Surface & Coatings Technology 232 (2013) 311–318

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Microstructure, chemical states, and mechanical properties of magnetron co-sputtered $V_{1-x}Al_xN$ coatings

Ping Zhu [a,b], Fangfang Ge [a], Shengzhi Li [b], Qunji Xue [a], Feng Huang [a,*]

[a] *Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China*
[b] *School of Materials Science and Engineering, Anhui University of Technology, Maanshan, Anhui 243002, China*

ARTICLE INFO

Article history:
Received 15 December 2012
Accepted in revised form 16 May 2013
Available online 25 May 2013

Keywords:
VAlN
Cubic phase
Al − N bonds
Reactive magnetron sputtering

ABSTRACT

Wear-resistant vanadium-containing nitride hard coatings are of special interest for tooling applications. We deposited $V_{1-x}Al_xN$ coatings by reactive magnetron co-sputtering from vanadium and aluminum targets, which were independently driven by dc and pulsed dc (350 kHz and 75% duty) power supplies, respectively. Over the range of $x = 0$–0.62, all $V_{1-x}Al_xN$ coatings were supersaturated cubic solid solutions stabilized in the metastable B1 structure. X-ray diffraction and transmission electron microscopy (TEM) studies revealed no evidence of the hexagonal AlN phase. In the cubic $V_{0.38}Al_{0.62}N$ coating, however, interconnected AlN-rich and AlN-deficient domains were identified by elemental mapping in the scanning TEM mode. Regarding the growth structure, the $V_{0.48}Al_{0.52}N$ and $V_{0.43}Al_{0.57}N$ coatings exhibited a dense and fibrous one, while the $V_{0.38}Al_{0.62}N$ coating exhibited a porous and columnar one with many through-thickness cracks. In the cubic $V_{1-x}Al_xN$ coatings with a high amount of AlN ($x \geq 0.52$), X-ray photoelectron spectroscopy analysis revealed two distinct Al − N states centered at 73.4 ± 0.1 eV and 73.1 ± 0.1 eV, respectively. The area fraction of the lower binding energy Al − N bond (73.1 eV) increased with the AlN content in the cubic coating. The hardness was steadily increased from 11 GPa for VN to > 30 GPa for those $V_{1-x}Al_xN$ coatings with $0.48 \leq x \leq 0.57$, among which the hardest $V_{0.48}Al_{0.52}$ N coating (> 40 GPa) showed a very dense, non-columnar, texture-free microstructure.

1. Introduction

Low-friction wear-resistant hard coatings are of special interest for tooling applications [1]. Recently, vanadium nitride (VN) coatings have attracted a lot of attention [2,3]. During dry ball-on-disk tests over the range from room temperature to 973 K (alumina or stainless steel balls, sliding speed of 0.1 m/s, normal load of 5 or 10 N), they constantly exhibited a lower coefficient of friction (μ) than titanium nitride (TiN) coatings [2,3]. Specifically, when the testing temperature was increased from 773 K to 973 K, the TiN coatings exhibited a pretty constant $\mu = 0.60 \pm 0.08$, while that for the VN coatings dropped from 0.40 ± 0.02 to 0.26 ± 0.03 [3]. In addition, vanadium has been incorporated into many ternary or quaternary nitride coatings, which could lead to markedly reduced friction [4–7]. For example, in ball-on-disk sliding tests against alumina at 973 K (sliding speed of 0.1 m/s, normal load of 5 N), replacing $Al_{0.71}Cr_{0.29}N$ coatings by $Al_{0.67}Cr_{0.05}V_{0.28}N$ coatings led to a significant reduction in μ from $\mu = 0.6 \pm 0.2$ to $\mu = 0.22 \pm 0.03$ [7]. Furthermore, its beneficial role in tribological properties can even be extended into multilayered hard coatings. As an illustration, nanostructured TiAlN/VN multilayers not only showed exceptionally low wear rates ($<1.0 \times 10^{-16}$ m^3/Nm) when sliding against alumina at room temperature (sliding speed of 0.1 m/s, normal load of 5 or 10 N) [8,9], but also outperformed other hard coatings in cutting aluminum alloys [10].

VN is inferior to TiN in terms of hardness and oxidation resistance [11,12]. Addition of AlN into VN to form metastable V–Al–N solid solutions is attractive because both properties can be enhanced [13]. Very few publications, however, have been dedicated to V–Al–N based coatings. Kolozsvári et al. prepared cubic $V_{1-x}Al_xN$ coatings with a fixed AlN content (x), using unbalanced magnetron co-sputtering, and investigated the effects of gas flow ratio and substrate bias, respectively, on the hardness and adhesion [14]. Rovere et al. examined the phase stability of magnetron sputtered $V_{1-x}Al_xN$ coatings, in considerable detail, with respect to the AlN content as well as annealing temperatures. They found a maximum solubility of $x = 0.54 \pm 0.02$ in cubic $V_{1-x}Al_xN$ coatings deposited at 723 K, but no indication of spinodal decomposition in $V_{0.5}Al_{0.5}N$ coatings annealed up to 1873 K [15].

Other related studies include coatings in the quaternary V–Al–C–N system, where interest arose from the expectation that cubic metastable $V_{1-x}Al_xC_{1-y}N_y$ coatings can be easily formed along the quasi-binary VC–AlN section, thereby combining the different properties of metallic VC and covalent AlN for further optimization [16,17]. Ziebert et al. used a combinatorial method to map the mechanical and tribological properties in reactive glow discharges. They varied structures from nanocrystalline solid solutions to carbon-based nanostructured composites, and thus

---

* Corresponding author. Tel.: +86 574 86685930; fax: +86 574 86685159.
E-mail address: huangfeng@nimte.ac.cn (F. Huang).

0257-8972/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.surfcoat.2013.05.023

succeeded in tuning the hardness, elastic modulus, and coefficient of friction of the coatings over a wide range [16]. Later, Stüber et al. magnetron sputtered nanocrystalline solid solutions in pure argon discharges, and investigated the effect of bias voltage on the resultant microstructure and hardness [17].

Here we report our recent study on metastable $V_{1-x}Al_xN$ coatings with various AlN contents ($x = 0$–0.62). The objective of this paper is to systematically explore the effect of the AlN on the microstructure, chemical states, and mechanical properties of these $V_{1-x}Al_xN$ coatings. To this end, we selected dual-target magnetron co-sputtering of vanadium and aluminum targets in mixed Ar–N_2 discharges. Independent powering of the two targets enabled a flexible adjustment of the AlN content in the coatings. Except for the power applied to the aluminum target, all other process parameters were the same for the coatings.

2. Experimental

2.1. Coating preparation

The $V_{1-x}Al_xN$ coatings ($x = 0$–0.62) were reactively magnetron co-sputtered in mixed Ar–N_2 discharges in a custom-built MS450 system (Keyou Instruments Inc., Shenyang, China). The system consists of a two-magnetron deposition chamber and a loadlock. Its schematic drawing has been reported in Ref. [18]. The vanadium target, 99.9 at.% in purity and 10 cm in diameter, was driven by a dc power supply (Advanced Energy MDX 1K), while the aluminum target, 99.999 at.% in purity and also 10 cm in diameter, was driven by a mid-frequency (MF) pulsed dc power supply (Advanced Energy Pinnacle Plus + 5/5) at 350 kHz with a duty factor of 75% (reverse time = 0.7 μs). Other processing details are given in Table 1.

Microscopic glass slides and (100) oriented silicon pieces were used as substrates. Prior to insertion into the load-lock chamber, the substrates were sequentially cleaned by acetone, alcohol, and distilled water, and then blown dry with nitrogen flow. The coating thickness of all samples was 900–1500 nm. Additionally, a ~100 nm thick Al adhesion layer was applied prior to depositing the $V_{0.38}Al_{0.62}N$ coating.

2.2. Coating characterization

The elemental compositions of all coatings were measured by the energy-dispersive X-ray spectrometry (EDX) using an EDAX Sapphire Si(Li) detector. Quantification was performed using the standard ZAF method, which incorporated individual corrections from the atomic number (Z), absorption (A), and fluorescence (F).

The microstructure of the coatings was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM). The XRD measurements were performed on a Bruker D8 Advance diffractometer, using Cu Kα radiation and at a step of $\theta = 0.01°$. Two SEM systems, a FEI Quanta™ 250 FEG SEM and a Hitachi S4800 high resolution field emission SEM, were used to examine the surface and cross-sectional morphologies, respectively. The TEM and STEM studies were performed on an FEI Tecnai F20 system operated at an acceleration voltage of 200 kV. Plan-view and cross-sectional specimens were made by mechanical grinding followed by Ar^+-ion milling down to electron transparency. A Gatan 691 Precision Ion Polishing System was used in the ion milling process. Initially the incident angle and energy of the Ar^+ ions were set at 9–9.5° and 4 keV, respectively. During the final step, they were reduced down to 6.5–7° and 3 keV, respectively.

The chemical states were investigated by X-ray photoelectron spectroscopy (XPS) on a Kratos Axis ULTRA DLD XPS system, which used a monochromatic Al Kα source ($h\nu = 1486.6$ eV) to record the core-level spectra. The base pressure was better than 6.7×10^{-7} Pa. Calibration was made with a pure gold standard sample by setting the Au $4f_{7/2}$ peak at 83.96 ± 0.08 eV. The spectra of Al 2p, N 1s, and V 2p were recorded at a step of 0.05 eV. Unless otherwise stated, each sample was sputter cleaned by 2 kV Ar^+ ions for 5–15 min, before taking a spectrum. Charge referencing was performed by setting the C 1s peak of adventitious carbon at 284.8 eV. The XPS data were analyzed using the Kratos Vision Processing software (version 2.2.7). In the deconvolution analysis, we used a Gaussian–Lorentzian mixed (70%–30%) line-shape and the Shirley-type baseline.

Mechanical properties of the coatings were investigated by nanoindentation on a MTS Nano Indenter G200 tool with a diamond Berkovich tip. The maximum indentation depth was controlled at ~160 nm. The hardness (H) and indentation modulus (E^*) of the samples were extracted from the load–displacement curves with the Oliver–Pharr method [19]. Each value of H and E^* was an average of no less than 6 indentation measurements.

3. Results and discussion

3.1. Composition and microstructure

Table 2 lists the elemental compositions of the $V_{1-x}Al_xN$ coatings measured by EDX. The Al/(V + Al) ratio increased linearly with the power applied to the Al target. Meanwhile, the nitrogen concentration decreased a little bit. We also found a very low level of Ar trapped in our coatings. Due to the overlapping of X-ray signals from the V and O atoms, it is hard to separate them reliably by the EDX technique. We thus checked the amount of residual oxygen using XPS. Fig. 1 presents two spectra taken from the $V_{0.38}Al_{0.62}N$ coating in the binding energy (BE) range of 508–537 eV, where the O 1s and V 2p signals are detectable yet well separated. The lower one, which reflected the typical conditions under which the core-level V 2p, Al 2p, and N 1s spectra were taken for our chemical state analysis (Section 3.2), included a well-defined peak from the O 1s electrons in addition to the V 2p doublet ($\Delta = 7.6$ eV). Quantification based on the peak areas found an oxygen concentration of 6–8 at.%. However, the oxygen impurities can be reduced down to a negligible level (~0.2%) after subjecting the sample to prolonged sputter cleaning (4 kV for 10 min), which is not surprising by noting the good base pressure in our coating system. Therefore, our exclusion of the oxygen in the mentioned EDX analysis was justified.

Fig. 2 shows the XRD patterns, of which a salient feature is that all the reflection(s) could be assigned to the cubic B1-structured δ-VN phase (c-VN). Even for the $V_{0.38}Al_{0.62}N$ coating, it was still hard to identify unambiguously any contribution from the crystalline B4-structured AlN phase (h-AlN), due to the proximity of the h-AlN

Table 1
Deposition conditions of $V_{1-x}Al_xN$ coatings.

Base pressure	$<5 \times 10^{-5}$ Pa
Process pressure	1.05 Pa
N_2 partial pressure	0.30 Pa
N_2/Ar gas flow rate	24/32 sccm
V target power (DC)	300 W
Al target power (MF)	0–450 W (350 kHz, 75% duty)
Deposition temperature	573 K
Deposition rate	0.6–1.5 μm/h
Substrate bias voltage (MF)	−90 V (250 kHz, 88% duty)
Substrate holder rotation	12 rpm

Table 2
Elemental compositions of the $V_{1-x}Al_xN$ coatings determined by EDX analysis. Please be aware that the nitrogen contents are subject to the inherent uncertainty.

Coating ID	V (±0.5 at.%)	Al (±0.4 at.%)	N (±1 at.%)	Ar (at.%)
VN	48.1	0	51.7	0.2
$V_{0.65}Al_{0.35}N$	32.6	17.3	49.9	0.2
$V_{0.61}Al_{0.39}N$	30.8	20.0	48.6	0.6
$V_{0.52}Al_{0.48}N$	27.1	24.9	47.8	0.2
$V_{0.48}Al_{0.52}N$	25.6	28.2	46.0	0.3
$V_{0.43}Al_{0.57}N$	22.3	29.8	47.3	0.6
$V_{0.38}Al_{0.62}N$	19.8	32.3	47.7	0.2