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Titanium nitride/vanadium nitride alloy coatings: mechanical properties and adhesion characteristics

B.A. Latella[a,*], B.K. Gan[b], K.E. Davies[b], D.R. McKenzie[b], D.G. McCulloch[c]

[a]Materials and Engineering Science, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, New South Wales 2234, Australia
[b]School of Physics, University of Sydney, New South Wales 2006, Australia
[c]Applied Physics, School of Applied Sciences, RMIT University, G.P.O. Box 2476V, Melbourne 3001, Australia

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Abstract

This study examines the mechanical properties and adhesion characteristics of thin coatings of TiN, VN and various compositions in the Ti–V–N system deposited on stainless steel. Nano-indentation was used to determine the Young's modulus and hardness of the coatings. Tensile tests have been used to introduce controlled strains in the coatings, through the stainless steel substrate, to characterise the strength, fracture toughness and adhesion behaviour. The external stresses applied result in multiple cracking and localised delamination of the coatings, which have been followed in situ using optical microscopy. The Young's modulus shows a simple linear variation with composition within experimental error while the hardness and fracture properties show a clear maximum for the ternary alloy containing 23% VN. The Young's modulus behaviour can be explained by linear mixing while the maximum in the other properties may arise from optimum pinning of dislocations at Vanadium sites in the ternary alloys.

Keywords: Hardness; Toughness; Coatings; Fracture; Adhesion; Ternary alloy

1. Introduction

Transition metal nitride coatings on metals show considerable promise in applications where severe contact-induced loading is common, such as cutting tools, due to their high hardness and wear resistance [1–4]. The load-bearing capacity of these extremely hard coatings provides superior protection to the underlying substrate from external contact stresses and spurious impacts with foreign bodies. In a companion paper [5], we examined the deposition, structure and intrinsic residual stresses of TiN, VN and a range of $Ti_{1-x}V_xN$ alloy compositions. We demonstrated that the composition $Ti_{0.77}V_{0.23}N$ produced the highest indentation hardness and hence yield stress. This composition also showed the highest intrinsic residual stress, which we explain in terms of its reduced flow during deposition. The microstructure of the alloys, analysed by transmission electron microscopy and electron diffraction, indicates that they are homogeneously mixed with the rocksalt structure. At higher Vanadium contents, a (200) preferred orientation develops as a result of the low surface energy of the VN (100) surface.

The questions addressed here are: How strong and tough are the $Ti_{1-x}V_xN$ coatings? And how well do they remain adhered to the surface on which they are deposited when subjected to external stresses? These questions are central to the potential uses of such coatings. The advantages of using hard protective coatings on metallic tools and engineering components are well known [6]. However, the mechanical improvement and resistance to contact damage, wear and corrosion offered by the deposited coating is strongly dependent on its toughness and adhesion properties to the metallic substrate [7–9]. Clearly, if defects exist and if cracking occurs at the coating–substrate interface after the deposition process or if such damaging processes are

* Corresponding author. Tel.: +61 297173330; fax: +61 295437179.
E-mail address: bal@ansto.gov.au (B.A. Latella).

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sustained during use, catastrophic failure of the system can occur leading to delamination of the coating exposing the underlying surface. Even the case of minor cracking or small-scale delamination of the functional coating may have significant repercussions particularly where corrosion is an issue and ultimately lead to premature failure.

Accordingly, we examine the mechanical properties and adhesion characteristics of the same coatings examined in the companion paper but here deposited on stainless steel. Tensile tests are used to reproducibly subject the coating–substrate systems to large strains while viewing the damage evolution in situ using optical microscopy. The study focuses on five different coatings: pure TiN, pure VN and three $Ti_{1-x}V_xN$ alloy compositions each with a nominal thickness of 70 nm. Along with the adhesion tests, nano-indentation experiments were performed to ascertain the hardness and Young's modulus of the entire suite of coatings [5].

2. Experimental

2.1. Coating deposition

A dual source pulsed cathodic arc system [10] was used to deposit the TiN/VN alloy films at ambient temperature using two 10-mm diameter cathodes, one each of V and Ti, separated by 20-mm centre-to-centre distance. A 0.7-mm diameter tungsten trigger wire was located centrally in each cathode 2 mm above the cathode surface. Each cathode was alternately triggered to deliver a preset number of pulses in each cycle, designed to obtain the desired composition. A pulse length of 0.5 ms and a frequency of 4.5 Hz were used. The arc current applied was 220 A and the system base pressure was 1×10^{-5} Torr (1.3×10^{-3} Pa). The nitrogen gas flow rate was fixed at 50 sccm and the chamber pressure was 6×10^{-4} Torr (0.08 Pa) during deposition. Further details of the deposition method can be found in Ref. [5]. The coatings were deposited on Silicon and stainless steel substrates (see Section 2.3) with the following compositions: (i) TiN, (ii) $Ti_{0.87}V_{0.13}N$, (iii) $Ti_{0.77}V_{0.23}N$, (iv) $Ti_{0.63}V_{0.37}N$ and (v) VN (refer to Table 1 from Davies et al. [5]). The surface roughness of all the coatings ranged between 1 and 2 nm.

2.2. Nano-indentation

Mechanical properties of the five coating–substrate combinations on Silicon (from wafer curvature measurements—see Ref. [5]) and stainless steel were measured by depth-sensing indentation tests. Indentations were made with an Ultra Micro Indentation System (UMIS 2000, CSIRO, Australia), configured with a Berkovich (3-sided pyramid) diamond tipped indenter. Calibration of the indenter tip was carried out using fused silica glass (elastic modulus, E=70 GPa and Poisson's ratio, v=0.2) at numerous loads to determine an effective tip radius profile over a range of penetration depths. The Berkovich tip was chosen to determine the hardness and Young's modulus as a function of indenter penetration. The pyramidal tip was used as a small radius spherical indenter suitable for studies of ultrathin coatings. Measurements of the load and depth penetration were recorded simultaneously using a load-partial unload procedure [11]. Peak contact loads, P, of 0.5, 1 and 2 mN were used with the maximum indenter penetration varying from ≈20% (for P=0.5 mN) to ≈60% (for P=2 mN) of the film thickness. A minimum of five indents at each load was made and the results averaged. A 50% unload from the maximum load for 20 increments (at 0.1 s duration for each increment to P_{max}) of loading was used. From the tests at each peak load, the average of the load-displacement data of those tests was used in the analysis to determine the composite Young's modulus, E^*:

$$E^* = \frac{3P}{4ah_e} \tag{1}$$

where a is the contact radius $\left(a = \sqrt{2Rh_p - h_p^2}\right)$ with R the tip radius and h_p the plastic penetration depth or depth of the circle of contact, h_e is the elastic penetration depth (h_e=h_t−h_r) with h_t the maximum penetration depth at full load P, and h_r the residual depth of the impression upon unloading. The depth of the residual impression is obtained from the measurement of load and displacement at a partial

Table 1
Coating properties for TiN, VN and the ternary alloy compositions

Coating[a]	% VN calculated	Thickness t (nm) (±2 nm)	Hardness H (GPa)	Young's Modulus E_f (GPa)	Residual Stress σ_r (GPa)	Cracking strain ε_{exp} (%) (±0.1%)	Coating Strength σ_c (MPa)	Coating Toughness K_{IC} (MPa m$^{1/2}$)
TiN	0	68	20.2±4	395±18	−6.56[b]	1.87	840±82	0.56±0.13
$Ti_{0.87}V_{0.13}N$	12.9	69	26.1±3	410±28	−5.97	1.83	1540±166	1.14±0.20
$Ti_{0.77}V_{0.23}N$	22.8	66	32.1±3.8	384±30	−7.20	2.27	1520±167	1.09±0.21
$Ti_{0.63}V_{0.37}N$	37.2	67	23.7±1.7	365±30	−5.94	1.75	460±58	0.29±0.15
$Ti_{0.43}V_{0.57}N$	56.8	66	23.1±2	385±30	−5.50	–	–	–
$Ti_{0.22}V_{0.78}N$	78.3	63	15.8±1.6	361±28	−4.45	–	–	–
VN	100	69	5.6±0.7	307±18	−3.63	1.39	640±81	0.40±0.21

[a] Ternary alloy formulae given are based on the calculated composition, which has been shown to agree with measured values using EDS and EELS [5].
[b] Negative values indicate compressive stress.