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Mechanisms of topography formation of magnetron-sputtered chromium-based coatings on epoxy polymer composites

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ABSTRACT

The tribological protection of stiff technical polymers like epoxy resins, being main component in fiber strengthened composites (CFC), gains increasing interest to enable their use in mechanical engineering applications. Besides hardening of the surfaces to achieve similar properties like low carbon steels, smooth surfaces are essential in sliding contact. However, the conditions of film growth during magnetron sputtering including thermal stresses result in high intrinsic film stresses, which trigger the formation of distinct surface topography. Especially chromium nitride (CrN_x) single layer coatings show a fragmentation of the coating by cracking during film growth. Preferential growth of crystallites in subsequent deposition closes these cracks, provides complete covering of the surface, and bulged topographical features. Goal of this work is describing the mechanisms of formation of these topographical features as well as emphasizing influences of higher film toughness by Cr-CrN_x multilayer coatings on the density and height of the bulges.

1. Introduction

Carbon fiber polymer composites (CFC) are used for a wide range of industrial products (aeronautics, automotive, medical devices, etc.). Their advantage is rather easy fabrication with complex shapes. However, CFC performance in terms of abrasion, sliding, and impact wear resistance is very limited. Thus, a replacement of steel components by light-weight CFC demands effective surface wear protection by appropriate coatings. Applicable coating techniques are electrochemical/galvanic deposition or thermal and plasma spraying, which provide thick coatings of high load support [1–3]. However, they lack in adhesion during overloading, since their stiffness is too high and their plastic deformability is too low to follow substrate deflection. Alternatively, thick soft polymer coatings (pure and micro-/nanoparticle strengthened lacquers) possess high elasticity for bending to follow substrate deflection, but they fail in tribological resistance [4]. Thin films of materials combining hardness and wear resistance with high compliance as well as high resistance to cohesive and adhesive crack propagation (high toughness) are future candidates for surface protection of high performance polymers [5–7]. Kääriäinen et al. [8] proposed chromium nitride (CrN_x) single layer coatings on CFC, but they were not effective in tribological protection. Although they achieved high adhesion of the magnetron-sputtered PVD coatings due to surface activation by high ion doses before film deposition or high substrate temperature, the realization of dense coatings was impossible. This was assigned to a very inhomogeneous and rough substrate surface, consisting of fibers with loose ends and polymer filler. For improved coatings, the authors stated that the surface of CFC should have a fiber-free layer to obtain a sufficiently smooth surface before deposition. We observed roughening of the CFC surface with thick, smooth epoxy top layer at the micrometer scale during coating deposition in own work [9]. This roughening occurs not homogenously over the whole coated surface, but is dominated by domed lines (bulges) between fragmented, tablet-like structures.

Here, we describe this bulping effect as it is observed for magnetron-sputtered Cr-based coatings on CFC in detail and explain its deformation mechanisms. Additionally, influences of tougher multilayer vs. brittle single layer coatings on the formation of these topographical features are emphasized

2. Experimental details

2.1. Coating deposition

For deposition of single layer CrN_x and multilayer Cr-CrN_x coatings with low friction top layers of diamond-like carbon (amorphous carbon, a-C), we used epoxy-based CFC plates (manufactured by Secar Technologie Ges.m.b.H., Hönigsberg, Austria), silicon (100) wafers, and

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polished austenitic steel substrates (DIN EN 1.4301, AISI 304). They were cleaned in an industrial washing machine by using commercial tenside agents, followed by a final cleaning with ethanol before mounting in the vacuum chamber. After pumping down to high vacuum (2×10^{-3} Pa), organic contaminations were removed and the polymer surfaces were chemically activated using plasma of an anode layer ion source [10,11]. Unbalanced magnetron sputtering from 4 rectangular cathodes (432 mm height) was afterwards applied to deposit Cr, CrN_x, and a-C coatings from high purity Cr (99.99%, RHP Technology GmbH, Seibersdorf, Austria) and electrographite carbon targets (99.9%, Schunk Group, Bad Goisern, Austria), respectively. The following coating architectures were developed based on former works [12,13]:

(1) single layer CrN_x coating with 3.94 ± 0.03 μm thickness,
(2) Cr-CrN_x multilayer coatings with totally 16 bilayers and a modulation ratio Cr:CrN_x = 1:2 (82 nm Cr + 164 nm CrN_x), total thickness 3.99 ± 0.04 μm,
(3) Cr-CrN_x multilayer coating with totally 32 bilayers and a modulation ratio Cr:CrN_x = 1:2 (42 nm Cr + 84 nm CrN_x), total thickness 4.18 ± 0.03 μm.

To improve adhesion, we started deposition with a 50 nm Cr interface. 1 μm a-C films were used as top layer on all three coating types, except for samples for dedicated topography and hardness investigations. Cr as well as a-C deposition occurred in an inert Ar process gas. For CrN_x, a mixture of Ar and N_2 with a flow ratio N_2:Ar = 3:1 was used in reactive deposition. The working pressure during deposition was set to 2.9 Pa. Bias voltage of –50 V was applied to increase the energy density on CFC substrates during deposition. The DC magnetron power, set to 12 – 18 W cm^{-2}, was controlled to prevent high substrate heating exceeding the low thermal stability of the epoxy matrix (degradation starting above ~140 °C). Finally, we achieved deposition rates of ~3.4 μm h^{-1} for Cr and ~2.3 μm h^{-1} for CrN.

The temperature measurement during deposition was performed by temperature measuring tapes (Testo, Testoterm), attached on the back side of the samples in the chamber. These tapes indicate, if a distinct maximum temperature is reached during deposition.

2.2. Coating characterization

To study the topographical formation phenomena in comparison between coated CFC and Si wafers, atomic force microscopy (AFM) was applied on an Asylum Research MFP-3D equipment in soft tapping mode. Olympus AC160TS Type 3 silicon probes with a nominal tip radius of 7 nm and an opening angle of about 35° were used for all measurements. From each surface a 30 × 30 μm^2 area was scanned as overview with additional 10 × 10 and 5 × 5 μm^2 scans for detailed analysis. Roughness analysis to obtain the root mean square (RMS) roughness (standard deviation of height values) was applied on whole images and selected areas.

Scanning electron microscopy (SEM, Zeiss EVO 50) was used to study surface morphology and growth structure of cross sections. For cross-section sample preparation, cutting with an ATM Brillant 221 system was performed up to $^2/_3$ of the sample thickness from backside. Fracturing of the coated CFC substrates occurred manually by tensile loading with pincers. For increasing the conductivity during microscopy imaging, the specimens were evaporated with thin gold layers.

Structural investigations for obtaining crystallographic phases and phase orientation on coated epoxy CFC and Si substrates were performed on a Bruker AXS D8 Advance diffractometer with CuKα radiation, equipped with Sol-X detector and Goebel mirror. Bragg–Brentano

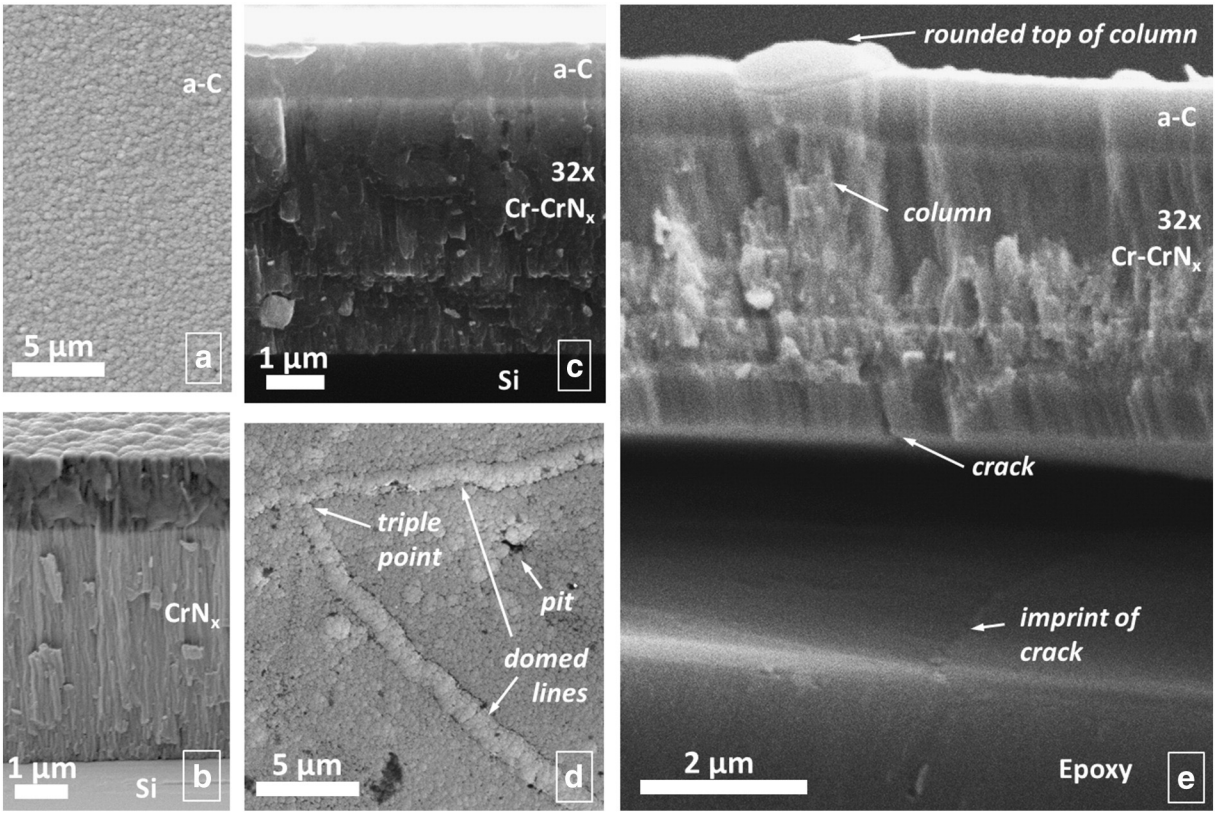

Fig. 1. SEM surface topography and cross-section images of CrN_x-based coatings with ~1 μm thick a-C top layers: (a) Surface of a 32 bilayer coating on Si substrate. (b) Cross section of a CrN_x single layer coating and (c) a Cr-CrNx multilayer coating on Si substrate. (d) Surface of a 32 bilayer coating on epoxy CFC substrate. (e) Cross section of a 32-bilayer Cr-CrN_x multilayer on epoxy CFC substrate. The gap between the substrate and coating is due to delamination during sample preparation for cross-section imaging (fracture in liquid nitrogen along a mechanically introduced notch at the back side of the sample).

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