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CrN/AlN nanolaminate coatings deposited via high power pulsed and middle frequency pulsed magnetron sputtering

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ABSTRACT

Nanolaminate coatings based on transition metal nitrides such as CrN, AlN and TiN deposited via physical vapor deposition (PVD) have shown great advantage as protective coatings on tools and components subject to high loads in tribological applications. By varying the individual layer materials and their thicknesses it is possible to optimize the coating properties, e.g. hardness, Young's modulus and thermal stability. One way for further improvement of coating properties is the use of advanced PVD technologies. High power pulsed magnetron sputtering (HPPMS) is an advancement of pulsed magnetron sputtering (MS). The use of HPPMS allows a better control of the energetic bombardment of the substrate due to the higher ionization degree of metallic species. It provides an opportunity to influence chemical and mechanical properties by varying the process parameters. The present work deals with the development of CrN/AlN nanolaminate coatings in an industrial scale unit by using two different PVD technologies. Therefore, HPPMS and mfMS (middle frequency magnetron sputtering) technologies were used. The bilayer period Λ, i.e. the thickness of a CrN/AlN double layer, was varied between 6.2 nm and 47.8 nm by varying the rotational speed of the substrate holders. In a second step the highest rotational speed was chosen and further HPPMS CrN/AlN coatings were deposited applying different HPPMS pulse lengths (40, 80, 200 µs) at the same mean cathode power and frequency. Thickness, morphology, roughness and phase composition of the coatings were analyzed by means of scanning electron microscopy (SEM), confocal laser microscopy, and X-ray diffraction (XRD), respectively. The chemical composition was determined using glow discharge optical emission spectroscopy (GDOES). Detailed characterization of the nanolaminate was conducted by transmission electron microscopy (TEM). The hardness and the Young's modulus were analyzed by nanoindentation measurements. The residual stress was determined via Si microcantilever curvature measurements. The phase analysis revealed the formation of h-Cr_2N, c-CrN and c-AlN mixed phases for the mfMS CrN/AlN coatings, whereas the HPPMS coatings exhibited only cubic phases (c-CrN, c-AlN). A hardness of 31.0 GPa was measured for the HPPMS coating with a bilayer period of 6.2 nm. The decrease of the HPPMS pulse length at constant mean power leads to a considerable increase of the cathode current on the Cr and Al target associated with an increased ion flux towards the substrate. Furthermore, it was observed that the deposition rate of HPPMS CrN/AlN decreases with shorter pulse lengths, so that a CrN/AlN coating with a bilayer period of 2.9 nm, a high hardness of 40.8 GPa and a high compressive stress (−4.37 GPa) was achieved using a short pulse length of 40 µs.

1. Introduction

Multilayer coatings formed of different metal nitrides such as CrN or TiN and AlN have been investigated during the past decade as protective coatings for different applications in corrosive and abrasive environments [1–5]. By varying the thickness of the individual layers and their composition it is possible to optimize the properties of CrN/AlN multilayer coatings, e.g. hardness, Young's modulus, fracture toughness, residual stress, thermal stability and oxidation behavior [3,6–10]. In a CrN/AlN nanolaminate coating, the CrN layers generally form a face centered cubic (fcc) (NaCl type, B1) phase and AlN presents a hexagonal structure. But it was found that a cubic AlN phase develops by coherent epitaxial growth onto cubic CrN when the AlN nanolayer thickness is thin enough (e.g. thinner than 4 nm) [9,11] combined with the condition that the CrN layers need to be at least as thick as the AlN layers [9]. Furthermore, Chawla et al. [12] reported that the stabilization of c-AlN within nanolaminate coatings strongly depends on the elastic properties, the crystallographic orientation and the lattice parameters of the other layer material, as well as the strength of the substrate.

Another alternative for further improvement of coating properties is the use of advanced PVD technology. CrN/AlN multilayer coatings are commonly prepared by reactive magnetron sputtering from Cr and Al

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targets using dc (direct current) or pulsed dc magnetron sputtering technology [9,11,13,14]. In recent years the modulated pulsed power (MPP) magnetron sputtering technique has been developed, which generates a very high degree of ionization of the target species by using long and modulated high power pulses [15–17]. Recent studies in Ref. [18] have shown the potential of MPP technique in combination with middle frequency pulsed dc magnetron sputtering in hybrid process for production of CrN/AlN coatings (up to 10 μm) with hardness values of 40–45 GPa and thermal stability after annealing at 1000 °C.

A further variation of the pulsed technique is the high power pulse magnetron sputtering (HPPMS) technology, which generally operates at low duty cycles (1-10%), short pulse lengths (t_{on}) from several μs and with frequencies in the range of 10 Hz to 10 kHz [19,20]. Thus, HPPMS provides high target peak current and high ionization degree, which are much higher than those of conventional radio frequency magnetron sputtering (rfMS), direct current magnetron sputtering (dcMS) and middle frequency magnetron sputtering (mfMS). The potential of the HPPMS technology has been investigated for the deposition of different transition metal nitride coatings, such as CrN [21–23], TiN [24], TiMoN [25], (Cr,Al)N [26,27] and (Cr,Al,Si)N [26], CrN/NbN [28], CrAlYN/CrN [29], CrN/TiN [31] and CrN/AlN [30].

The variation of the HPPMS pulse parameters, e.g. frequency and pulse length, allows a control of the energetic bombardment of the substrate [32]. It provides an opportunity to influence the chemical composition, the microstructure, the mechanical properties and the phase composition of the coatings. Greczynski et al. showed in investigations of CrN_x coatings that an increasing frequency results in nano-sized grain structure and suppression of columnar growth [33]. In previous works, we have investigated the impact of the variation of HPPMS pulse parameters on the properties of Cr-rich monolithic $(Cr_{1-x},Al_x)N$ coatings. The results have shown that short pulse lengths (t_{on}) lead to a densification of the coating microstructure and a hardness of 32.4 GPa for $x = 0.24$ [34]. Furthermore, by using a short pulse length an increase of the N content was observed in $(Cr_{1-x},Al_x)N$ resulting in a change of the chemical composition of the coating bulk and of the surface near region [35]. Recent investigations of Al-rich $(Al_x,Cr_{1-x})N$ monolithic coatings deposited at different pulse on/off time configuration reveal that the hardness increased with an increasing frequency at a constant duty cycle of 2% and reached a value of 39.9 GPa for $x = 0.75$ [36].

However, there have been few studies that reported on the effects of the HPPMS pulse parameters on the properties of CrN/AlN nanolaminate coatings. The presented work deals with the investigation of the influence of the variation of HPPMS pulse lengths (t_{on}) on the structural, the chemical and the mechanical properties of CrN/AlN multilayer coatings deposited in an industrial scale unit. The results were compared to other coatings obtained via a mfMS process in bipolar pulse mode with similar process conditions.

2. Experimental

2.1. Coating deposition

For the coating deposition two industrial coating units were used, which are identical in design. The coating unit CC800/9 Custom by CemeCon AG, Würselen, is equipped with two HPPMS power supplies made by ADL GmbH (Fig. 1). This coating unit was used for the deposition of the HPPMS coatings. An identical CC800/9 SinOx equipped with two pulsers made by Melec GmbH operating in the bipolar pulse mode was used for the mfMS coatings (Fig. 1).

The coating processes were preceded by a plasma cleaning process in order to clean the substrates. In HPPMS and mfMS deposition processes one cathode was equipped with a Cr target (purity: 99.9%) and the other with an Al target (purity 99.5%). The size of all used targets was 88 mm × 500 mm. The N_2 concentration was pressure controlled. The pressure was chosen in order to achieve approximately the same N_2/Ar ratio (33–34%) in HPPMS as well as in mfMS processes. A dc bias voltage of −100 V was applied to the substrate holder during the coating deposition.

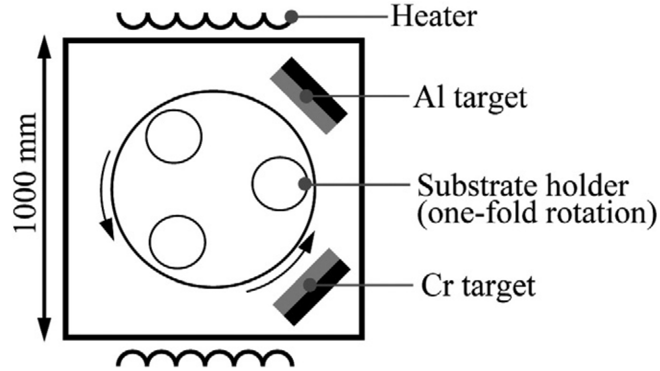

Fig. 1. Schematic of the coating deposition setup (top view).

For the deposition of the nanolaminate coatings with different bilayer period the rotation of the substrate table was varied. During all deposition processes the samples were moved in a one-fold rotation. In a first step, the rotational speed was varied in the range of 0.63, 1.30, 2.30 and 2.97 min^{-1} (maximal table rotation 3 min^{-1}) for the deposition of the HPPMS and mfMS CrN/AlN coatings. While the pulse length and the frequency in the HPPMS process were 200 μs and 500 Hz, the values in the mfMS process were 7 μs and 18.51 kHz, respectively. The Cr mean cathode power was fixed at 4 kW and the Al was fixed at 3 kW during the HPPMS and the mfMS processes.

In a second step the highest table rotation of 2.97 min^{-1} was kept constant, whereas the pulse length (t_{on}) was varied in the HPPMS processes from 200 μs, to 80 μs and to 40 μs. The frequency (500 Hz) and the mean cathode power (Cr: 4 kW, Al: 3 kW) were fixed, so that the duty cycle was varied from 10% (t_{on}: 200 μs) to 4% (t_{on}: 80 μs) and to 2% (t_{on}: 40 μs). All coatings were deposited on cemented carbide (THM12) and on Si-based substrates (100). The substrates were mounted using a sample holder which was positioned parallel to the cathodes. Further process parameters are shown in Table 1.

2.2. Process and coating characterization

The current and the voltage at both cathodes were recorded during the deposition process using an oscilloscope TDS3014B, Tektronix, in order to further analyze the HPPMS CrN/AlN deposition process. The cathode peak current density was estimated considering the whole target area (88 mm × 500 mm). Furthermore, the substrate current was measured during the HPPMS CrN/AlN process via a current probe. The morphology and the thickness of the coatings were evaluated using a scanning electron microscope (SEM) ZEISS DSM 982 Gemini. The bilayer period Λ was calculated by means of the coating thickness d and the

Table 1
Process parameters for deposition of the CrN/AlN coatings using HPPMS and mfMS.

Deposition parameters	Unit	HPPMS	mfMS
Substrate temperature	°C	375	375
Mean cathode power Cr	kW	4	4
Mean cathode power Al	kW	3	3
Pulse length t_{on}	μs	200/80/40	7
frequency	Hz	500	$18.51 \cdot 10^3$
Duty cycle	%	10/4/2	13
Bias voltage	V	−100	−100
Ar flow	sccm	200	200
N_2 flow	sccm	69 (pressure controlled)	66 (pressure controlled)
Pressure	mPa	550	500
Type of rotation		One-fold motion	One-fold motion
Rotational speed	min^{-1}	0.63/1.30/2.30/2.97	0.63/1.30/2.30/2.97