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Hybrid dcMS/HPPMS PVD nitride and oxynitride hard coatings for adhesion and abrasion reduction in plastics processing

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ABSTRACT

During plastics extrusion, machine components such as extruder screw and extrusion die are exposed to the plastics melt. The resulting tribological loads can lead to excessive wear. In this regard, chromium based nitride and oxy-nitride hard coatings deposited via physical vapor deposition offer great potential in order to protect machine components against wear. In order to produce PVD coatings with increased mechanical properties on complex geometries such as extruder screws the high power pulsed magnetron sputtering/high power impulse magnetron sputtering technology seems to be promising. In this paper Cr-Al-N and Cr-Al-O-N coatings deposited on plasma nitrided steel 34CrAlNi7 10 (1.8550) by a direct current magnetron sputtering hybrid PVD process are investigated. The Cr/Al ratio and the O content of the coatings were varied. Chemical composition, morphology and structure were analyzed by means of scanning electron microscopy, X-ray photo spectroscopy and X-ray diffraction, respectively. High temperature contact angle measurements at the processing temperatures of the plastics were conducted in order to analyze the adhesion behavior of the (coated) surfaces towards industrial relevant types of polyamide, polycarbonate and polypropylene. The tribological behavior of the (coated) surfaces against plastic pins at ambient temperature was investigated in a pin-on-disc tribometer. The contact zones between the (coated) surfaces and the plastics were analyzed by Raman spectroscopy. Furthermore, the wear behavior was investigated. The results reveal a correlation between the chemical composition of the coatings and the adhesion towards the investigated plastics.

1. Introduction

The global plastics production increased continuously over the last decades reaching 311 mio. t in 2014 [1]. The plastics polyamide (PA), polycarbonate (PC) and polypropylene (PP) represent about 22% of the requested plastic types in Europe. These plastics are mainly used for automotive and electrical products as well as packaging applications [1]. Driven by the increasing amount of plastics production, the demand for plastics processing machinery increases as well. With regard to environmental and economical aspects efficient processing machines in the mass production of plastics products are required [2,3]. In plastics processing the technologies injection molding and extrusion are highly relevant [1].

Machine components exposed to the plastics melt and the plastics pellets during plasticizing are subject to adhesive and abrasive wear as well as corrosion [4,5]. Excessive wear on machine components like extruder screw or extrusion die reduces the service life. Processing of filled plastics can increase abrasive wear in the feed zone and also lead to abrasion in the metering zone [4]. Excessive wear in these areas will lead to increased gaps between the screw and the barrel resulting in decreasing melt quality [4,6]. Furthermore, plastics melt is likely to thermally degrade which has been investigated elsewhere [7–11], and adhere on the machine components which causes defects in the extrudate. Therefore, a decreased adhesion between the plastics melt and the machine components and an increased abrasion resistance of the machine components exhibit high potential in order to extend the life time and product quality in the extrusion process. Furthermore, small batch sizes lead to an increasing amount of purging processes in order to flush a prior processed plastics out of the extrusion line. An optimization of process parameters like flow rate and temperature has been proven to affect the purging times [12]. Besides that a decreased adhesion between plastics and the machine components can lead to reduced purging times. Especially, in high wage countries highly efficient production facilities are required [13]. Which particular aspect affects the production efficiency most significantly, strongly depends on the particular boundary conditions like intervals of material changes, processed plastics type, filler material etc.

In order to improve the extrusion and injection molding process, surface modifications and coatings are widely investigated. Physical vapor deposition (PVD) hard coatings offer high potential to reduce the adhesion and abrasive wear between plastics melt and machine components

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[14,15]. Especially chromium based hard coatings are promising candidates for the application on the components of plastics processing machines [16–18]. Adding Al into CrN coatings leads to ternary (Cr,Al)N coatings. Due to the substitution of Cr by Al in the CrN crystals the mechanical properties of the cubic structured coatings like universal hardness HU and indentation modulus E_{IT} can be increased [19–21]. The Cr in the coatings can lead to the formation of a Cr_2O_3 passive layer on the coatings which can improve the corrosion resistance and reduce the adhesive interactions [22,23]. Based on the desirable advantages of CrN and (Cr,Al)N coatings (Cr,Al)ON coatings were developed. The introduction of O_2 during the deposition process can enhance the formation of Cr and Al oxides. The addition of O into the (Cr,Al)N coatings can influence the phase formation of the coatings. Furthermore, the hardness of the coatings correlates with the O content. Low oxygen contents can lead to an increase of the universal hardness, whereas a further increase of the O content in (Cr,Al)N coatings leads to a decreasing universal hardness [24,25]. Due to this combination of properties, (Cr,Al)ON coatings show a high potential for tribological applications ranging from plastics processing to metal cutting applications [26]. Therefore, quaternary (Cr,Al)ON coatings were investigated for applications in plastics processing and revealed promising results [27]. Nevertheless, the aforementioned demand for high efficient production machinery for the plastics processing emphasizes the necessity of coatings ensuring low wear and low adhesion. Besides the chemical composition, the surface roughness of the tools has a significant effect on the adhesive interaction between tool and plastics melt. Investigations revealed that a low surface roughness correlates with low adhesive interactions [28]. Cathodic arc evaporation (CAE) and magnetron sputtering (MS) are the most relevant industrially applied PVD technologies [18]. Due to the droplet emission during conventional CAE the MS technology offers high potential for the deposition of smooth coatings. Detrimental for the MS technology are the lower ionization rates compared to CAE. In order to increase the ionization during MS processes pulsed power supplies were developed [29]. State of the art in this field are high power impulse/pulse magnetron sputtering (HiPIMS/HPPMS) power supplies. In order to achieve increased mechanical properties combined with high deposition rates, HPPMS and dcMS can be combined in hybrid coating processes [30–32]. In this paper (Cr,Al)N and (Cr,Al)ON coatings deposited by a dcMS/HPPMS hybrid coating process on the nitrided steel 34CrAlNi7-10 (1.8550) were investigated regarding their mechanical and chemical properties. Furthermore, the influence of the coatings on the adhesion towards PA, PC at processing temperatures of the polymers and the tribological behavior against PA, PC and a PP masterbatch are presented. The plastics PA, PC and PP were chosen due to their high relevance for packaging applications [33]. They provide different permeabilities and barrier properties towards several gases and steams [33]. Therefore, PA, PC and PP are common plastics for thin film extrusion. In order to investigate the abrasion resistance of the samples, a PP highly filled with $CaCO_3$ has been chosen. High temperature contact angle (HTCA) measurements at the processing temperatures T_P of the plastics and pin-on-disc (PoD) tests at ambient temperature were conducted to evaluate the adhesion. Due to the high $CaCO_3$ content, the PP could not be tested in the high temperature contact angle measurements. This is especially relevant for extruder screws which are in contact with the pellets and the plastics melt as well. The steel 34CrAlNi7-10 (1.8550) is commonly used for extruder screws and has therefore been chosen as substrate material and reference.

2. Experimental details

The employed physical vapor deposition (PVD) technologies for the deposition of the (Cr,Al)N and (Cr,Al)ON coatings were direct current magnetron sputtering (dcMS) and high power pulsed/impulse magnetron sputtering (HPPMS/HiPIMS). Both technologies were combined in a dcMS/HPPMS hybrid process. An industrial scale coating unit of the type CemeCon CC800/9 HPPMS, CemeCon AG, Würselen, Germany, was used. The coating unit was equipped with four dcMS cathodes and two HPPMS cathodes. The arrangement of the cathodes and the layout of the deposition chamber are depicted in Fig. 1 a. The substrate table consisted of six satellites. The substrate table and the satellites were driven by a planetary gear box, allowing a double rotation of the substrates during the deposition process. In order to vary the Cr/Al ratio of the coatings Al plugged Cr targets or Cr plugged Al targets, respectively were used, Fig. 1 b. The notation CrAl20 refers to a Cr target with 20 Al plugs, AlCr20 to a target which is assembled vice versa.

During the deposition process a constant Ar flow of $Q_{Ar} = 200$ sccm was maintained. The deposition parameters are summarized in Table 1. The dcMS cathodes operated at a power $P_{dc} = 3$ kW and the HPPMS cathodes at an average power $P_{HPPMS} = 5$ kW. A pulse frequency $f_{HPPMS} = 500$ Hz and a pulse on time $t_{on} = 40$ µs were used. The heating power was set to $P_{heat} = 4$ kW, which lead to a maximum deposition temperature $T_{deposition} < 350$ °C. The specimen (Ø25 mm × 8 mm) were polished with 3 µm diamond suspension to a surface roughness Ra = 0.01 µm–0.02 µm and plasma nitrided afterwards with an effective nitride case depth $d_N = 0.3$ mm and a hardness H = 950 HV. The specimen were ultrasonically cleaned and mounted in the deposition chamber. Prior to the deposition process the substrates were etched in an Ar plasma for a time $t_{etch} = 75$ min. The coating deposition consisted of two phases for the (Cr,Al)N coatings and three phases for the (Cr,Al)ON coatings. First a metallic interlayer was produced using the two HPPMS cathodes, which were equipped with CrAl20 targets. In a second step N_2 was introduced into the coating process and the dcMS cathodes were powered, equipped with four CrAl20 or AlCr20 targets, respectively. Regarding the (Cr,Al)ON coatings during the third step of the deposition process O_2 was introduced in order to produce an oxygen rich toplayer. The O_2 flow Q_{O2} has been varied between $Q_{O2} = 15$–25 sccm. The pressure of the deposition chamber was set to p = 650 mPa for the coatings with low Al content and p = 620 mPa for the coatings with high Al content.

Surface rougnesses of the coated samples were determined by means of confocal laser scanning microscopy (CLSM), VK-X210, Keyence, Neu-Isenburg, Germany. Coating thicknesses and morphology were investigated by scanning electron microscopy (SEM), DSM982 Gemini, Carl Zeiss GmbH, Jena, Germany. The Cr/Al ratio of the coatings was measured by energy dispersive X-ray analysis (EDX), Oxford Link ISIS, Oxford Instruments plc, UK. SEM and EDX analyses were conducted at the Central Facility for Electron Microscopy (GfE), RWTH Aachen University, Aachen, Germany. Further investigations regarding the chemical composition of the reaction layer on the coating surface were carried out by X-ray photoelectron spectroscopy (XPS) at DWI Leibniz Institut für Interaktive Materialien e.V., Aachen, Germany. The measurements were carried out in an Ultra Axis™ spectrometer, Kratos Analytical, Manchester, UK. The samples were irradiated with monoenergetic Al $K\alpha_{1,2}$ radiation at 1486.6 eV and the spectra were taken at a power of 144 W, 12 kV × 12 mA. The aliphatic carbon (C-C, C-H) at a binding energy of 285 eV (C 1 s photoline) was used to determine the charging. The elemental concentration is given in at.%. The information depth is about 6 nm nanometers for metals. The mechanical properties indentation hardness HU and indentation modulus E_{IT} were determined by nanoindentation measurements, Nanoindenter XP, MTS Nano Instruments, Oak Ridge, TN, USA, and evaluated according to Oliver and Pharr [34]. The indentation depth was limited to 10% of the coating thickness d in order to prevent influences of the substrate on the nanoindentations. A value of $\nu = 0.25$ was assumed for the Poisson ratio of the coatings [34]. Phase analyses of the coatings were conducted by X-ray diffraction (XRD) measurements using grazing incidence diffraction (GID), XRD 3003, GE Energy Germany GmbH, Ratingen, Germany. The measurements were carried out by means of Cu-Kα radiation, wavelength $\lambda = 0.1540598$ nm, U = 40 kV, I = 40 mA, diffraction angle $2\Theta = 20°$–$80°$, incidence angle $\omega = 2°$, step width s = 0.01°, step time t = 10 s. High temperature contact angle measurements (HTCA) were conducted to investigate the adhesion of the plastics PA and PC towards the uncoated substrate and coatings at