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Influence of HPPMS pulse length and inert gas mixture on the properties of (Cr,Al)N coatings

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ABSTRACT

During the production of plastic products by injection molding processes adhesion and abrasion wear as well as corrosion take place in the molding tools. Concerning this, (Cr,Al)N coatings deposited via physical vapor deposition (PVD) have a good potential to be used as protective coatings on injection tools. For an effective protection of coated tools a uniform layer of coating material is also required. In this regard, the HPPMS (high power pulse magnetron sputtering) technology offers possibilities to improve coating thickness uniformity as well as to adapt the chemical and mechanical properties. The present work deals with the investigation of influence of HPPMS pulse length and the argon/krypton ratio in the deposition process on (Cr,Al)N coating properties. For this reason, (Cr,Al)N coatings were deposited with HPPMS pulse length of 40, 80 and 200 μs at constant Ar/Kr ratio (120/80 sccm). The results were compared with a coating deposited with DC Magnetron Sputtering (DC-MS) with the same Ar/Kr ratio. Afterwards, a (Cr,Al)N coating was deposited with constant pulse length (200 μs) without Kr. The chemical composition, morphology and phase composition of the coatings were analyzed by means of EDS (Energy Dispersive Spectroscopy), SEM (Scanning Electron Microscopy) and XRD (X-ray Diffraction), respectively. The composition of the surface near region in the samples was investigated by means of XPS (X-ray Photoelectron Spectroscopy). Mechanical properties were measured by means of nanoindentation. Decreasing of pulse length at constant mean power leads to a considerable increase of cathode current. It could be observed that the deposition rate of the HPPMS process reduces with decreasing pulse length. Nevertheless, short HPPMS pulse lengths and high peak currents lead to an increase of hardness from 25 GPa to 32 GPa while the DC-MS coating displays a hardness of 18 GPa. The use of krypton within the sputter process leads to a marginal increase of the deposition rate while the mechanical properties are not significantly changed. In addition, EIS (electrochemical impedance spectroscopy) was employed to investigate the defect structure of the coatings.

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1. Introduction

During processing of plastic products using injection molding machines the surfaces of molding tools are often subject to adhesion and abrasion wear as well as corrosion [1]. Limited tool life of molding tools represents an issue for mass production especially of plastic products with complex geometries. Concerning this, coatings deposited via physical vapor deposition (PVD) have a good potential to be used as protective coatings on molding tools. It was demonstrated that the protection of molding tools can be improved and the adhesion of plastic melts can be reduced by using e.g. titanium and chromium based coatings [2,3]. Especially, (Cr,Al)N is an important hard transition metal nitride coating that exhibits high hardness, good abrasion wear resistance and high corrosion resistance [4–8], which makes this coating system a promising candidate for many different applications, e.g. cutting and forming operations [9–12]. Thus, (Cr,Al)N was chosen to be investigated in this work.

HPPMS (High Power Pulsed Magnetron Sputtering) is a physical vapor deposition (PVD) technology. Due to high-energy pulses a plasma density can be achieved which is higher by three orders of magnitude in comparison to conventional direct current (DC-MS) sputtering [13]. Furthermore, the MPP (Modulated Power Pulse) technique enables a creation of highly ionized sputtered species leading to deposition of dense coatings with deposition rates up to 15 μm/h and high hardness [14,15]. A detailed review of HPPMS/HIPIMS technology and its advantages is given from Sarakinos et al. [16] and Lundin et al. [17]. The main advantage of using HPPMS is that it provides high plasma densities and a high grade of ionization. First analysis using optical emission spectroscopy (OES) during sputtering of Cr and Ti targets have shown a considerable enhancement of ion/atom ratio by highly ionized plasmas compared to DC-MS sputtering [18,19]. Thus, the use of HPPMS allows for a better control of the energetic bombardment of the substrate. It offers the possibility to influence phases, microstructure, and composition of the coating by variation of the process parameters [20], e.g. peak current, frequency and pulse length. Investigations of CrN_x coatings show changes of the density and the surface roughness as the peak target current increased, while the deposition rate decreases drastically [21]. Other

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investigations of CrN_x reveal that an increasing frequency leads to a nano-sized grain structure and a partial suppression of the columnar growth [22]. Jing et al. reported that the crystal size and the surface roughness of titanium coatings increased with increasing pulse length [23].

The most commonly utilized inert gas for magnetron sputter deposition is argon, due to its combination of physical and chemical properties and its relatively low cost. However, the choice of the process gas may significantly affect the production and transport of a range of energetic species to the substrate, and subsequently the growth and properties of the deposited material [24]. Krypton is used for its greater atomic mass and size compared to argon, which leads to lower gas incorporation and may have beneficial effects on the kinetics of the coating growth. Its potential and kinetic secondary electron emission yields are somewhat lower than those for argon [25].

The presented work deals with the investigation of the influence of HPPMS pulse length on the properties of (Cr,Al)N coatings deposited with an argon/krypton mixture. The results were compared to other coatings obtained via a DC-MS process. For this reason, (Cr,Al)N coatings were deposited with HPPMS pulse lengths of 40, 80 and 200 μs at constant Ar/Kr ratio (120/80 sccm). The properties of these coatings were compared with a coating deposited with DC Magnetron Sputtering (DC-MS) with the same Ar/Kr ratio. Afterwards, a (Cr,Al)N coating was deposited with constant pulse length (200 μs) without Kr in the gas mixture. In addition, the chemical composition of the coatings was measured by EDS (Energy Dispersive Spectroscopy). An investigation of the chemistry of the surface near region of these coatings is of crucial importance towards understanding the interaction of the polymer melt with the (Cr,Al)N substrate such as adhesion, wear and related phenomena. To study the composition of the surface near region, X-ray photoelectron spectroscopy (XPS) was used. Tempez et.al. reported angle resolved XPS measurements for amorphous TiAlN coatings showing that the surface near region was partially oxidized and enriched with Al [26]. The information depth of XPS is limited to a few nanometers, so the results are representative for the composition of the native oxide layer of the coating. As our study focuses on (Cr,Al)N as a protective coating for tools within polymer processing it is straight forward to perform a comparative analysis of the bulk composition by means of EDS and an analysis of the surface near region by XPS as the interaction with the polymer melt is determined by the surface chemistry of the coating. Mechanical properties, morphology and phase composition were analyzed by means of Nanoindentation, SEM (Scanning Electron Microscopy) and XRD (X-ray Diffraction) measurements, respectively. EIS (electrochemical impedance spectroscopy) was employed in order to investigate the electrochemical properties and defect structure of the coatings.

2. Experimental

2.1. Materials and processes

The investigated coatings were deposited on cemented carbide (THM12), on silicon wafer (100) and on stainless steel AISI 304 (1.4301, X5CrNi18-10) via an industrial CC800/9 coating unit from CemeCon AG, equipped with one HPPMS power supply and one DC source, which were operated at constant mean power of 5 kW. A Cr target (500 × 80 mm) with 20 Al plugs (purity: Cr: 99.9% and Al: 99.5%) was applied for the deposition of the coatings. HPPMS (Cr,Al)N coatings were deposited using different pulse lengths (40, 80, 200 μs) at constant Ar/Kr ratio (120/80 sccm). The gas composition was chosen in order to achieve an Ar/Kr ratio of approximately 1.5 as reported by other authors [27–29]. Furthermore, a HPPMS (Cr,Al)N coating was deposited in pure Ar atmosphere (200 sccm) at 200 μs pulse length. In addition, a DC-MS coating was deposited with a Ar/Kr ratio of 120/80 sccm. During deposition samples were moved in a two-fold rotation. Other process parameters are shown in Table 1.

Table 1
Process parameters for deposition of the (Cr,Al)N coatings.

Deposition parameters	Unit	HPPMS	DC
Substrate	Cemented carbide, silicon, AISI 304 (1.4301, X5CrNi18-10)		
Mean cathode power	kW	5	5
Pulse length	μs	200/ 80/ 40	–
frequency	Hz	500	–
Bias voltage	V	−100	−100
Nitrogen flow		Pressure controlled	Pressure controlled
Pressure	mPa	450	450

2.2. Analytical methods

Morphology, topography and chemical composition of the samples were analyzed using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) for elemental analysis. The surface roughness was measured by means of a Hommel-Tester T2000 profilometer. The phase analysis was carried out via X-ray diffractometry with a grazing incidence X-ray diffractometer XRD 3003, General Electric. All measurements were performed using Cu-Kα (wavelength $\lambda = 0.15406$ nm) radiation operated at 40 kV and 40 mA. Hardness and Young's modulus were determined using a Nanoindenter XP, MTS Nano Instruments. The evaluation of the measured results was based on the equations according to Oliver and Pharr [30]. A Poisson's ratio of $\nu = 0.25$ was assumed.

XPS measurements were performed by means of an Omicron ESCA+Sytem (Omicron NanoTechnology GmbH, Taunusstein, Germany) with a base pressure of $<3 \cdot 10^{-4}$ mPa. The system is equipped with a hemispherical energy analyzer, the element spectra were recorded at pass energies of 25 eV. For photoelectron excitation a monochromated Al-Kα (1486.7 eV) X-ray source with a spot diameter of 600 μm was used. The take-off angle of the detected photoelectrons was 30° with respect to the surface normal. The calibration of the spectra was performed using the C 1 s peak (binding energy, BE = 285.0 eV) as an internal reference. For data evaluation the CasaXPS software (version 2.3.15) was used. All quantifications of the XPS data were done by integration of the peaks with regard to the relative sensitivities of the elements. As the core level energy of Al 2p overlaps with Cr 3 s, for the evaluation of the Al content the Al 2 s peak was used. Estimating the attenuation length of the electrons in a solid to $\lambda = \sim 2$ nm (for an Al-K_α X-ray source at 1486.7 eV), the information depth d can be estimated to about $3\lambda \cdot \cos(30) = 5.0$–$5.5$ nm [31].

Electrochemical impedance spectroscopy (EIS) measurements were performed with a Reference 600 (Gamry, Germany) potentiostat. A gold wire and a saturated Ag/AgCl electrode were used as counter and reference electrodes, respectively. Impedance data was collected in a borate buffer electrolyte (pH ~ 8.4, 19.1 g/L sodiumtetraborate decahydrate, 12.4 g/L boric acid und 7.1 g/L sodium sulfate) for a frequency range of 1–10^5 Hz by superimposing a 10 mV AC voltage at open circuit potential.

3. Results and discussion

3.1. Cathode voltage and current measurement during HPPMS discharge

The generated pulse shape during HPPMS discharge is demonstrated in Fig. 1 representative for a pulse length of 200 μs (left) and 40 μs (right) at constant mean power (5 kW) and frequency (500 Hz). When the pulse length is reduced, the current and voltage are increased in order to keep the same mean power. It can be observed that the peak current increases drastically from 260 A at 200 μs, to 280 A at 80 μs and to 660 A at 40 μs. Higher peak currents can be associated with an increased plasma ionization rate as it was reported by Alami et al. [21,32] for Cr sputtering. Therefore, it can be assumed that the ionization rate of the metal atoms is dramatically increased with increasing peak current.

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