Surface & Coatings Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

(Cr,Al)N/(Cr,Al)ON Oxy-nitride Coatings deposited by Hybrid dcMS/HPPMS for Plastics Processing Applications

K. Bobzin [a], T. Brögelmann [a], G. Grundmeier [b], T. de los Arcos [b], M. Wiesing [b], N.C. Kruppe [a],*

[a] *Surface Engineering Institute, RWTH Aachen University, Kackertstr. 15, D-52072 Aachen, Germany*

[b] *Technical and Macromolecular Chemistry, University of Paderborn, Warburger Str. 100, D-33098 Paderborn, Germany*

ARTICLE INFO

Article history:
Received 30 March 2016
Revised 6 June 2016
Accepted in revised form 8 July 2016
Available online xxxx

Keywords:
PVD
HiPIMS
HPPMS
Passive film
plastic
wetting behavior
oxy-nitride

ABSTRACT

In plastics industry injection molding and extrusion tools are subjected to adhesive and abrasive wear by the flowing hot melt during extrusion process and adhering solidified melt. Due to their beneficial properties, Cr-based nitride hard coatings deposited by physical vapor deposition (PVD) are applied as protective coatings. In this regard, especially Cr-based oxy-nitride coatings with increased oxygen contents have a high potential to be used on plastic processing tools. In the presented work, five different oxy-nitride monolayer and bilayer coatings (Cr,Al)N/(Cr,Al)ON were synthesized on tool steel substrate AISI 420 (X42Cr13, 1.2083) by means of a hybrid direct current and high power pulsed magnetron sputtering (dcMS/HPPMS) process. Further, the coating architecture was varied in order to compare oxy-nitride monolayers with nitride coatings comprised of thin oxy-nitride top layers. All coatings were investigated with regard to their coating properties and, as defined by the corresponding coating/substrate interactions, with regard to their compound properties. The interactions between the coatings and Makrolon® 2408 polycarbonate (PC_{2408}) were also characterized by means of high temperature contact angle and adhesive tensile strength measurements. Complementary, in-depth chemical analysis of the surface oxide regions of the coatings by means of X-ray photoelectron spectroscopy (XPS) was performed and revealed that the surface oxide composition is primarily determined by the oxygen concentration in the coating bulk. Further, this resulted into high contact angles of the polycarbonate melt, which is desirable for injection molding. All coated samples exhibited a better demolding behavior of the solidified plastic melt as compared to uncoated AISI 420.

1. Introduction

The tools used for the processing of plastics in the industry are subjected to a complex load spectrum. The plastic extrusion can be divided into feed zone, melting zone, metering zone, and the respective tool [1]. The highest thermo-mechanical loads are effective in the metering zone. In this zone a complex load spectrum of adhesive and abrasive wear as well as corrosion has effect on the working tools which consequently lead to a reduction in tool lifetime and product quality [2]. Coatings deposited by physical vapor deposition (PVD) offer high potential to protect tools in the plastics processing against wear and corrosion as well as to minimize the wetting behavior of the plastic melt and the adhesive strength of the solidified plastic on the coated surface. The resistance against abrasion can be increased by the application of ceramic-like coatings [2,3,4,5]. The low coatings thickness of typically between 2 and 5 μm and the high uniformity of the coating allow preserving the tools geometry [6]. Due to the high mechanical loads during plastics processing a high wear resistance of the PVD coating is one of the main requirements in order to improve the durability of the tool [6,7,8]. This can be further increased by means of high power pulsed magnetron sputtering (HPPMS) technology [4,9,10]. HPPMS provides high target peak current and high ionization degree of the sputtered metallic atoms, which are much higher than those of conventional direct current magnetron sputtering (dcMS). Though higher deposition rates can be achieved by means of dcMS technology than HPPMS [11,12], HPPMS leads to more dense coatings with promising mechanical properties such as a high universal hardness HU or indentation modulus E_{IT} [13,14,15,16,17,18]. A hybrid process dcMS/HPPMS will thus combine the advantages of both technologies.

Transition metal nitrides like titanium-nitride (TiN) and chromium-nitride (CrN) deposited using PVD offer a high potential as protective coatings due to their good wear and corrosion resistance [19,20,21,22,23]. Within the binary system CrN the face-centered cubic phase (fcc) CrN and the hexagonal phase (hex) Cr_2N do exist. Depending on the nitrogen flux these phases can be synthesized by PVD. Nitrogen atoms are interstitially incorporated into the chromium metallic lattice. Thus, the metallic character of chromium is maintained [9]. In comparison to other nitride hard materials, such as TiN, CrN has a higher amount of metallic bonding [24]. This results in good adhesion on metallic

---

* Corresponding author.
E-mail address: kruppe@iot.rwth-aachen.de (N.C. Kruppe).

http://dx.doi.org/10.1016/j.surfcoat.2016.07.093

substrates. Therefore CrN is often used as bond coat [9,24]. By extending the binary system CrN with aluminum to the ternary system chromium aluminum nitride (Cr,Al)N, the properties of the coating can be varied by altering the chromium/aluminum ratio. (Cr,Al)N coatings exhibit enhanced mechanical properties, increased abrasion resistance, and a higher adhesion resistance in comparison to CrN coatings [25,26,27]. Furthermore, (Cr,Al)N coatings have been reported exhibiting a good oxidation and corrosion resistance as well as good tribological properties and high hardness [28,29,30,31,32,33]. Due to the formation of protective passivating Cr_2O_3 layers Cr-based nitride coatings offer a better oxidation resistance compared to Ti-based coatings as TiN or TiC [34,23]. The lower melting temperature of Cr-based nitride coatings ($T \approx 1740$ °C) compared to Ti-based nitride TiN ($T \approx 2950$ °C [35]) usually results in denser morphologies [36], which is beneficial for the corrosion resistance. Protection against adhesive wear caused by the formation of passivating Cr_2O_3 layers is a further reason for the industrial application of Cr-based nitride coatings on plastics processing tools [37].

Recently, several investigations focus on quaternary oxy-nitride coatings as (Cr,Al)ON for the use as potential hard coatings for tools in cutting and forming applications due to their mechanical properties and oxidation resistance [38,39,40,41]. Besides increasing the oxidation resistance, the incorporation of oxygen in ternary nitride coatings as (Cr,Al)N strongly influences the properties of oxy-nitride (Cr,Al)ON coatings, which is attributed to differences in the nature of metal-anion bonds [40,42,43]. Here, the incorporation of oxygen in the nitride structure and the incorporation of the nitrogen atoms in the oxide structure in combination with the transition region between the oxide and nitride structure can be considered responsible for the favorable mechanical properties and thermal stability of the oxy-nitride coatings [43,44,45,46]. In comparison to (Cr,Al)N-coatings (Cr,Al)ON-coatings have a lower adhesion tendency towards plastic melts of optical plastics such as polycarbonate (PC), poly(methyl methacrylate) (PMMA), cyclic olefin copolymer (COC) and polyethersulfon (PES) [38].

In the presented work, five different synthesized nitride and oxy-nitride coatings of the system Cr-Al-O-N deposited on tool steel substrate AISI 420 (X42Cr13, 1.2083) by hybrid dcMS/HPPMS technology were investigated. All coatings were investigated with regard to their coating properties and, as defined by the corresponding coating/substrate interactions, with regard to their compound properties. The interactions between the coatings and Makrolon® 2408 polycarbonate (PC_{2408}) was also characterized by means of high temperature contact angle and adhesive tensile strength measurements. The interactions between the coatings and molten polycarbonate were investigated complementary by means of in-depth chemical analysis using x-ray photoelectron spectroscopy (XPS).

2. Experimental details

2.1. Materials

Round samples (Ø = 25 mm, h = 8 mm) made of industrially used plastic mold steel AISI 420 (1.2083, X40Cr14) hardened to (51 ± 1) HRC were used for all experiments. The investigated plastic was polycarbonate Makrolon® 2408, Corvestro AG, Leverkusen, Germany, which is industrially used in the plastic extrusion. In the following, polycarbonate Makrolon® 2408 will be referred to as PC_{2408}.

2.2. Coating deposition

All coatings were synthesized using an industrial PVD coating unit (CC800/9 Custom, CemeCon AG, Würselen, Germany). The unit is constructed with a chamber volume of $V = 1\ m^3$. Inside, the coating chamber is equipped with two HPPMS and four dcMS cathodes placed around a rotating substrate table. The configuration is schematically shown in Fig. 1. Each of the six cathodes was loaded with a plugged CrAl20 target with the size of 500 mm × 88 mm. Each of the twenty Al plugs within the Cr target has a diameter of d = 15 mm. For reason of comparability all coatings were deposited with coating thicknesses of approximately $s \approx 3$ µm. Since the nitride and the oxy-nitride coatings exhibit similar deposition rates, a deposition time of $t = 60$ min was used for all coatings.

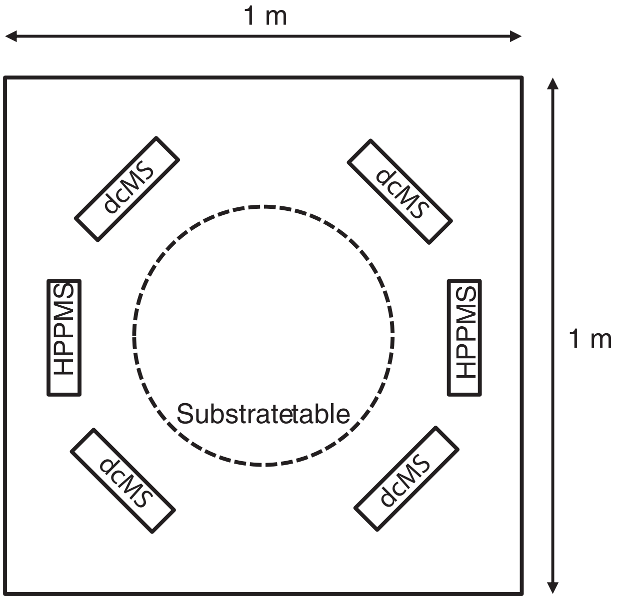

Fig. 1. Schematic depiction of the PVD dcMS/HPPMS hybrid unit in top view.

Argon was used as process gas, whereas a mixture of O_2/N_2 was used as reactive gas (Table 1). The oxygen flux was fixed for the synthesis of (Cr,Al)ON coatings while the nitrogen flux was pressure controlled in order to maintain a constant total pressure. To ensure comparable coating thickness s = (3.0 ± 0.4) µm for all coatings, the coating time was adjusted accordingly.

Table 1 shows the process parameters of the different coating processes. These mainly differ in the variation of the reactive gas mixture. Due to the increased oxygen flux into the coating chamber nitrogen was decreased pressure controlled to achieve a constant pressure of $p = 620$ mPa. The oxygen flux was varied from $F(O_2) = 0$ sccm (pressure controlled $F(N_2) = 160$ sccm) over $F(O_2) = 25$ sccm (pressure controlled $F(N_2) = 143$ sccm) to $F(O_2) = 50$ sccm (pressure controlled $F(N_2) = 122$ sccm). Thus, five different coatings where synthesized (Fig. 2).

All five coatings were bonded to the substrate AISI 420 using a (Cr,Al)-bond coat. The notation $[(Cr,Al)N]_{Ref.}$ refers to the nitride monolayer coating which is deposited as reference coating synthesized with an oxygen flux of $F(O_2) = 0$ sccm. It is used for the comparison between nitride and oxy-nitride coatings with regard to the wetting behavior of

Table 1
Process parameters for the deposition of dcMS/HPPMS hybrid coatings.

Process parameter	Unit	Value
Max. substrate temperature T_S	°C	420
Total pressure p	mPa	620
Ar flux F(Ar)	sccm	200
N_2 flux $F(N_2)$	sccm	Pressure controlled
O_2 flux $F(O_2)$	sccm	0/25/50
Heating power P_H	kW	4
Bias voltage U_{Bias}	V	-100
Avg. cathode power HPPMS per cathode P_{HPPMS}	kW	5
Avg. cathode power dcMS per cathode P_{dcMS}	kW	3
Pulse frequency f	Hz	500
Pulse duration t_{on}	µs	40

Please cite this article as: K. Bobzin, et al., Surf. Coat. Technol. (2016), http://dx.doi.org/10.1016/j.surfcoat.2016.07.093