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Seed layer stimulated growth of crystalline high Al containing $(Al,Cr)_2O_3$ coatings deposited by cathodic arc evaporation

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ABSTRACT

Single layer and dual layer $(Al_xCr_{1-x})_2O_3$ coatings were synthesised by cathodic arc evaporation with different Al contents to study their growth characteristics. It was demonstrated that variations in the Al content, the energy of incident particles and the coating thickness control the crystallinity and the coating texture. Analysis by X-ray diffraction revealed a distinct (110) out of plane orientation after transition from a fine grained nucleation zone to a columnar growth mode. Furthermore, the impact of $(Al_xCr_{1-x})_2O_3$ seed layers with $x = 0.25$ and 0.5 on the growth of $(Al_xCr_{1-x})_2O_3$ top layers with $x = 0.7$ and 0.85 was evaluated in detail. According to X-ray diffraction and transmission electron microscopy, the development of the corundum-type crystal structure of the top layer was promoted by local epitaxy if the low Al containing seed layer exhibited a pronounced columnar structure. In this way, crystalline corundum-type coatings with an Al content up to $x = 0.85$ were obtained.

1. Introduction

Corundum-type $(Al_xCr_{1-x})_2O_3$ coatings have been intensively studied within the last decade since they are considered to be promising candidates to partially substitute wear resistant α-Al_2O_3 coatings, e.g. in cutting tool applications. Their properties in terms of thermal stability, hardness and wear resistance are reported to be comparable to α-Al_2O_3. However, the synthesis temperature using different physical vapour deposition (PVD) techniques, e.g. sputter deposition or cathodic arc evaporation, could be reduced to below 600 °C [1–5]. This provides the opportunity to use a wider range of substrate materials as compared to typical chemical vapour deposition techniques with deposition temperatures between 800 °C and 1000 °C for α-Al_2O_3 [6].

Alloying of the isostructural binary oxides, corundum α-Al_2O_3 and eskolaite Cr_2O_3 (space group R-3c), leads to formation of a system with limited solubility with an upper consolute temperature of ~1300 °C (at $x \sim 0.65$). Within the miscibility gap decomposition of the single phase $(Al_xCr_{1-x})_2O_3$ solid solution is predicted for $0.25 < x < 1$ [7]. However, the high cooling rates encountered during film growth in PVD processes allow for the synthesis of metastable single-phase $(Al_xCr_{1-x})_2O_3$ coatings that are stable during annealing up to a temperature of 1050 °C [8].

Even though, the addition of eskolaite Cr_2O_3 aids the nucleation of the corundum-type crystal structure of Al_2O_3 below 600 °C, the formation of the latter showed an upper limit in the Al content x which depends on the used PVD synthesis method. Ashenford et al. [9] reported a maximum of about $x = 0.35$ using molecular beam epitaxy, whereas Ramm et al. [1] as well as Diechle et al. [5] showed the existence of crystalline corundum-type $(Al_xCr_{1-x})_2O_3$ up to an Al content of about $x = 0.7$ using cathodic arc evaporation and reactive magnetron sputtering, respectively. Beyond those limits an amorphous-like structure was described. If the development of a corundum Al–Cr–O phase is hindered, a cubic polymorph may form as reported by Khatibi et al. [10,11] and Najafi et al. [12] for magnetron sputtered as well as arc evaporated coatings.

Another way of growing corundum-type Al_2O_3 at low temperatures also makes use of Cr_2O_3. In this case, Cr_2O_3 is used as a template in order to stimulate the growth of crystalline α-Al_2O_3 due to structural epitaxy [13–15]. The easy forming eskolaite Cr_2O_3 can support the growth of α-Al_2O_3 by the low lattice mismatch between both materials and heteroepitaxial growth. Thereby, a strong influence of the seed layer texture on the top layer microstructure was observed. Nevertheless, the thickness of the α-Al_2O_3 top layer seems to be restricted to a few hundreds of nm before the structure reverts. A transition into one of the several Al_2O_3 polymorphs occurs resulting in a multiphase coating structure.

The motivation for the present study was to extend the range of crystalline corundum-type $(Al_xCr_{1-x})_2O_3$ to higher Al contents x by applying a combined approach that included both, solid solution as

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well as seed layer enhanced stimulation of corundum-type crystal growth. This work aims to elucidate the growth characteristics of cathodic arc evaporated Al–Cr–O coatings, in particular dual layer Al–Cr–O/Al–Cr–O architectures with layers of different Al/Cr ratios. A detailed analysis of morphology and microstructure of several Al–Cr–O single and dual layer coatings by means of scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and transmission electron microscopy (TEM) is provided.

2. Experimental details

Single layer and dual layer $(Al_xCr_{1-x})_2O_3$ coatings were grown by cathodic arc evaporation using a commercial Oerlikon Balzers Innova coating unit. All coatings were synthesised from powder metallurgically produced metallic Al_xCr_{1-x} composite cathodes with Al contents $x = 0.25, 0.5, 0.7$ and 0.85 providing for different coating compositions. For the synthesis of each layer of the (single and double layer) coatings, two of the six available arc sources were equipped with cathodes of identical composition. In case of the dual layer coatings, four different combinations of the Al content x were synthesised (seed layer + top layer): (1) 0.25 + 0.7, (2) 0.25 + 0.85, (3) 0.5 + 0.7 and (4) 0.5 + 0.85. In all cases a direct and sharp transition from the seed layer to the top layer was conducted.

Due to the insulating character of $(Al_xCr_{1-x})_2O_3$ coatings, a bipolar pulsed bias voltage with a pulse frequency of 25 kHz and negative pulse duration of 38 μs was used. Two different voltage peak amplitudes of 60 V and 160 V (symmetrically pulsed around 0 V) were applied during the deposition of the single layer coatings as well as the seed layers to vary the energy of the incident ions and to study the influence on the coating's microstructure. The voltage amplitude for the top layers of the dual layer coatings, however, was kept constant at 60 V in all cases.

All depositions were carried out in a pure O_2 atmosphere and the arc sources were operated by DC power supplies. The deposition parameters for the synthesis of the different coatings concerning arc current and oxygen pressure are summarized in Table 1.

Polished and ultrasonically pre-cleaned (in ethanol) Si (100) platelets as well as cemented carbide cutting inserts were used as substrates and were mounted on a carousel allowing for two-fold rotation during the deposition process. The chamber was pumped down to a base pressure below 10^{-3} Pa and the substrates were etched in a pure Ar plasma prior to deposition. The deposition temperature was 550 °C for all deposition runs.

The resulting coating thickness was determined by cross sectional SEM measurements using a Zeiss EVO 50 microscope. The room temperature residual stress was calculated from the wafer curvature of Si strips (7 mm × 20 mm) by the modified Stoney equation. The technique is described in more detail in ref. [16].

XPS using an Omicron Nanotechnology Multiprobe surface analysis system with monochromatic Al-Kα_1 radiation was applied to identify the binding states as well as the chemical composition of the coatings. The analysed sample area was about 1 mm in diameter and is given by the spot size of the used X-ray beam. The core-level electron binding energy was investigated by analysing the position of the Cr-2p, Al-2s and O-1s bands using the Unifit 2009 software package. The binding energy scale was calibrated using the C-1s peak at 285 eV. In order to remove volatile surface contaminations, especially to reduce the content of absorbed water and different C-compounds, the samples were heated up to 350 °C in an ultra-high vacuum chamber prior to the measurements.

Elastic recoil detection analysis (ERDA) applying a 35 MeV Cl^{7+} ion beam was used for quantitative element analysis. The analysed area was 1.5 mm × 1.5 mm with a depth of information of about 600 nm. The obtained spectra were fitted using the NDF software package.

The crystallographic structure of the coatings was examined by XRD in Θ-2Θ mode as well as in grazing incidence (GIXRD) geometry with an angle of incidence of 2°. The measurements were performed on a Bruker-AXS D8 Advance diffractometer applying Cu-Kα (λ = 1.54056 nm) radiation. The device was equipped with a Goebel mirror and an energy-dispersive X-ray detector. For analysing the phases present in the XRD patterns, the ICDD database [17] as well as lattice parameters for different $(Al_xCr_{x-1})_2O_3$ solid solutions given in ref. [18] were used.

Further details about the coatings' microstructure were obtained from cross sectional TEM investigations that also included selected area electron diffraction (SAED). The measurements were carried out on a FEI Tecnai 12 microscope using an acceleration voltage of 120 kV and a LaB_6-cathode. The TEM lamellas were prepared with a FEI Nova focused ion beam work station.

Table 1
Deposition parameters for single layer and dual layer $(Al_xCr_{1-x})_2O_3$ coatings synthesised from Al-Cr composite cathodes in a pure oxygen atmosphere.

	Target composition Al [at.%] – Cr [at.%]		Arc current [A]		Oxygen pressure [Pa]	
Single layer	25 – 75		180		1.4	
	50 – 50		180		1.4	
	70 – 30		180		2.2	
	85 – 15		150		2.2	
	Seed layer	Top layer	Seed layer	Top layer	Seed layer	Top layer
Dual layer	25 – 75	70 – 30	180	180	1.4	2.7
	25 – 75	85 – 15	180	150	1.4	2.2
	50 – 50	70 – 30	180	180	1.4	2.2
	50 – 50	85 – 15	180	150	1.4	2.2

3. Results

3.1. Single layer coatings

The thickness of the synthesised single layer coatings was between 2.2 and 3.3 μm with the corresponding deposition rates (normalised to an arc current of 180 A, see Table 1) changing from ~2.4, ~2.2, ~1.9 to ~1.8 μm/h with increasing Al content. The deposition rate slightly decreases with increasing Al content in the cathode. In addition, the higher pressure during deposition of the coatings synthesised from the cathodes with x = 0.7 and 0.85 also seems to reduce the rate.

In our previous studies we have reported that stoichiometric coatings can be achieved with the deposition conditions used within this work [8,19,20]. It was also shown that the metal ratio of the cathode material was preserved in the deposited coatings [8,19–21]. For a uniform coating composition along the coating thickness, a sufficiently high O_2 pressure, as used in this work, is necessary [21]. The oxygen content of the single layer coatings, was measured by XPS, yielding a value of 60.3 ±1 at.% for all coatings, which indicates the presence of stoichiometric oxides regardless of the Al content. However, the quantitative analysis of the derived spectra with regard to the Cr content is not straight forward [22] and further difficulties may arise when using XPS for analysing non-conductive coating materials with high surface roughness. Therefore, the single layer coating deposited from the cathodes with the highest Al content (x = 0.85) was analysed by means of ERDA. Thereby, an oxygen content of 59.2 at.% ±1 at.% and an Al/(Al + Cr) ratio of 0.85 was obtained. This result corroborates the XPS measurements in terms of oxygen content and denotes a metal ratio in the coating close to the cathode composition. Thus, for simplicity, the cathode composition is used to refer to the different coatings in the following.

However, despite the difficulties in determining the chemical composition using XPS, the recorded core level spectra revealed binding energies for the O-1s, Al-2s and Cr-2p3/2 bands at of ~530.9 eV, ~119.5 eV and ~576.4 eV, respectively, independent of the metal ratio in the coatings. These values are in agreement with values reported in literature where predominant Al_2O_3 and Cr_2O_3 bindings were considered [23–25].