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Influence of HPPMS pulse parameters on the reactive gas N_2 and on the properties of (Cr, Al)N coatings

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A B S T R A C T

In plastics industry molding tools are subjected to adhesive and abrasive wear as well as to corrosion. In this regard, (Cr, Al)N hard coatings deposited by physical vapor deposition (PVD) have a high potential to be used as protective coatings. The high power pulse magnetron sputtering (HPPMS) technology offers several advantages with regard to the deposition of hard coatings. Variation of the pulse length has a significant influence on the current–voltage-characteristic (I–U) of the cathodes, the chemical composition and the mechanical properties of the (Cr, Al)N coatings as well as on the reaction layer on the coating surface, which affect the interactions between the coated tool and the plastic melt in terms of adhesion. The present work deals with investigations of the influence of HPPMS pulse length at constant pulse frequency on the reactive gas N_2 in the deposition process and on the adhesion behavior of (Cr, Al)N coatings towards plastic melt. For this reason, the HPPMS plasma was analyzed at the substrate side via a retarding field energy analyzer (RFEA) and energy resolved mass spectrometer (MS). The RFEA was used to determine ion current densities at different HPPMS pulse length of $t_{on} = 40$ µs, 80 µs and 200 µs. The MS was used to analyze the intensities of Cr^+, Al^+, N^+ and N_2^+ in the HPPMS plasma. The results revealed that a decrease of the pulse length leads to an increased ion current density as well as an increased dissociation of molecular nitrogen, which has a significant influence on the chemical composition of the coating. Furthermore the adhesion behavior between coating and plastic melt is influenced by the pulse parameters via the changed chemical composition of the reaction layer on the coating surface. Based on these results, coatings with desirable mechanical properties with regard to wear resistance in plastics processing and a passive layer designed to ensure low adhesion of the plastic melt shall be developed.

1. Introduction

Molding tools in plastics industry are often subject to adhesive and abrasive wear as well as corrosion. A way to protect the molding tools is the application of hard coatings, which can be deposited by physical vapor deposition (PVD). Titanium and chromium based coating systems are known to have the possibility to reduce the adhesion of plastic melt on molding tools [1,2]. One of these systems is (Cr, Al)N, which was used for the investigations presented here.

The application of high power pulsed magnetron sputtering (HPPMS) technology expands the maximal applicable power at the cathode as well as the possibility for process control [3–5]. The high peak power, which is possible due to the pulsed operation, is achieved by a significant high cathode current, which leads to an ionization up to more than 60% in HPPMS processes [6–11]. Current and voltage characteristics at the cathode in a HPPMS process can be further influenced by the HPPMS pulse parameters, e.g. frequency and pulse length. This enables a control of the coating process. Keeping the HPPMS frequency constant, peak current and hereby peak power can be influenced by changing the pulse length and i.e. the duty cycle. A reduction of pulse length results in greater peak current and peak power density at the target, when the mean cathode power remains constant. Especially, the raising peak current at the cathode is reported to be responsible for an increased ionization and therefore, in a (Cr, Al)N PVD process, higher metal and reactive gas ion flux to the substrate is expected [9–13].

In [6,14] the influence of the higher ionization of the HPPMS technology on coating properties is discussed. Using the HPPMS technology, (Cr, Al)N coatings were produced under variation of pulse length at constant frequency and mean cathode power in our previous works [15,16]. It was reported, that the reduction of the pulse length at constant frequency influences the mechanical properties as well as the microstructure [15] and the chemical composition of the coatings [16]. In Table 1 properties of the coatings produced in a HPPMS (Cr, Al)N process for three different pulse lengths (t_{on} = 40, 80, 200 µs) are given. As can be seen from Table 1, the pulse length has significant influence on the mechanical properties of the coatings. The coating produced using t_{on} = 40 µs pulse length presented higher hardness HV and moderate indentation E_{IT} modulus compared to the coating produced at t_{on} =

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Table 1
Universal hardness HU, indentation modulus E_{IT} and roughness Ra of coatings produced in HPPMS (Cr, Al)N process using substrate bias of $U_B = -100$ V for three different pulse lengths ($t_{on} = 40, 80, 200$ µs) [15,16].

Pulse length t_{on}	200 µs	80 µs	40 µs
Universal hardness HU	25.0 GPa	30.1 GPa	32.4 GPa
Indentation modulus E_{IT}	425 GPa	408 GPa	453 GPa
Roughness Ra	0.02 µm	0.01 µm	0.01 µm

200 µs. With regard to the roughness Ra it can be seen that there is only a marginal influence of the pulse duration on the topography. There was no difference observed between the topography of the coatings with regard to waviness or surface asperity. Hence, the best mechanical properties are revealed by the coating produced using $t_{on} = 40$ µs pulse length. (Cr, Al)N coatings produced in a HPPMS process at $t_{on} = 40$ µs are therefore promising candidates for wear protection in plastics processing.

The chemical composition of the coatings determined in the coating bulk region by glow discharge optical emission spectroscopy (GDOES) is shown in Fig. 1 for different pulse lengths ($t_{on} = 200, 80, 40$ µs) in combination with data published in [16] regarding the chemical composition at the surface measured by X-ray photoelectron spectroscopy (XPS). On the basis of these results, a significant influence of the pulse length on the chemical composition can be observed. The nitrogen content in the coating produced with a pulse length of $t_{on} = 40$ µs is higher than the nitrogen content in the coating produced at $t_{on} = 200$ µs and $t_{on} = 80$ µs pulse length. Measurements by using GDOES showed a sub-stoichiometry in the bulk of all coatings. For the coatings deposited at $t_{on} = 200$ µs and $t_{on} = 80$ µs a nitrogen content of approximately 30 at.-% and for the coating deposited at $t_{on} = 40$ µs of approximately 30 at.-% were determined. Furthermore it was found, that the deposition rate and corresponding the nitrogen gas consumption decreases with decreasing pulse length [15,16]. Interestingly, the high nitrogen content in the coating produced at $t_{on} = 40$ µs does not lead to an increasing reactive gas consumption. This behavior can be explained by the results shown in Section 3.3.

Also the oxygen passive layer at the surface of the (Cr, Al)N coating, which is formed by oxygen from the air [17], is influenced by variation of the pulse length. Analysis of the chemical composition and a phase analysis of the coatings were carried out by Bagcivan et al. [15]. The oxygen content of 27 at.-% at the surface is lower at the coating produced at $t_{on} = 40$ µs compared to the coatings produced at $t_{on} = 200$ µs and $t_{on} = 80$ µs. The higher nitrogen content in the bulk of the coating leads to a lower oxygen content within the passive layer at the surface compared to $t_{on} = 200$ µs and $t_{on} = 80$ µs, where higher oxygen contents of 42 and 39 at.-% were measured, respectively [15]. The metal (Cr + Al) to nonmetal (N + O) ratio for all coatings was determined by Bagcivan et al. [15].For all coatings, a nonmetal content in the surface near region between 60 and 61 at.-% was measured. For the application of PVD-coated tools in plastics processing the composition of the passive layer on the coating surface has a great importance. Due to the fact that the passive layer gets directly in contact with the molten plastic (Fig. 2) it significantly influences the adhesion affinity against the plastic melt.

In order to understand this behavior of the chemical composition with different pulse length, it is necessary to correlate process parameters, plasma ion composition and coating composition. Therefore, the present work deals with the investigation of the influence of the HPPMS pulse length on plasma ion composition at the substrate side. The measurements reported here were carried out using the same industrial scale coating unit of [15,16], in order to enable the possibility of a correlation with coating properties reported in the previous works. Measurements of the effective mean ion temperature and ion current density at the substrate side were done by retarding field energy analyzer (RFEA) in a HPPMS (Cr, Al)N coating process. Furthermore, also measurements on the plasma ion composition at substrate side were carried out using energy resolved mass spectrometer (MS). In a second step the interaction between different coatings and plastic melt was investigated using high temperature contact angle measurements in order to determine the influence of formed passive player and therefore of the changed chemical composition at the coating surface on the interaction between plastic melt and (Cr, Al)N coating.

2. Experimental details

2.1. Process and plasma characterization

The investigations were carried out using an industrial scale PVD coating unit, CC800/9 Custom, CemeCon AG, Würselen, Germany. The coating chamber had a dimension of

100 × 100 × 100 cm^3. The coating unit had two cathodes, one equipped with a dcMS power supply and one with a HPPMS power supply. The angle between the cathodes and the wall was approx. 45°. For the presented investigations only the HPPMS cathode was used. Onto the HPPMS cathode a chromium target with 20 aluminum plugs was mounted, chromium purity 99.9% and aluminum purity 99.5%, respectively. The target size was 500 mm × 88 mm. Measurements were carried out during a HPPMS-(Cr, Al)N process with argon and krypton as process gases (F(Ar) = 120/F(Kr) = 80 sccm). Nitrogen was used as

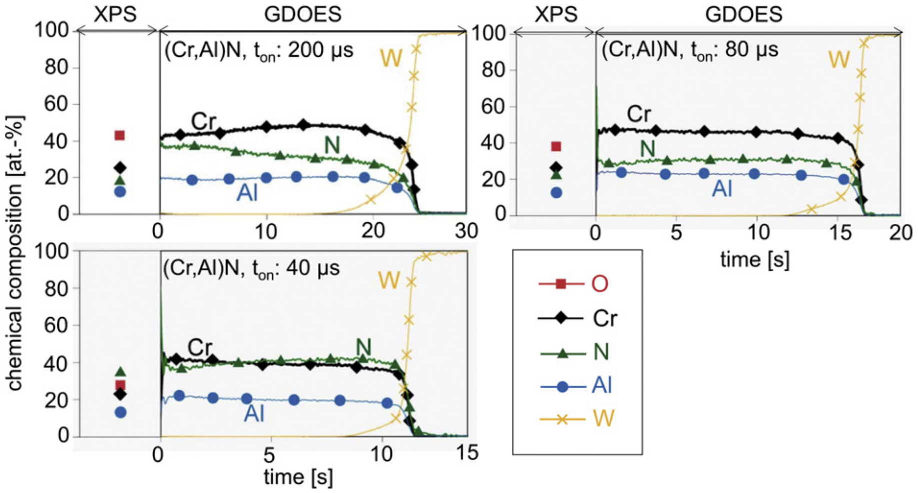

Fig. 1. Chemical composition of HPPMS-(Cr, Al)N coatings deposited at P = 5 kW mean cathode power, f = 500 Hz frequency and different pulse lengths ($t_{on} = 40$ µs, 80 µs, 200 µs) at the surface using XPS and in the bulk region using GDOES, data from [15,16].