Thin Solid Films 581 (2015) 20–24

Contents lists available at ScienceDirect

Thin Solid Films

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

# Effect of wavelength modulation of arc evaporated Ti–Al–N/Ti–Al–V–N multilayer coatings on microstructure and mechanical/tribological properties

Martin Pfeiler-Deutschmann [a,1], Paul H. Mayrhofer [b,2], Kerstin Chladil [b,3], Marianne Penoy [c], Claude Michotte [c], Martin Kathrein [d,4], Christian Mitterer [b,*]

[a] *Materials Center Leoben Forschung GmbH, Roseggerstraße 12, A-8700 Leoben, Austria*
[b] *Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria*
[c] *CERATIZIT Luxembourg Sàrl, Route de Holzem, B.P. 51, L-8201 Mamer, Luxembourg*
[d] *CERATIZIT Austria GmbH, A-6600 Reutte, Austria*

## ARTICLE INFO

Available online 30 October 2014

*Keywords:*
Hard coatings
TiAlN
Multilayer coatings
Cathodic arc evaporation
Mechanical properties
Tribological properties

## ABSTRACT

Ti–Al–N/Ti–Al–V–N multilayer hard coatings were grown by industrial-scale cathodic arc evaporation on cemented carbide and silicon substrates, and the wavelength of compositional modulation of the coatings was systematically varied by changing the rotation speed of the substrate carousel. The face-centered cubic $Ti_{1-x}Al_xN$ template epitaxially stabilizes growth of the originally dual-phase cubic and wurtzite Ti–Al–V–N layer up to layer thicknesses of ~20 nm. Suppressing the formation of the wurtzite phase leads to a significant enhancement of mechanical and tribological properties, outperforming single-layer Ti–Al–N coatings.

## 1. Introduction

The addition of vanadium has recently been suggested to further improve Ti–Al–N based hard coatings. The incorporation of V in the form of a TiN/VN multilayer or as solid solution Ti–Al–V–N coating led to potential low friction and enhanced wear behavior [1–3]. Additionally, it has been shown that V as a substitutional atom in the $Ti_{1-x}Al_xN$ solid solution has a stabilizing effect for the face-centered cubic (fcc) structure, which is characterized by high hardness and Young's modulus [1,4,5]. Also suppressing the formation of the wurtzite AlN phase in the Ti–Al–V–N system by applying high bias voltages has been mentioned to significantly improve the mechanical properties [6].

Multilayered structures were intensively investigated and a hardness enhancement well above the hardness of the individual monolithic layers was reported, initially for TiN/VN superlattices. In particular, a maximum hardness was obtained for a wavelength (i.e. a bilayer thickness) of roughly 10 nm [7,8]. This hardness enhancement is attributed to the so-called superlattice effect and is based on differences in the shear modulus between the individual layer materials. Long et al. [9] reported that this substantial hardness increase due to the superlattice effect is not generally observed. The reported huge hardness enhancements are not consistent with the idea of increased dislocation line energy. Consequently, no significant variation of hardness with the wavelength of the multilayer has been found [9]. However, a smaller increase of ~5 GPa might be observed and connected with differences in shear modulus, whereas the high values initially reported are suggested to be associated with high internal stress. Ljungcrantz et al. [10] reported on nanoindentation and abrasive wear tests of TiN/NbN multilayers synthesized with various wavelengths. No significant influence on hardness and wear resistance was observed; values in between those of the single-layer materials have been observed.

Multilayer arrangements can also be used for epitaxial stabilization of the phases present in the individual layers. This template effect enables the stabilization of fcc AlN by a fcc template layer, although the wurtzite phase of AlN is thermodynamically favored and fcc AlN is normally unstable at pressures below 22 bar [11]. Similar observations are also reported by other authors [8,12].

The aim of the present work was to deposit Ti–Al–N/Ti–Al–V–N multilayers with various multilayer wavelengths by an industrial scale cathodic arc evaporation process. The multilayer wavelength was modulated by changing the rotation speed of the substrate carousel. Here, we report on the hardness increase from Ti–Al–V–N single-layers to Ti–Al–N/Ti–Al–V–N multilayers, where in particular we

---

[*] Corresponding author. Tel.: +43-3842-402-4220; fax: +43-3842-402-4202.
*E-mail address:* christian.mitterer@unileoben.ac.at (C. Mitterer).

[1] Present address: Tridonic Jennersdorf GmbH, Technologiepark 10, A-8380 Jennersdorf, Austria.

[2] Present address: Institute of Materials Science and Technology, Vienna University of Technology, A-1040 Vienna, Austria.

[3] Present address: Materials Center Leoben Forschung GmbH, Roseggerstraße 12, A-8700 Leoben, Austria.

[4] Present address: PLANSEE SE, A-6600 Reutte, Austria.

http://dx.doi.org/10.1016/j.tsf.2014.10.051

concentrate on the fcc stabilizing effect by the use of the $Ti_{1-x}Al_xN$ solid solution as a fcc epitaxial template and its influence on the resulting mechanical and tribological properties by suppressing the wurtzite phase. Furthermore, the influence of multilayer wavelength on hardness and wear resistance was investigated.

## 2. Experimental details

An industrial scale cathodic arc evaporation facility, type Oerlikon Balzers RCS, and powder metallurgically produced targets with compositions (in at.%) Ti16.5Al67V16.5 and Ti50Al50 were used to deposit the coatings. Due to the use of two Ti–Al–V and two Ti–Al targets and the substrate rotation, coatings with compositional modulations could be synthesized (these coatings are termed multilayers in the following). The deposition runs were conducted at four different rotation speeds, ranging from 0.75 to 3 rpm and resulting in different multilayer wavelengths, in pure $N_2$ atmosphere at a pressure of $3.2 \times 10^{-2}$ mbar. The bias voltage was −40 V for all multilayer deposition runs. The multilayers were topped with a 150 nm thick, decorative TiN top-layer, grown by cathodic arc evaporation using two Ti targets and the same growth conditions as for the multilayers. For comparison, single-layer coatings were deposited from the Ti16.5Al67V16.5 targets at −40 and −120 V bias voltage, respectively. The coatings were grown onto cemented carbide (CC) SNUN cutting inserts, CC disks (Ø 30 × 4 mm) and single-crystal silicon (100) samples (21 × 7 × 0.38 mm). The SNUN samples were used for glancing angle X-ray diffraction (GAXRD) and for nanoindentation. Tribological tests were performed on CC disks, whereas for transmission electron microscopy (TEM) investigations the silicon samples were used.

The chemical composition of the single-layer coatings was determined by energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments INCA) in a Zeiss EVO 50 scanning electron microscope (SEM). Crystallographic investigations were performed by GAXRD (Panalytical X'Pert Pro) applying Cu Kα radiation at an angle of incidence of 2°. TEM and selected area electron diffraction (SAED) investigations were conducted using a Philips CM12 microscope, operated at 120 keV. The samples were prepared by cross-sectional tripod polishing followed by Ar-ion milling using a Gatan PIPS 691 device. Hardness and Young's modulus of the coatings were assessed by nanoindentation using a UMIS ultra micro indentation system with a Berkovich indenter. To reduce surface roughness and to remove the decorative TiN top-layer, the samples were polished for 5 min with 1 μm diamond suspension prior to the nanoindentation measurement. To evaluate hardness and Young's modulus, correction of compliance, initial penetration and contact area were applied to the raw data. The tribological behavior was investigated by dry sliding tests at room temperature, 500 and 700 °C on a CSM high-temperature ball-on-disk tribometer. The normal load, sliding speed, pre-heating time, sliding distance, and radius of wear track were kept constant at 5 N, 10 cm/s, 90 min, 300 m, and 7 mm, respectively. All tests were performed in ambient atmosphere at a relative humidity of 35 ± 5% against an alumina ball (Ø 6 mm). After tribometer testing, a Wyko NT 1000 3D white light profiling system was used to investigate the wear tracks and to derive the worn volume from the worn area determined by two-dimensional cross-sections. The wear coefficients were calculated from the wear volume, the normal load and the sliding distance. In addition, the wear tracks were examined by SEM to illuminate the wear mechanisms.

## 3. Results and discussion

Fig. 1 presents a summary of the microstructure evolution of Ti–Al–N/Ti–Al–V–N multilayer coatings grown at different substrate rotation speeds. In addition, the diffractograms shown at the bottom of Fig. 1 correspond to Ti–Al–V–N single-layer coatings deposited at −40 and −120 V bias, respectively. The single-layer −40 V coating with chemical composition of $Ti_{0.09}Al_{0.34}V_{0.10}N_{0.48}$, as determined by EDX (corresponding to an atomic ratio $^{Al}/_{Ti+V+Al}$ of ~0.65), exhibits a dual-phase structure and contains both fcc and wurtzite crystals. Due to the incorporation of the smaller Al and V atoms into the lattice, the peaks of the fcc Ti–Al–V–N phase are shifted towards higher diffraction angles compared to the TiN phase [13]. In contrast, the peaks of the wurtzite phase are shifted towards lower angles due to incorporation of the larger Ti atoms. By raising the bias voltage up to −120 V, the coating can be grown in a single-phase fcc structure (see Fig. 1). Thus, increasing the bias voltage reduces the Al content slightly to $Ti_{0.08}Al_{0.32}V_{0.01}N_{0.50}$ ($^{Al}/_{Ti+V+Al}$ of ~0.64) and, consequently, hinders the formation of the wurtzite phase and promotes a single-phase fcc structure, which has been already reported earlier [1,6]. The upper four diffractograms in Fig. 1 represent Ti–Al–N/Ti–Al–V–N multilayer coatings deposited at various rotation speeds of the substrate carousel at −40 V bias. In none of the diffractograms, the wurtzite phase can be detected; all peaks visible can be ascribed to the fcc Ti–Al–V–N phase. Thus, it can be concluded that the Ti–Al–N layer (with the chemical composition determined for the single-layer grown at −40 V bias of $Ti_{0.52}Al_{0.48}N_{0.49}$) acts as a fcc epitaxial template, which enables growth of a single-phase Ti–Al–V–N layer at low bias voltages due to epitaxial stabilization of the fcc crystals. The variation of rotation speed does not have a significant influence on the crystal structure. This indicates that the fcc stabilizing effect of the Ti–Al–N layer is also working for the lowest rotation speed, which causes the highest multilayer wavelength.

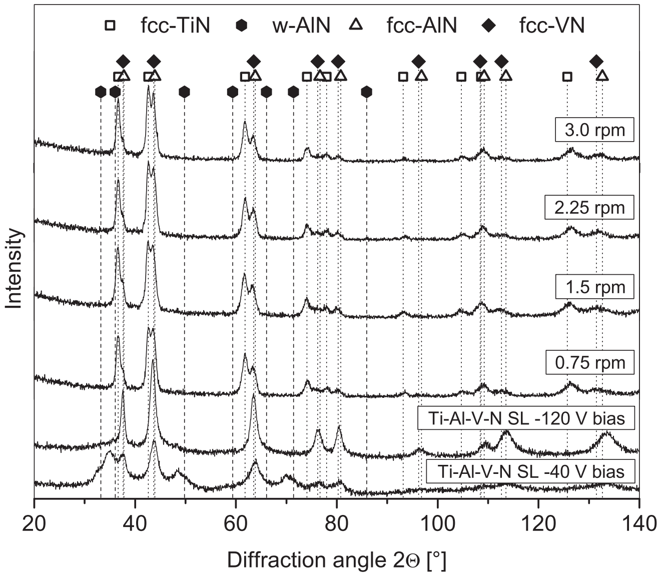

**Fig. 1.** XRD diffractograms of Ti–Al–V–N single-layers (SL) deposited at −40 and −120 V bias voltage, respectively, and Ti–Al–N/Ti–Al–V–N multilayers deposited at −40 V bias and various rotation speeds of the substrate carousel.

The TiN top-layer is also detected in the diffractograms, appearing at the TiN standard positions. Due to the topmost position of the TiN-layer and the glancing angle measurements, the TiN phase appears dominant with respect to intensity, despite its low thickness.

In order to support the XRD results, additional TEM investigations were conducted, enabling to correlate the rotation speed of the substrate carousel to the resulting multilayer wavelength. The phase contrast between the Ti–Al–N and Ti–Al–V–N layers in the TEM micrographs in Fig. 2 is due to the compositional similarity quite low; nevertheless, brighter and darker layers are observable. The lowest rotation speed of 0.75 rpm resulted in a multilayer wavelength of 40–45 nm (see the TEM bright-field cross-sectional micrograph in Fig. 2a), corresponding to Ti–Al–V–N layer thicknesses of at least 20 nm. It should be noted that the additional layers visible within the individual layers of the Ti–Al–N/Ti–Al–V–N multilayer structure are related to compositional modulations caused by the double rotation of