatings 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 mechanical properties of the coatings were determined by nanoindentation technique. Sharp indentation experiments were performed using a MTS Nano Indenter II^{TM} tester. A diamond Berkovich indenter with a tip radius of about 220 nm was used in the experiments with a maximum load of 10 mN. The loading and unloading phases of the indentations were carried out under load control at a nominal rate of 0.5 mN/s. At the maximum load, a dwell period of 20 s was imposed before unloading. Another dwell period of 30 s was imposed at 80% of unloading to correct for thermal drift in the system. The adjacent indents were separated by at least 50 μm. The hardness and elastic modulus values were averaged over five measurements. Hardness and elastic modulus of the coatings were calculated in accordance with the method as described by Oliver and Pharr [16]. The plasticity parameter of the coatings was determined as a ratio of the work of the plastic deformation to the total work done by the indenter in deforming the material.

3. Results
Microstructural evolution

Typical structures of the (Ti,V)N, (Ti,Al)N and (Cr,Al)N coatings deposited under the current experimental conditions are shown in Fig. 1. It was found that both (Ti,V)N and (Ti,Al)N contained a densified faceted grain structure but the grain size of (Ti,Al)N was much finer than that of (Ti,V)N. On the other hand, the (Cr,Al)N coatings had a more fibrous structure. Cross-sections of the coatings were examined in this study. A columnar grain structure was contained in the cross-sections of all the three coatings.



(a) (b) (c)

Fig. 1 SEM micrographs showing microstructure of (a) (Ti,V)N, (b) (Ti,Al)N and (c) (Cr,Al) coatings produced at 0.4 mTorr nitrogen pressure.

Typical features of the coatings are shown in Fig. 2.

Grain size and surface roughness

The grain diameter and surface roughness of the coatings were determined by AFM measurements. The results for the grain diameter and surface roughness of the coatings deposited at 0.40 and 0.96 mTorr are given in Tab. I. It was found that the (Ti,V)N coatings were generally of a larger grain size and a higher surface roughness. At a nitrogen deposition pressure of 0.4 mTorr, the grain diameter of the (Ti,V)N coatings was ~200 nm compared to ~90 nm of (Ti,Al)N and ~100 nm of (Cr,Al)N.

The surface roughness of the (Ti,V)N coatings was ~10 nm compared to 4.2 nm of (Ti,Al)N and 3.9 nm of (Cr,Al)N. As the nitrogen deposition pressure increased, the grain diameter and surface roughness increased for the coatings. At 0.96 mTorr, the grain diameter of the (Ti,V)N coatings was ~350 nm and those of (Ti,Al)N and (Cr,Al)N were 136 and 200 nm. The surface roughness of the (Ti,V)N, (Ti,Al) and (Cr,Al)N coatings was 15, 8.1 and 8.0 nm respectively.

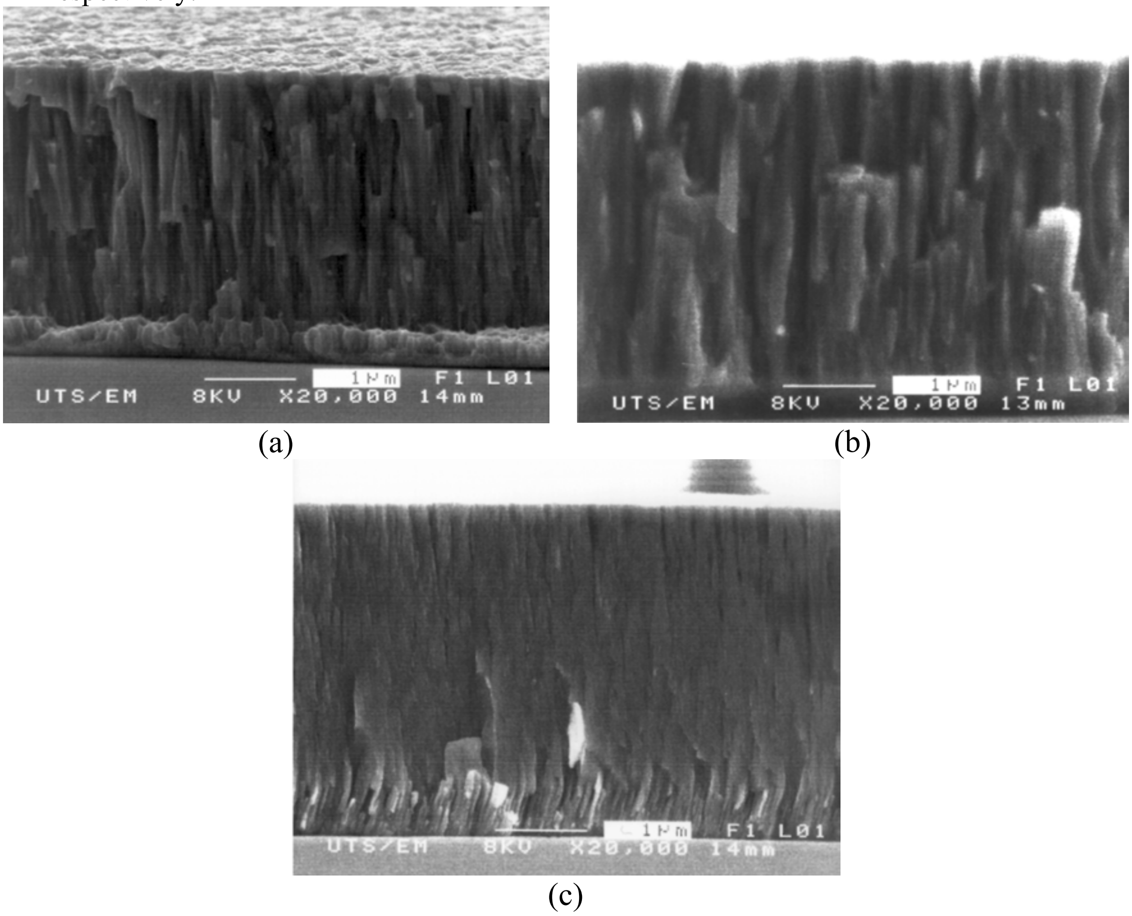


Fig. 2 SEM micrographs showing microstructure of the cross-section of (a) (Ti,V)N, (b) (Ti,Al)N and (c) (Cr,Al) coatings produced at 0.4 mTorr nitrogen pressure.

Nanoindentation

Nanoindentation measurements with a diamond Berkovich indenter were performed on the coatings. The load-displacement curves for the (Ti,V)N, (Ti,Al)N and (Cr,Al)N coatings are shown in Fig. 3 – Fig. 5 respectively. It was found that the three coatings generally exhibited typical load-displacement behaviour under nanoindentation and the depth of the indent monotonously increased with increasing load. However it was found that the penetration depth of the indenter at the maximum load of 10 mN substantially increased for the coatings deposited at the higher nitrogen pressure of 0.96 mTorr. The difference in the penetration depth was more significant in the coatings of (Ti,V)N and (Ti,Al)N and was less significant in the coatings of (Cr,Al)N. Using the load vs displacement curves of Fig. 3 – Fig. 5, the values of the hardness (H) and elastic modulus (E) of the coatings were calculated. The plasticity parameter (δ_H) was also determined for the coatings. The results are given in Tab. I. It was found that hardness and elastic modulus were much higher in the coatings deposited at 0.4 mTorr. At a nitrogen deposition pressure of 0.4 mTorr, despite its larger grain size, the

(Ti,V)N coating had the highest hardness of 18.6 GPa and the highest elastic modulus of 264 GPa. The hardness and elastic modulus of (Ti,Al) coatings were 17.3 GPa and 238 GPa and those of (Cr,Al)N coatings were 18.4 GPa and 214 GPa respectively. As the nitrogen deposition pressure increased, the grain diameter of the coatings increased, hardness and elastic modulus of the three coatings dropped to lower values. The changes in hardness and elastic modulus with grain size of the coatings are shown in Fig. 6 and Fig. 7 respectively. It was found as the nitrogen deposition pressure increased to 0.96 mTorr, hardness of (Ti,V)N and (Ti,Al)N coatings dropped to 13.6 and 15.8 GPa respectively whilst hardness of (Cr,Al)N maintained a more moderate drop to 16.7 GPa. Elastic modulii of (Ti,V)N and (Ti,Al)N coatings dropped to 196 and 158 GPa respectively and that of (Cr,Al) decreased to 194 GPa.

Tab. I Comparison of the grain diameter, surface roughness and mechanical properties of the coatings deposited at different nitrogen pressure.

	(Ti,V)N		(Ti,Al)N		(Cr,Al)N	
Nitrogen Pressure (mTorr)	0.4	0.96	0.4	0.96	0.4	0.96
Grain Diameter, d (nm)	200	350	90	136	100	200
Surface Roughness, R (nm)	10.0	15.0	4.2	8.1	3.9	8.0
Hardness, H (GPa) (Approximate HV value)	18.6 (1711)	13.6 (1251)	17.3 (1592)	15.8 (1454)	18.4 (1693)	16.7 (1536)
Elastic Modulus, E (GPa)	264	196	238	158	214	194
Plasticity Parameter, δ_H	0.53	0.51	0.53	0.51	0.48	0.48

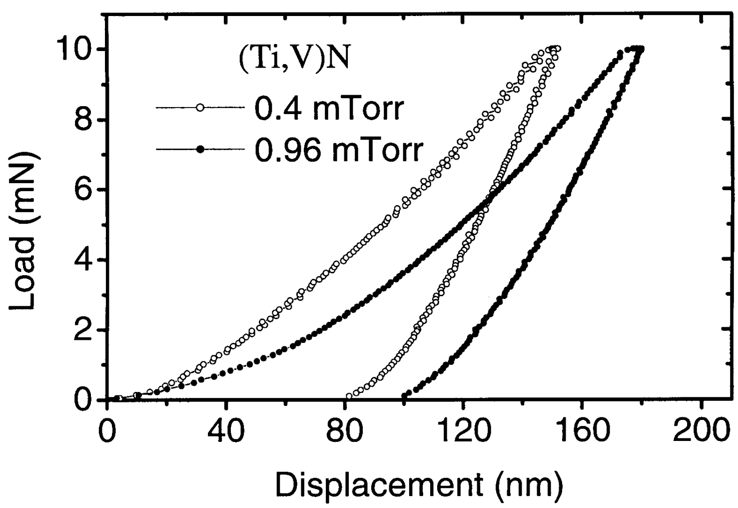


Fig. 3 Load-displacement curves of (Ti,V)N coatings deposited at nitrogen deposition pressures of 0.4 and 0.96 mTorr.

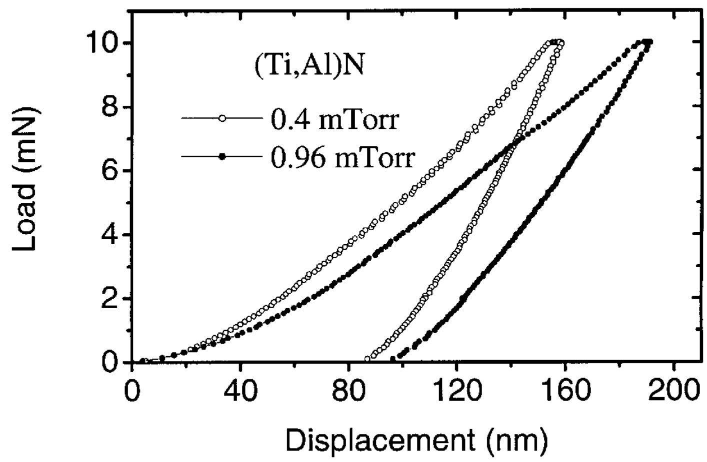


Fig. 4 Load-displacement curves of (Ti,Al)N coatings deposited at nitrogen deposition pressures of 0.4 and 0.96 mTorr.

On the other hand, the plasticity parameters of (Ti,V)N and (Ti,Al)N coatings were higher than that of the (Cr,Al)N coatings. But, as the nitrogen deposition pressure increased, the plasticity parameters of the (Ti,V)N and (Ti,Al)N coatings decreased to lower values and that of (Cr,Al)N was unchanged.

4. Discussion

Superhard coatings for advanced engineering applications are generally of a small thickness. Because of the small thickness of the coatings, their mechanical properties such as the elastic modulus and plasticity characteristic cannot be readily obtained by the conventional mechanical testing methods. Information about the mechanical properties of these complex ternary nitride coatings is therefore very scarce.

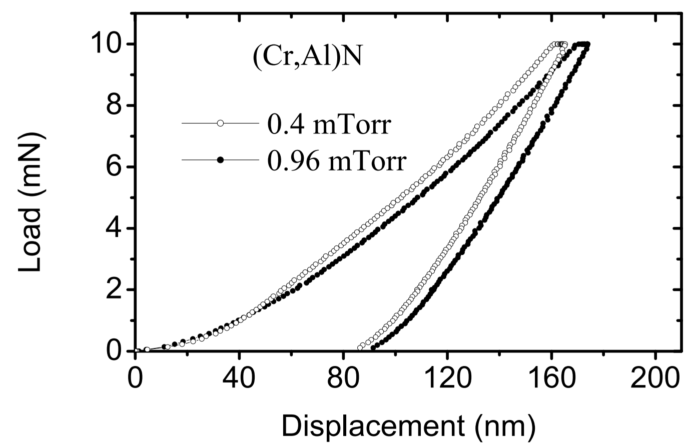


Fig. 5 Load-displacement curves of (Cr,Al)N coatings deposited at nitrogen deposition pressures of 0.4 and 0.96 mTorr.

The present investigation aims to use the nanoindentation method to determine the hardness, elastic modulus and plasticity parameter of three newly developed coatings of (Ti,V)N, (Ti,Al)N and (Cr,Al)N. Using the load-displacement curves of nanoindentation and the methods developed by Oliver and Pharr [16] and Milman and co-workers [19,20], hardness, elastic modulus and plasticity parameter of the coatings have been determined. It was found that at a nitrogen deposition pressure of 0.4 mTorr, the hardness values and elastic modulii of the coatings were in the order of 17 - 18.5 GPa (1600 – 1700 HV) and 240 – 265 GPa respectively, and the plasticity parameters of the coatings were within 0.48 to 0.53. Scanning electron microscopy and atomic force microscopy showed that these coatings were associated of densified and nanograin sized structures. As the nitrogen deposition pressure increased, the grain size of the coatings increased, the hardness values, elastic moduli and plasticity parameters of the coatings decreased. The (Cr,Al) coatings however maintained a more moderate value drop.

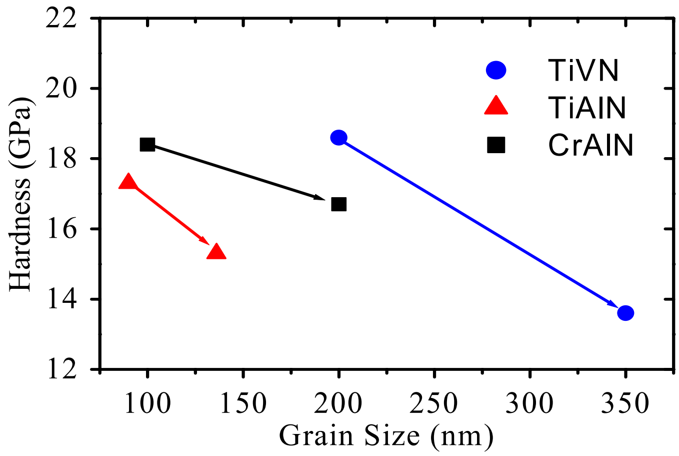


Fig. 6 Variation of hardness versus grain diameter of the coatings.

In a nanoindentation test, the mechanical properties of the test materials are calculated from the load-displacement curve of the indentation process. Despite several models [16-18] developed for the calculation of hardness (H) and elastic modulus (E) of materials, the analysis by Oliver and Pharr [16] is generally accepted as the standard method for nanoindentation calculation. In the method by Oliver and Pharr [16], the elastic modulus is computed from the slope of the unloading portion of the load-displacement curve at the maximum load. In determination of the material hardness, while the conventional microhardness indentation uses the indented area (after removal of the indenter) as contact area in hardness calculation, the hardness of the material in a nanoindentation test is determined at the maximum load with the load divided by the cross-sectional area of the indenter at the depth of penetration. The instrument determines this cross-sectional area during indentation by assuming a known tip shape and back computing the area based on the tip displacement of the indenter with correction for elastic recovery. For low loads on hard thin coatings, nanoindentation appears to be an appropriate approach to generate more accurate results. On the other hand, by adopting the principle developed by Milman and co-workers for instrumental indentation [19,20], material plasticity of the coatings could be determined in this study. Taking into account the elastic and plastic stress-strain relationship of the material, a plasticity parameter is defined as $\delta_H = \varepsilon_p/\varepsilon = 1 - \varepsilon_e/\varepsilon$ where ε_p, ε_e and ε are the mean strain values of the plastic, elastic and total deformation on the contact area of the indenter with specimen in the loading direction, respectively [19,20]. Knowing the defined geometry of the indenter, plasticity of the material or coating can then be determined using the H and E values of the materials. The plasticity parameters of metals generally fall in a range of $0.9 < \delta_H < 1.0$ and fcc metals have higher values of δ_H. Ceramic materials are of δ_H values lower than those of metals and alloys. For high hardness ceramic materials, polycrystalline TiN and TiB_2 have δ_H values of 0.57 and 0.44 respectively. It has been shown in literature [16, 17] that for bulk materials, the plasticity characteristic, δ_H of the materials should be above a value of 0.90 in order to demonstrate plasticity prior to fracture under the standard tensile or bending tests. Otherwise brittle failure occurs. However, the situation is different for thin ceramic coatings. An effective application of thin ceramic coatings can be achieved without brittle failure even if the plasticity characteristic δ_H of the coatings is smaller than the critical value of 0.9. This is possibly because the coating thickness is very small, elastic deformation of bending preferably develops under the applied force and helps in decreasing the risk of brittle fracture. In a more recent study [24], it has been found that for some engineering applications the plasticity characteristic of $\delta_H = 0.45$ is an adequate property for effective usage of ceramic coatings.

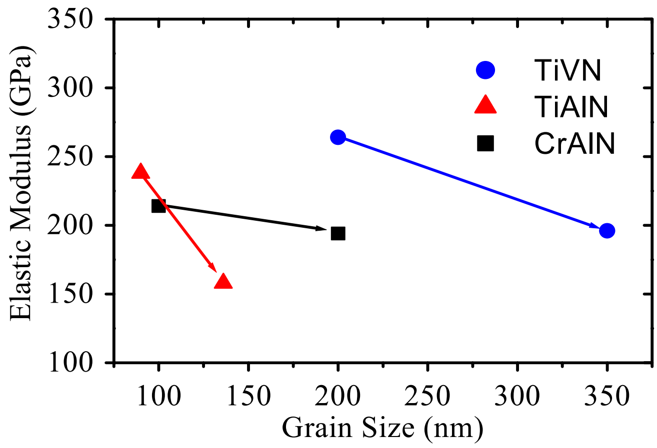


Fig. 7 Variation of elastic modulus versus grain diameter of the coatings.

In the present study, a direct approach was used to calculate the δ_H values of the coatings from the load-displacement curves of nanoindentation. The total work done by the indenter in deforming the material (W), the work of plastic deformation (W_p) and the work of elastic deformation (W_e) were determined from the load-displacement curve of the loading and unloading phases of the nanoindentation process, and the δ_H value was calculated as a ratio of W_p/W. The results showed that the ternary nitrides under investigation had δ_H values slightly lower than TiN but higher than TiB_2. Furthermore, the nanostructured coatings deposited at a nitrogen pressure of 0.4 mTorr achieved some higher values of both hardness and plasticity parameters. In general, the plasticity characteristic δ_H depends on the hardness (H) and elastic modulus (E). δ_H increases with increasing elastic modulus but decreases with increasing hardness [19]. For the ternary nitride coatings investigated presently, a decrease of the grain size led to an increase in both H and E values, and the plasticity characteristic δ_H changed weakly with the change of grain size. In other words, as the nitrogen deposition pressure decreased the grain diameter of coatings decreased, and this led to increasing H and E values with conservation (or even with a small increase) of the plasticity characteristic δ_H. The results showed the beneficial effects of developing a fine grained structure in these coating materials.

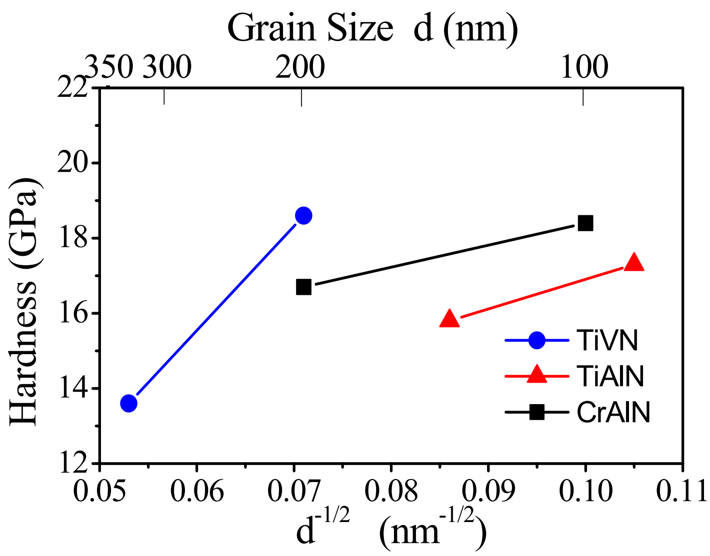


Fig. 8 Variation of hardness versus reciprocal of square root of grain diameter of the coatings.

Nanoindentation testing also provided results consistent with those of some previous studies. In a recent study of (Ti,Al)N and (Cr,Al)N by Wuhrer and Yeung [15], it was found that the intrinsic properties of the coating elements played an important role in the magnetron sputter process. While the hardness of both (Ti,Al)N and (Cr,Al)N coatings decreased with increasing nitrogen pressure and grain size, the hardness decrease in (Cr,Al)N was found to be much less significant, showing that (Cr,Al)N could maintain its properties better with variation of deposition conditions. The current work showed the same trend of property development of the coatings. The results of Figs. 6 and 7 showed that the hardness and elastic modulus of the (Cr,Al)N coatings decreased at a much slower rate with increasing grain diameter of the coating structure. It was found that, with the data obtained in this study, the hardness of the coatings decreased at a rate (w.r.t. grain size) of 0.033 GPa/nm for (Ti,Al)N and (Ti,V)N and 0.017 GPa/nm for (Cr,Al)N, and the elastic modulus (w.r.t. grain size) decreased at 1.739 GPa/nm for (Ti,Al)N, 0.453 GPa/nm for (Ti,V)N and 0.2 GPa/nm for (Cr,Al)N. The plasticity parameter of the (Cr,Al)N coatings also remained the same as the grain diameter of the coatings increased from 100 to 200 μm. The results confirmed advantages of chromium ternary nitrides over the titanium ternary nitrides. By re-plotting the results of Fig. 6 with hardness versus $d^{-1/2}$ where d is the grain diameter of the coatings, the Hall-Petch constant can be obtained for the coatings. The results are shown in Fig. 8. Assuming that the Hall-Petch relation of $\sigma_y = \sigma_o + k_y d^{-1/2}$ and the Tabor relation of $H \approx 3\sigma_y$ are applicable to the coatings, the Hall-Petch constant (k_y) was estimated to be 2.94, 0.66 and 0.63 $MN/m^{3/2}$ for (Ti,V)N, (Ti,Al)N and (Cr,Al)N correspondingly. In an early experiment on refractory metals, Milman and co-workers determined k_y = 0.63, 0.88 and 1.80 $MN/m^{3/2}$ for low carbon steel, chromium and molybdenum respectively [25]. Estimation of the k_y values of the coatings of this study showed a reasonable order of magnitude compared with other materials, suggesting that nanoindentation testing could be a capable tool in assessing the mechanical properties of thin coatings, which otherwise could not be determined by the conventional mechanical testing methods. With more data points obtained from further tests on the coatings, empirical relationships between the elastic modulus, plasticity and other mechanical properties of these ternary nitride coatings and the deposition conditions could be formulated.

5. Conclusions

Nanoindentation testing was used to determine the hardness, elastic modulus and plasticity parameter of three newly developed ternary nitride coatings of (Ti,V)N, (Ti,Al)N and (Cr,Al)N. It was found that the hardness values and elastic modulii of the nanostructured coatings were in the order of 17 - 18.5 GPa and 240 – 265 GPa respectively, and the plasticity parameters of the coatings were within 0.48 to 0.53. With a reduction of the nitrogen deposition pressure, the grain diameter of the coatings decreases that leads to both higher nanohardness and elastic modulus with conservation of satisfactory values of the plasticity characteristic.

Acknowledgements

Financial support from the University of Technology, Sydney under an internal research grant is gratefully acknowledged. The authors also wish to thank G. McCredie for his technical support in preparation of the coatings and D. Attard, S. Kim and D. Tallis for their assistance in this study. This work was partially supported by the National Ukrainian Academy of Sciences (project H43-04).

References

1. H.A. Jehn, S. Hofmann, W.D. Munz, Thin Solid Films, 153 (1987) 45.
2. O. Knotek, T. Leyendecker, J. Solid State Chem., 70 (1987) 318.
3. J.R. Roos, J.P. Celis, E. Vancoille, H. Veltrop, S. Boelens, F. Jungblut, J. Ebberink, H. Homberg, Thin Solid Films 193/194 (1990) 547.
4. L. Hultman, G. Hakansson, U. Wahlstrom, J.E. Sundgren, I. Petrov, F. Adibi, J.E. Greene, Thin Solid Films, 205 (1991) 153.
5. U. Wahlstrom, L. Hultman, J.E. Sundgren, F. Adibi, I. Petrov, J.E. Greene, Thin Solid Films, 235 (1993) 62.
6. B.Y. Shew, J.L. Huang, Surf. Coat. Technol., 71 (1995) 30.
7. K. Tonshoff, A. Mohlfeld, T. Leyendecker, H.G. Fub, G. Erkens, R. Wenke, T. Cselle, and M. Schwenck, Surf. Coat. Technol., 94/95 (1997) 603.
8. R. Wuhrer, W.Y. Yeung, J. Mats. Sci., 37 (2002) 3477.
9. R. Wuhrer, W.Y. Yeung, Scripta Mater., 49 (2003) 199.
10. Y. Makino, K. Nogi, Surf. Coat. Technol., 98 (1998) 1008.
11. M. Kawate, A.K. Hashimoto, T. Suzuki, Surf. Coat. Technol., 165 (2003) 163.
12. O. Banakh, P.E. Schnid, R. Sanjines, F. Levy, Surf. Coat. Technol., 163 (2003) 57.
13. A. Sugishima, H. Kajioka, Y. Makino, Surf. Coat. Technol., 97 (1997) 590.
14. O. Knotek, F. Loffler, H.J. Scholl, C. Barimani, Surf. Coat. Technol., 68 (1994) 309.
15. R. Wuhrer, W.Y. Yeung, Scripta Mater., 50 (2004) 1461.
16. W.C. Oliver, G.M. Pharr, J. Mater. Res., 7 (1992) 1564.
17. M.F. Doerner, W.D. Nix, J. Mater. Res., 1 (1986) 601.
18. J.B. Pethica, R. Hutchings, W.C. Oliver, Phil. Mag. A, 48 (1983) 593.
19. Yu.V. Milman, B.A. Galanov, S.I. Chugunova, Acta Metall. Mater., 41 (1993) 2523.
20. B.A. Galanov, Yu.V. Milman, S.I. Chugunova, I.V. Goncharova, Superhard Mats., 3 (1999) 25.
21. S.N. Dub, Yu.V. Milman, D.V. Lotsko, A.N. Belous, J. Mats. Sci. Letters, 20 (2001) 1043.

22. S. Dub, N. Novikov, Yu.V. Milman, Phil. Mag. A, 82 (2002) 1261.
23. A.V. Byakova, Yu.V. Milman, A.A. Vlasov, Science of Sintering, 36 (2004) 27.
24. A.V. Byakova, Yu.V. Milman, A.A. Vlasov, Science of Sintering, 36 (2004) 93.
25. V.I. Trefilov, Yu.V. Milman, S.A. Firstov, Physical Aspects of Strength of Refractory Metals, Naukova Dumka, Kiev, (1975) p.315.

Садржај: *Тестирање наноурезивањем је коришћено за одређивање тврдоће, еластичног модула и параметра пластичности за три ново развијене тернарне нитридне превлаке са зрнима величине наночестица. Са умањењем притиска депозиције азота опада и пречник зрна превлаке што доводи до веће микротврдоће и вредности еластичног модула уз очување задовољавајућих вредности пластичности.*
Кључне речи*: Нанокристални материјали, танки филмови, спатеровање, наноурезивање.*