



Seed layer stimulated growth of crystalline high Al containing $(\text{Al,Cr})_2\text{O}_3$ coatings deposited by cathodic arc evaporation

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ABSTRACT

Single layer and dual layer $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ 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 $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ seed layers with $x = 0.25$ and 0.5 on the growth of $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ 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.

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1. Introduction

Corundum-type $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings have been intensively studied within the last decade since they are considered to be promising candidates to partially substitute wear resistant $\alpha\text{-Al}_2\text{O}_3$ coatings, e.g. in cutting tool applications. Their properties in terms of thermal stability, hardness and wear resistance are reported to be comparable to $\alpha\text{-Al}_2\text{O}_3$. 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 $\alpha\text{-Al}_2\text{O}_3$ [6].

Alloying of the isostructural binary oxides, corundum $\alpha\text{-Al}_2\text{O}_3$ and eskolaite Cr_2O_3 (space group R-3c), leads to formation of a system with limited solubility with an upper consolute temperature of $\sim 1300^\circ\text{C}$ (at $x \sim 0.65$). Within the miscibility gap decomposition of the single phase $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ 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 $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ 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 $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ 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 $\alpha\text{-Al}_2\text{O}_3$ due to structural epitaxy [13–15]. The easy forming eskolaite Cr_2O_3 can support the growth of $\alpha\text{-Al}_2\text{O}_3$ 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 $\alpha\text{-Al}_2\text{O}_3$ 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 $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ 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 $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings were grown by cathodic arc evaporation using a commercial Oerlikon Balzers Innova coating unit. All coatings were synthesised from powder metallurgically produced metallic $\text{Al}_x\text{Cr}_{1-x}$ 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 $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ 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 $\times$ 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-K α_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 $\times$ 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 -2 Θ 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-K α ($\lambda = 1.54056$ 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 $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ 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.

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 $\mu\text{m}/\text{h}$ 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 ± 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-2p $_{3/2}$ 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].

Table 1

Deposition parameters for single layer and dual layer $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ 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

The microstructural evolution of as-deposited single layer $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings with Al contents x from 0.25 to 0.85 is given in Fig. 1. For coatings with $x \leq 0.7$ a corundum-type $(\text{Al,Cr})_2\text{O}_3$ crystal structure in R-3c space group symmetry is found. These coatings show a continuous shift of the diffraction peaks to higher diffraction angles for increasing Al content following the changing lattice parameters of the Al_2O_3 – Cr_2O_3 solid solution described in ref. [18]. Nevertheless, a clear dependence of the peak intensities on the overall Al content is visible. Even though the coating with $x = 0.7$ still shows a corundum-type crystal structure, the peak intensities are significantly reduced compared to the coatings with $x = 0.25$ and 0.5 . For an Al content of $x = 0.85$, only weak diffraction information with broad peaks and ambiguous phase composition can be observed indicating a very fine crystalline or amorphous like coating structure. Thus, the maximum Al content in the cathode in order to obtain a predominant crystalline corundum-type microstructure of $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings for the used deposition parameters seems to be close to $x = 0.7$. For the coatings with an Al content $x \geq 0.5$ there is evidence for an additional Al–Cr–O phase with noticeable diffraction peaks at $\sim 45^\circ$ and $\sim 66^\circ$ (not shown) 2θ . Thereby, the peak at $\sim 45^\circ$ 2θ is overlapped by the corundum-type (202) orientation. Nevertheless, with increasing Al content a moderate shift of these peaks to higher diffraction angles can be observed indicating an Al and Cr containing solid solution. Such phase could be correlated to a cubic Al–Cr–O polymorph as suggested in ref. [10]. However, in the further sections of the text, the discussion of the crystallographic investigations will be exclusively focused on the development of the dominating corundum-type $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ modification.

The obtained results concerning the crystal structure are in good agreement with ref. [1] where also a decreasing crystallinity with increasing Al content was reported for arc evaporated $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings. The nearly perfect match of the diffraction signals with the calculated solid solution peak positions (especially for $x = 0.25$ and 0.5) confirms a stoichiometric coating composition with an Al/Cr ratio similar to the used cathodes. Furthermore, the well defined XRD peak positions strongly suggest a low level of residual stress in the coatings. This

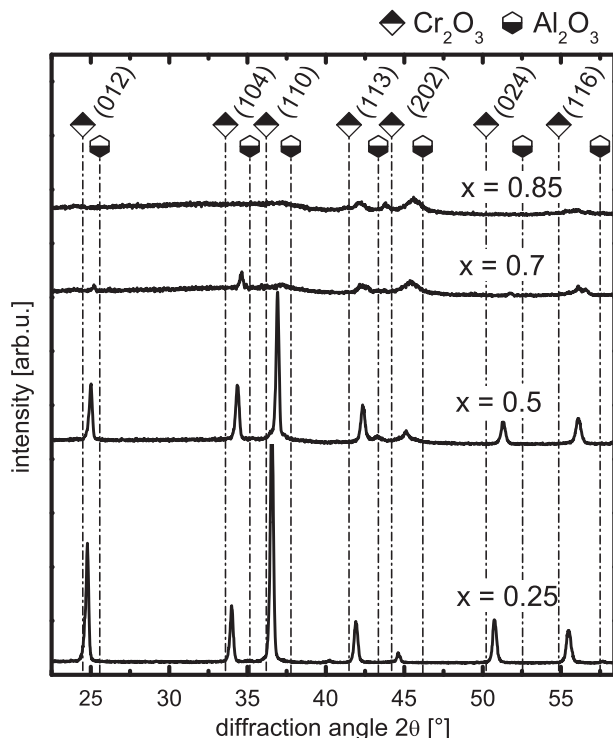


Fig. 1. GIXRD patterns of single layer $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings on Si substrates as a function of the coating composition.

is corroborated by biaxial residual stress measurements on Si substrates where in-plane tensile stresses of ~ 220 , ~ 270 , ~ 330 and ~ 570 MPa were observed for the coatings with $x = 0.25$, 0.5 , 0.7 and 0.85 , respectively. The slightly increasing stress with increasing Al content might be correlated with the decreasing crystallinity, a reduction in the domain size within the coatings or the appearance of the above mentioned second phase, which may be in particular the case for the samples with $x \geq 0.7$.

The above described reduction in crystallinity can be correlated with the SEM top view images of Fig. 2 (cemented carbide substrates), where a significant change of the coating surface morphology with increasing Al content can be observed. For $x = 0.25$ and 0.5 (Fig. 2(a) and (b)), a polygonal and fine grained structure is visible suggesting a pronounced crystal formation. This is accompanied by considerable coarsening of the surface structure with increasing Al content. It also has to be pointed out, that both coatings contain a considerable amount of droplets originating from the evaporation of the cathodes by cathodic arc as discussed in more detailed in ref. [19]. To a large fraction these droplets were

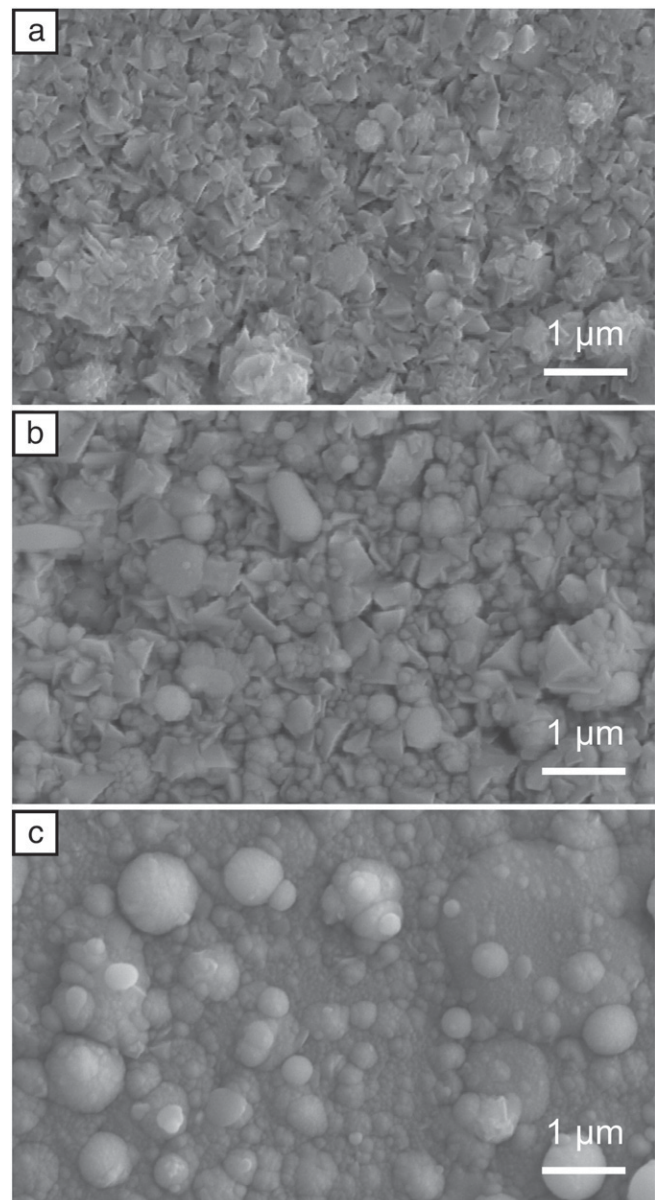


Fig. 2. SEM surface top views of $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings with (a) $x = 0.25$, (b) $x = 0.5$ and (c) $x = 0.7$ on cemented carbide substrates.

overgrown by crystallites as can be seen in Fig. 2(a). The surface top view of the coatings with $x \geq 0.7$ (see Fig. 2(c) for $x = 0.7$) does not show a faceted appearance, but a rather droplet dominated morphology appears.

3.2. Dual layer coatings

A possible strategy to stimulate the crystalline growth of high Al containing $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings is the introduction of a highly crystalline seed layer. Within the current study, combinations of the single layers described in the previous section were evaluated. The coatings with low Al content served as seed layers, i.e. $x = 0.25$ or 0.5 , while the Al-rich coatings were deposited as top layers, i.e. $x = 0.7$ or 0.85 , to study changes in their crystal structure. The chemistry within the different layers is assumed to be similar to the already presented single layer coatings since identical deposition parameters were used. In the further course of the text, the Al content of the seed layer will be labelled as x_s and that for the top layer as x_t . The seed layer thickness (t_s) is $\sim 0.9 \mu\text{m}$ for both seed layer compositions, whereas the top layer thickness (t_t) is $\sim 1.9 \mu\text{m}$ and $\sim 1.5 \mu\text{m}$ for $x_t = 0.7$ and 0.85 , respectively. This variation in the top layer thickness results from an adjustment of the deposition parameters for the respective cathode composition.

3.2.1. Seed layer $x_s = 0.25$

According to the X-ray diffractograms shown in Fig. 3, a significant improvement of the crystallinity of the top layers was noticed if a seed layer with $x_s = 0.25$ was used. The peak intensities of the high Al containing top layers in the dual layer coatings are considerably increased compared to that of the single layer reference coatings. Especially in case of $x_t = 0.85$, a distinct corundum-type crystal structure appears after the addition of the highly crystalline seed layer. This represents a significant improvement compared to the amorphous like single layer reference coating with $x = 0.85$. The high conformity of the top layer peaks with the corresponding corundum-type $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ standard positions strongly indicates a nearly unstrained growth of the top layer and thus only minor influence of the seed layer on the top layer's stress

state. Therefore, the impact from the seed layer seems to be confined to the stimulation of the formation of a corundum-type crystal structure.

A detailed representation of the growth characteristics of the dual layer coatings is given in Fig. 4(a) where a cross sectional TEM image of the coating with $x_s = 0.25$ and $x_t = 0.7$ (cf. GIXRD in Fig. 3(a)) is shown. While the morphology of the top layer is rather homogeneous throughout the layer thickness, the growth of the low Al containing seed layer is split into two stages (A and B). During the early stage of film growth a nucleation zone exhibiting a very fine structured morphology is developed. This substrate facing section "A" has a thickness of roughly $0.3 \mu\text{m}$. The adjacent section "B", on the other hand, shows a distinct columnar structure. These columns exhibit a slightly V-shaped appearance, as it is typical for competitive crystal growth in the zone T structure [26], and terminate with a maximum column width of about 60 nm . The transition between the fine grained section "A" and the columnar section "B" is rather diffuse and occurs over a length of about 80 nm . Nevertheless, the seed layer as well as the top layer exhibits a dense structure over the whole layer thickness except in zones affected by the incorporation of droplets. Similar to the V-shaped columns of the seed layer also the column width within the top layer slightly increases with increasing coating thickness resulting in a maximum column width of $\sim 90 \text{ nm}$.

Instead of developing a distinct fine grained initial growth stage as evident for the seed layer, the Al rich top layer shows a columnar structure even at the very beginning, as can be seen in the higher magnification image of the interface between seed and top layer in Fig. 4(b). A so called column to column alignment denoted by dotted lines, as known from, e.g., Cr/CrN dual layer coatings [27], dominates the transition from the seed to the top layer and confirms the existence of a template effect or even local epitaxy. In addition to the described morphology, a distinct layered coating structure on the nm scale is visible in the cross sectional TEM images in Fig. 4(a) and (b). This multilayered morphology was reported to result from moderate fluctuations in the coating composition and is caused by the used two fold substrate rotation during the deposition process [20,28].

A representative SAED pattern of section "A" of the seed layer (see Fig. 4(c)) was recorded and proves the presence of a corundum-type

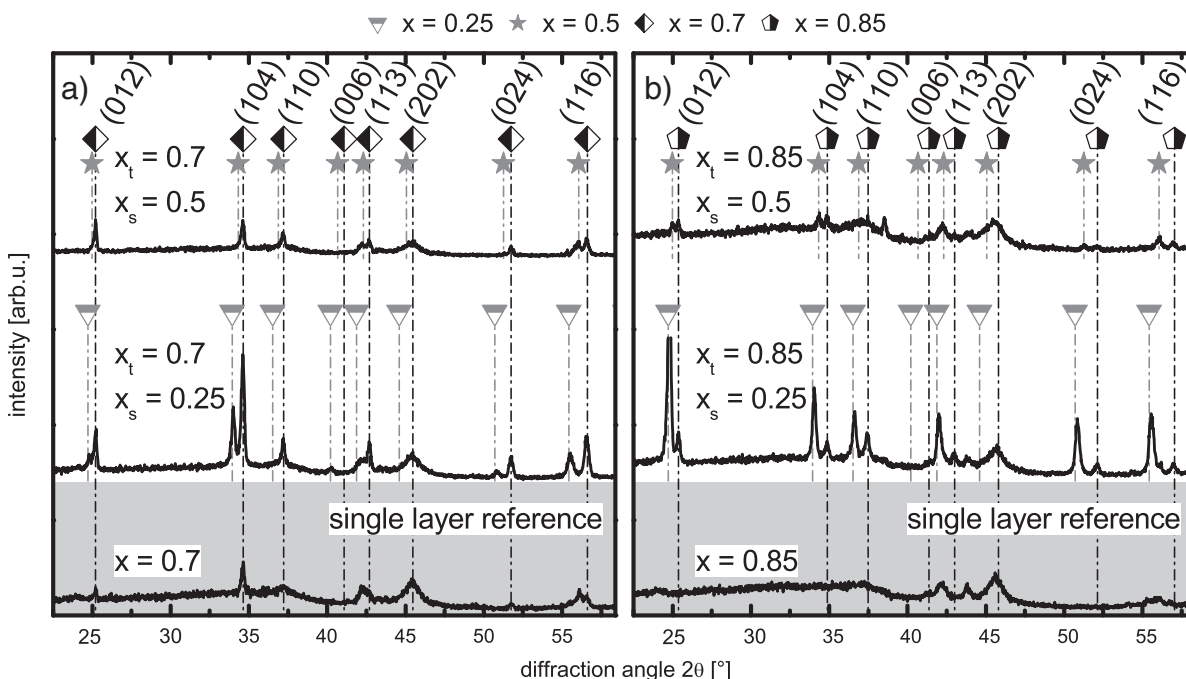


Fig. 3. GIXRD patterns of single layer coatings with (a) $x = 0.7$ and (b) $x = 0.85$ as well as dual layer coatings with different seed layer (x_s) – top layer (x_t) combinations. The calculated standard positions for $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ solid solutions with $x = 0.25$, $x = 0.5$, $x = 0.7$ and $x = 0.85$ are indicated by triangles, stars, diamonds and pentagons, respectively (seed layer bias voltage: 60 V in all cases).

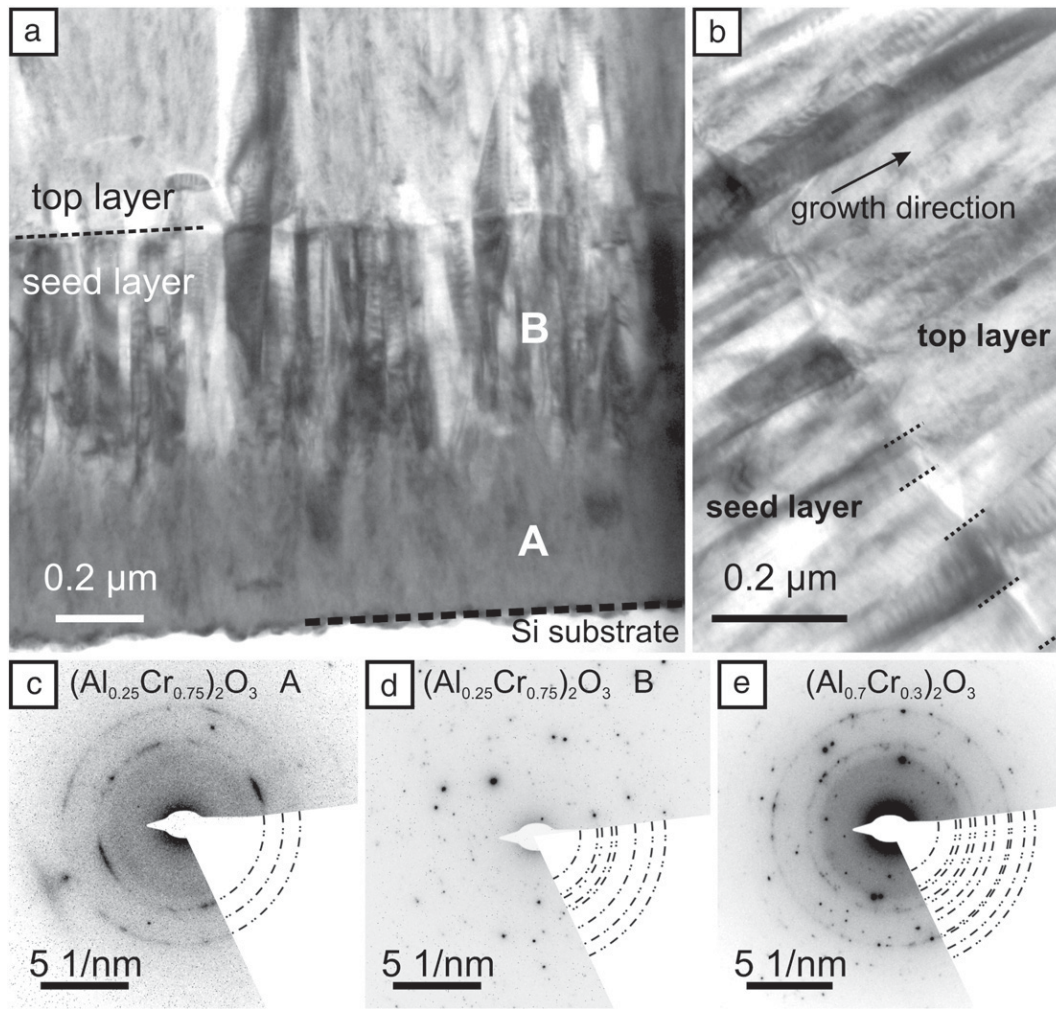


Fig. 4. (a) TEM cross section of an $(\text{Al}_{0.25}\text{Cr}_{0.75})_2\text{O}_3 - (\text{Al}_{0.7}\text{Cr}_{0.3})_2\text{O}_3$ dual layer coating. (b) Detail of the interface region between seed and top layer. SAED patterns (c) of section “A” and (d) section “B” of the $(\text{Al}_{0.25}\text{Cr}_{0.75})_2\text{O}_3$ seed layer and (e) of the $(\text{Al}_{0.7}\text{Cr}_{0.3})_2\text{O}_3$ top layer with the corresponding corundum-type standard diffraction rings.

$(\text{Al,Cr})_2\text{O}_3$ structure. The apparent diffuse diffraction rings corroborate the assumption of a fine crystalline structure. The SAED pattern of the columnar section “B” is presented in Fig. 4(d), featuring as well a corundum-type structure. However, in contrast to Fig. 4(c) the diffraction rings are replaced by discrete diffraction spots, which are related to an increased grain size with respect to section “A”. The SAED pattern of the top layer shown in Fig. 4(e) reveals again a randomly oriented corundum-type crystal structure and is therefore in good agreement with the XRD results presented in Fig. 3(a). The increased SAED aperture used for the top layer investigations (Fig. 4(e)) and the therefore increased number of diffracting crystallites leads to the development of the displayed diffraction rings. In summary, the results strongly indicate the suitability of the used seed layer with $x_s = 0.25$ as a crystallographic template for higher Al containing $(\text{Al,Cr})_2\text{O}_3$ coatings.

3.2.2. Seed layer $x_s = 0.5$

An increase of the Al fraction in the seed layer from $x_s = 0.25$ to 0.5 still aids the growth of crystalline top layers with $x_t = 0.7$ and 0.85, but, as shown in Fig. 3(b), the effect is less pronounced. Here, the GIXRD measurements reveal only moderately increased intensities for the peaks resulting from the top layers compared to the corresponding single layer coatings. However, the template effect seems to be still active as the growth of the (012), (110) or (024) out of plane domains of the coating with $x_t = 0.7$ as well as the appearance of weak but well defined corundum-type peaks in case of $x_t = 0.85$ confirm. It has to be noted, that the remaining crystallographic information from the seed

layer is considerably reduced compared to the coatings with the low Al containing seed layer $x_s = 0.25$. Since both seed layers and the corresponding top layers have the same thickness, compositionally driven differences in the growth characteristics of different $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings have been identified to cause such a behaviour as will be shown in the following section.

3.3. Influence of seed layer deposition parameters

In order to obtain a better understanding of the correlations between seed and top layer in cathodic arc evaporated Al–Cr–O dual layer coating systems, the bias voltage and seed layer thickness were varied and their impact on the top layer microstructure has been studied.

3.3.1. Bias voltage

The intensity of the particle bombardment on the film during deposition is a fundamental tool to control the growth and, hence, the microstructure [27,29,30]. Further, an increased substrate bias voltage is feasible to promote the development of a corundum-type crystal structure in arc evaporated coatings [31–34]. Thus, the role of the seed layer substrate bias voltage on the development of the top layer structure was chosen to be studied in more detail.

The influence of an increased bias voltage from 60 to 160 V on single layer $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings with $x = 0.25$ is depicted in the XRD scans in Fig. 5. For both applied bias voltages a single-phase corundum-type

structure is obvious. However, raising the bias voltage from 60 to 160 V leads to the formation of a preferred (110) out of plane orientation and to a pronounced reduction in the domain size as evidenced by a distinct peak broadening. The slight peak shift to lower diffraction angles with increasing bias voltage indicates the formation of an in-plane compressive stress state in the coating which is probably induced by the formation of defects due to the high-energetic ion bombardment [35,36]. This change in the residual stress state was confirmed by biaxial stress measurements on Si substrates, which revealed a variation from ~0.2 GPa tensile to ~2.5 GPa compressive stress for the coatings synthesised at bias voltages of 60 V and 160 V, respectively.

The effect of increased substrate bias voltage during seed layer growth on the top layer microstructure is shown in Fig. 6, where GIXRD scans of two dual layer coatings with $x_s = 0.25$ (bias voltage 160 V) and $x_t = 0.7$ and 0.85 (bias voltage 60 V) are presented. The diffraction patterns reveal the presence of a corundum-type $(\text{Al}_{0.25}\text{Cr}_{0.75})_2\text{O}_3$ phase, which can be related to the seed layer, as well as corundum-type $(\text{Al}_{0.7}\text{Cr}_{0.3})_2\text{O}_3$ and $(\text{Al}_{0.85}\text{Cr}_{0.15})_2\text{O}_3$ phases originating from the respective top layer. It can be seen that the preferred (110) orientation of the seed layer, which arises due to the enhanced substrate bias voltage (cf. Fig. 5), is transferred to the top layer as indicated by the increased relative peak intensities at $2\theta \sim 36\text{--}37^\circ$. The top layer peaks, however, are still at their standard positions and show no shift with respect to the top layer XRD signal of the coatings presented in Fig. 3 which have been deposited on the same seed layer with $x_s = 0.25$, but applying a bias of 60 V during its growth. Therefore, a distinct influence of the seed layer bias voltage on the top layer stress state seems to be absent. Nevertheless, the positive impact of the seed layer on the top layer crystallinity still remains even with 160 V bias voltage as demonstrated by the formation of a corundum-type crystal structure for $x_t = 0.85$.

To verify the obtained XRD results and in order to elucidate the morphology of the currently discussed dual layer coatings, cross sectional TEM investigations of the described dual layer coating with $x_s = 0.25$ and $x_t = 0.85$ have been performed and are presented in Fig. 7. Similar to the dual layer coating described in Fig. 4, the $(\text{Al}_{0.85}\text{Cr}_{0.15})_2\text{O}_3$ top layer depicted in Fig. 7(a) possesses a dense and columnar structure with a slightly increased maximum column width of approximately 170 nm. The highly biased (160 V) and low Al containing seed layer, on the other hand, shows distinct differences with respect to the seed layer in Fig. 4(a), which was synthesised with a substrate bias of 60 V. Even though the division into a fine structured near-substrate section "A" and a columnar section "B" is still possible, the thickness of section "A" with ~170 nm is reduced by almost 50%.

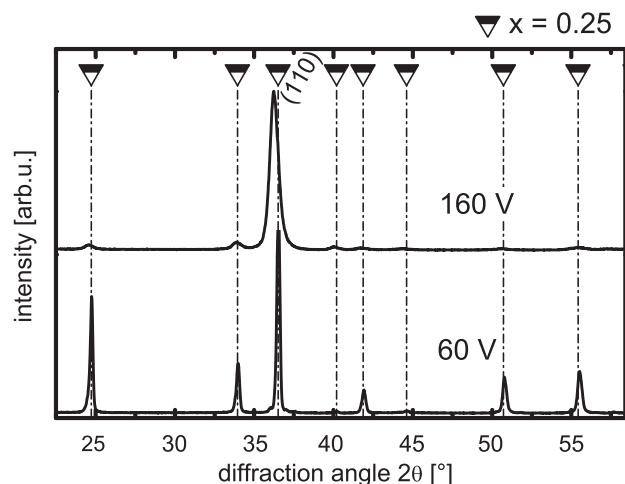


Fig. 5. XRD patterns of single layer $(\text{Al}_{0.25}\text{Cr}_{0.75})_2\text{O}_3$ coatings synthesised with a substrate bias of 60 V and 160 V.

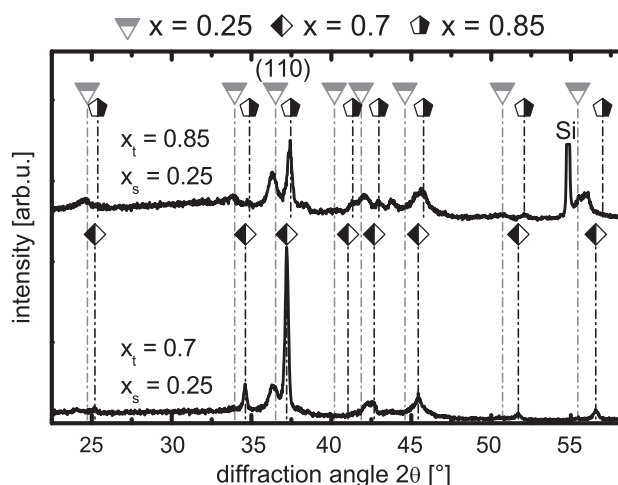


Fig. 6. XRD patterns of dual layer coatings with two seed layer (x_s) – top layer (x_t) combinations. The seed layer substrate bias voltage was 160 V. The calculated standard positions for $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ solid solutions with $x = 0.25$, $x = 0.7$ and $x = 0.85$ are indicated by triangles, diamonds and pentagons, respectively. The peak marked with Si originates from the silicon substrate.

The corresponding SAED patterns of the near-substrate section "A" and the adjacent section "B" are shown in Fig. 7(b) and (c), respectively. They reveal the presence of a corundum-type crystal structure for both regions as well as an increasing grain size as a function of the seed layer thickness and are thus in good agreement with the SAED patterns of the seed layer presented in Fig. 4. The appearance of distinct diffraction rings for the seed layer section "B" (cf. Fig. 7(c)), however, indicates an increased number of crystallites contributing to diffraction and therefore a reduced grain size compared to the same region in the seed layer synthesised with 60 V substrate bias where only single diffraction spots are visible (cf. Fig. 4(d)). The analysis of the SAED pattern for the high Al containing top layer with $x_t = 0.85$ (Fig. 7(d)) also reveals the existence of a corundum-type crystal structure and corroborates the above discussed XRD results.

3.3.2. Seed layer thickness

The presented structural investigations on the dual layer coatings with seed layers that were synthesised with either 60 V or 160 V substrate bias strongly suggest the importance of the seed layer thickness on the microstructural evolution of the coatings. However, the impact of the different growth stages within the seed layer on the structural evolution of the top layer has been not considered up to now.

The structural development of single layer $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings with $x = 0.25$ and 0.5 is presented in Fig. 8(a) and (b), respectively. Therein, the GIXRD patterns of coatings with a thickness of ~0.2, ~0.9 and ~2.5 μm deposited with a bipolar pulsed substrate bias of 60 V on Si substrates are shown. It can be seen that an increasing coating thickness is accompanied with increased peak intensities as well as a moderate reduction of the peak widths. The latter can be explained with slightly increased domain sizes and is, thus, consistent with the results of the TEM investigations discussed above. Furthermore, a variation in the preferred out of plane orientation of the single layer $(\text{Al}_{0.25}\text{Cr}_{0.75})_2\text{O}_3$ coatings as a function of the coating thickness is obvious. The (012), (104) and (116) oriented grains are dominating the early stages of growth, whereas with proceeding coating thickness the (110) orientation evolves and finally a preferred (110) and (012) out of plane orientation appears at the expense of (104) and (116). The corresponding texture coefficients according to the formula of Harris [37] as a function of the coating thickness are given in Fig. 9. Only the four most intense lattice orientations according to the Cr_2O_3 standard diffraction file [17] were taken into account for the calculation of the coefficient in order to get an indication for the preferred out of plane orientation. For the

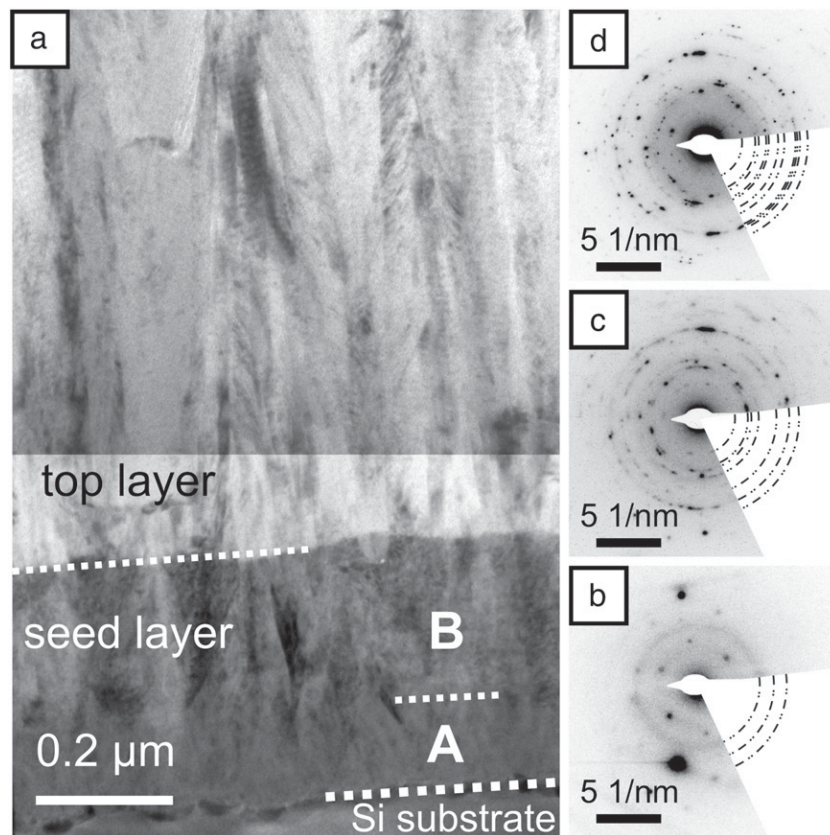


Fig. 7. (a) Cross sectional TEM image of an $(\text{Al}_{0.25}\text{Cr}_{0.75})_2\text{O}_3 - (\text{Al}_{0.85}\text{Cr}_{0.15})_2\text{O}_3$ dual layer coating synthesised with a seed layer substrate bias of 160 V. (b)–(d) SAED patterns of the seed layer section “A”, “B” and of the top layer, respectively. The SAED patterns also contain the corresponding corundum-type standard diffraction rings.

coating with $x = 0.5$ on the other hand, the growth of the corundum-type phase is almost suppressed for the first $\sim 0.9 \mu\text{m}$ and only minor contributions of the (012), (104), (110), (113) and (116) orientations are visible. The broad peak at $\sim 45^\circ 2\theta$ which arises for a coating thickness of about $0.9 \mu\text{m}$ can be assigned to the (200) plane of the cubic Al–Cr–O polymorph [10] which was already mentioned in Section 3.1. However, for thicker coatings ($2.5 \mu\text{m}$) the cubic peak decreases and a highly crystalline corundum-type structure with (110) preferred out of plane orientation evolves similar to the coatings with $x = 0.25$. This thickness triggered transition from the cubic to the corundum-type structure for coatings with $x = 0.5$ is in good agreement with results recently published by Najafi et al. [12]. Comparing the evolution of the two coating compositions ($x = 0.25$ and 0.5) it is obvious, that the fine grained or even amorphous like structure reaches a thickness of more than $0.9 \mu\text{m}$ for $x = 0.5$, while pronounced crystalline growth occurs between 0.2 and $0.9 \mu\text{m}$ for $x = 0.25$.

The GIXRD patterns in Fig. 10 show the effect of the seed layer thickness ($x_s = 0.25$) on the microstructure of the top layer ($x_t = 0.85$). Two dual layer configurations with seed layer thicknesses of $\sim 0.2 \mu\text{m}$ and $\sim 0.9 \mu\text{m}$ as well as a constant top layer thickness of $\sim 1.5 \mu\text{m}$ were compared. Beside a considerable increase in intensity for the seed layer diffraction peaks with rising thickness, the results also reveal a crucial dependence of the crystallographic template effect on the seed layer thickness. The positive effect on the development of a corundum-type structure in the top layer is reduced for the thin seed layer ($\sim 0.2 \mu\text{m}$) as compared to the thick one ($\sim 0.9 \mu\text{m}$), which is reflected in reduced top layer ($x_t = 0.85$) peak intensities. However, even for the configuration with the thin seed layer, traces of a corundum-type $(\text{Al}_{0.85}\text{Cr}_{0.15})_2\text{O}_3$ are detectable. It can therefore be concluded that an increased seed layer grain size and especially the formation of a columnar structure is beneficial for the effectiveness of a crystallographic template effect.

4. Discussion

As it was shown, the addition of Cr_2O_3 into Al_2O_3 is a feasible way to prevent the formation of various Al_2O_3 polymorphs apart from the thermodynamically stable corundum structure, even at moderate deposition temperatures of 550°C . Similar to previous studies on arc evaporated $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings, the miscibility gap predicted in the Al_2O_3 – Cr_2O_3 phase diagram [7] was not observed and a solid solution is formed at least up to $x = 0.7$. Nevertheless, with increased Al content a reduction in the coating's crystallinity and the existence of an additional cubic structured Al–Cr–O phase modification is observed. It seems that the threshold energy for the formation of corundum-type crystals, which was investigated for pure Al_2O_3 in ref. [34], is not reached during deposition of the high Al containing $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings.

4.1. Structural template effect

The application of a dual layer coating concept (i.e., seed + top layer) and in particular the use of seed layers with $x_s = 0.25$ and 0.5 was observed to have a strong effect on the growth of high Al containing coatings with $x_t = 0.7$ and 0.85 . Although high crystallinity for both investigated seed layer compositions was observed if they are deposited as single layers, they exhibit distinct differences in their effectiveness as seed layers. While the improvements on the top layer microstructure for $x_s = 0.25$ are well-defined, only moderate structural variations in the top layer can be achieved using $x_s = 0.5$.

According to the models for epitaxial growth, a narrow lattice mismatch between seed and top layer is one of the main preconditions in order to stimulate the transfer of the crystal structure throughout the grain boundaries [38]. The lattice mismatch concerning the lattice parameter a between $x_t = 0.85$ and $x_s = 0.25$ or 0.5 is $\sim 2.5\%$ or $\sim 1.6\%$,

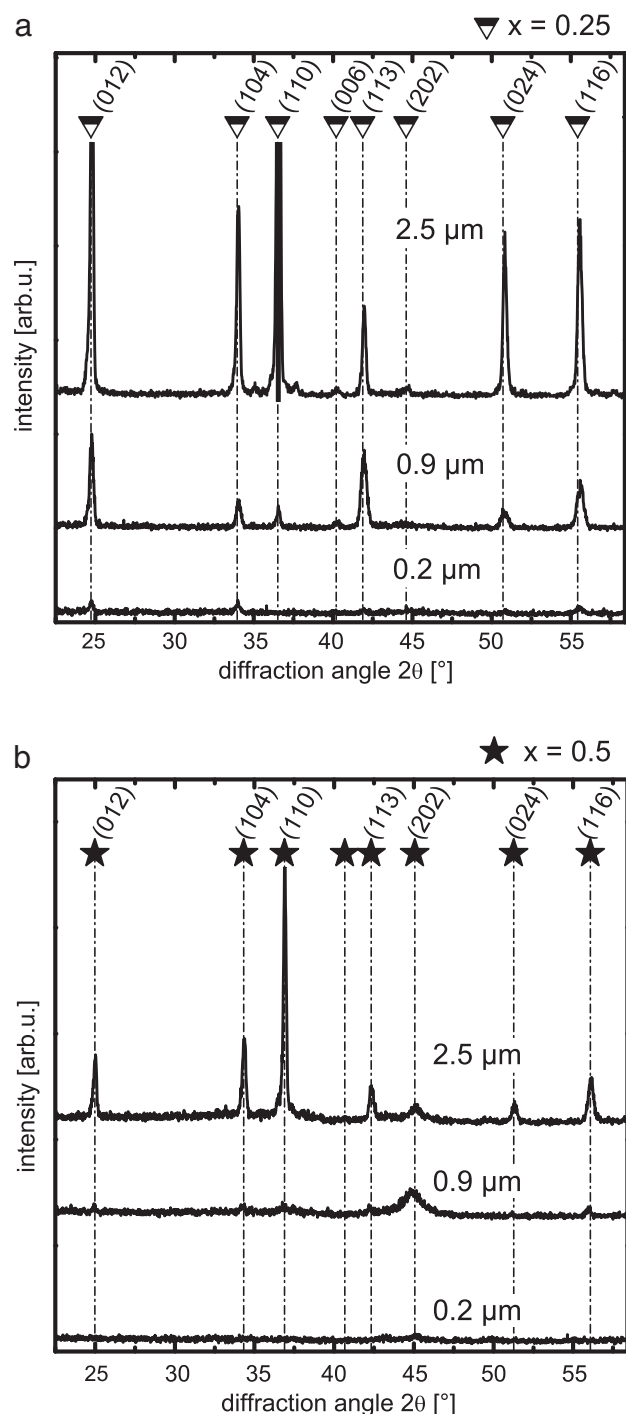


Fig. 8. XRD patterns of single layer $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings as a function of their thickness (0.2, 0.9 and 2.5 μm) for (a) $x = 0.25$ and (b) $x = 0.5$.

respectively. From that point of view, a seed layer with $x_s = 0.5$ would fulfil the requirements for crystallographic epitaxy even better compared to $x_s = 0.25$. However, the best results were obtained with the seed layer $x_s = 0.25$ and, therefore, other factors seem to be dominant.

An essential mechanism governing the ability of a seed layer to act as a crystallographic template can be found in the evolution of the crystal structure as a function of the coating thickness. As shown in Fig. 4 the investigated arc evaporated $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings undergo several stages of growth and their cross-sectional area can be sub-divided into different sections. Starting with a fine grained and probably equiaxed part (section A), the coating growth is continued with the evolution of

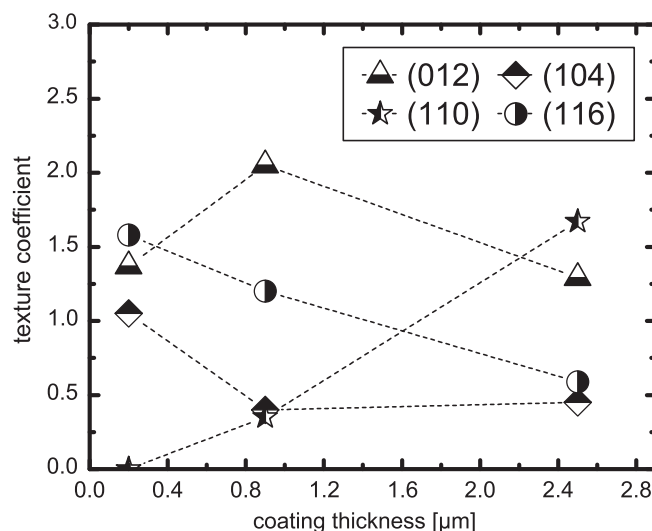


Fig. 9. Texture coefficients for the (012), (104), (110) and (116) out of plane lattice orientations as a function of the coating thickness for the coatings presented in Fig. 8(a).

an initially fine grained columnar structure (beginning of section B) and finally reaches a competitive growth situation of the columns accompanied with distinct coarsening of the crystallites.

4.2. Growth of arc evaporated $(\text{Al,Cr})_2\text{O}_3$ coatings

For the coating composition $x = 0.25$ the first 200 nm, which roughly represent section A, are dominated by preferred (012), (116) and (104) out of plane orientations. With increasing coating thickness especially the (116) and (104) oriented grains are gradually overgrown by the (110) orientation. A similar result was observed for rf magnetron sputtered Cr_2O_3 coatings where also a strong (110) texture was reported by Pang et al. [39]. A review of calculated surface energies for pure Cr_2O_3 reveals that the {102} and {116} families represent the low surface energy facets [40]. Therefore, repeated nucleation and thus minimisation of the surface energy are supposed to control the early stages of growth until the (110) dominated columnar growth starts. The {001} orientations, which were reported to show the lowest surface energy for pure $\alpha\text{-Al}_2\text{O}_3$ and which have been observed to be the preferred out of plane orientation in bias free sputtered Cr_2O_3 coatings [3], are negligible for the studied coating systems.

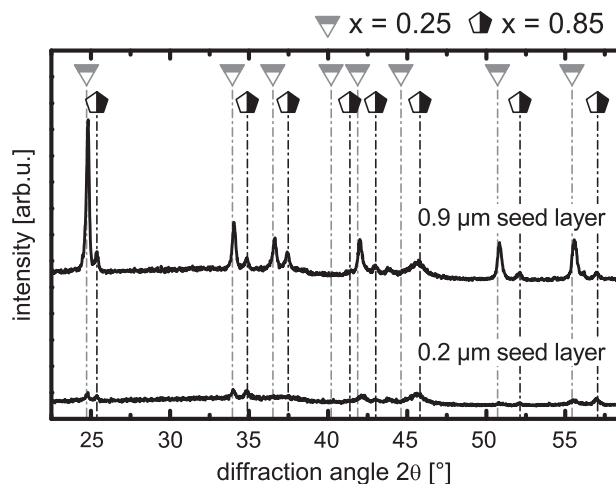


Fig. 10. XRD patterns of dual layer $(\text{Al}_{0.25}\text{Cr}_{0.75})_2\text{O}_3 - (\text{Al}_{0.85}\text{Cr}_{0.15})_2\text{O}_3$ coatings with a seed layer thickness of 0.2 μm and 0.9 μm (seed layer bias voltage: 60 V).

Nevertheless, the formation of a very fine grained and several 100 nm thick (depending on the deposition parameters) initial growth stage was also documented in previous studies on PVD Al_2O_3 [33,41,42] and Cr_2O_3 coatings [43]. Several mechanisms are contributing to the evolution of the rather thick fine grained zone of repeated nucleation in the investigated $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings. One is poor adatom mobility due to the low homologous temperature T_s/T_m of about 0.3 (depending on the coating composition). Here, T_s is the substrate and T_m the melting temperature of the coating material in Kelvin. It has been reported, that insufficient mobility of the surface adatoms promotes continued nucleation and therefore a fine grained coating structure [26,44].

On the other hand, the formation of corundum structured Al_2O_3 is highly sensitive to the incorporation of impurities from the deposition chamber into the coating, e.g. hydroxides developed from residual H_2O [45–47]. Restricted grain growth and repeated nucleation are the results. Due to the fact that a production scale deposition unit with an industrial common residual base pressure of about 10^{-3} Pa was used, the existence of such impurities, especially during the early stages of growth, cannot be neglected.

4.3. Impact of the substrate bias

The transition from equiaxed to columnar growth mode and thus the evolutionary selection of the (110) orientation tend to be strongly supported by increased energetic bombardment of the coating surface during growth. This is, however, again in contrast to sputter deposited pure Cr_2O_3 coatings described in ref. [3] where the development of a strong (104) texture was observed after using a substrate bias voltage of -50 V. On the other hand, it was shown that an increase in bias voltage leads to a significant reduction in thickness of the fine grained section A. This is in good agreement with ref. [33] where also a reduction of the fine grained initial growth stage for an increased substrate bias was described.

The reasons for the beneficial effect of a high bias voltage on the development of the corundum-type structure can be found in the increased energy of the impinging particles (ions and electrons) since they stimulate the adatom mobility, enable the rearrangement of atoms in the near surface zone of the coating as well as increase the surface temperature of the growing coating compared to the substrate due to the transfer of kinetic energy [48,49]. This should also lead to a shift of the columnar growth regime to lower homologous temperatures as reported by Anders [50], who provides a structure zone model for energetic deposition.

Moreover, the removal of the above mentioned surface impurities due to high energy surface bombardment may further facilitate the growth of the corundum structure [51,52]. Considering partial removal of adatoms, consequently also the $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ grains should be affected by, e.g., resputtering processes. However, it was demonstrated that especially the (110) oriented grains present fast growing surface facets whose growth is not significantly constrained by the impinging particles.

The early stages of growth, on the other hand, seem to remain unaffected by the substrate bias at least within the investigated voltage range, as confirmed by the similar morphology and microstructure of the coatings deposited with 60 V and 160 V substrate bias (cf. Figs. 4 and 7), until the transition to the columnar structure occurs.

4.4. Dual layer coatings

It can be concluded that the described transition from the fine grained to the columnar growth state in the seed layer is essential for the development of the crystallographic template effect. If the seed layer thickness does not reach the columnar growth stage, as it is the case for the coating with a seed layer thickness t_s of only $0.2 \mu\text{m}$ presented in Fig. 10, the beneficial impact on the top layer crystallinity is strongly decreased. Therefore, a reduced thickness of section A in the seed layer, as it can be achieved with increased bias voltage (cf. Fig. 7), should

allow a reduced seed layer thickness with concurrently retained template effect. Such an example is shown in Fig. 6, where a t_s of only $\sim 0.3 \mu\text{m}$ was used. The interplay between the pronounced coating texture and accelerated transition from the equiaxed to the columnar coating structure might cause the therein observed highly developed template effect.

Taking all these effects into consideration, it turned out that in particular the retarded transition to the columnar structure as well as smaller average grain size during the early stages of growth for increasing Al contents, as shown in Fig. 8, causes the poor template effect for $x_s = 0.5$. Then, it could be concluded that for high Al contents a reduced adatom surface diffusion due to a reduction in the homologous temperature and increased sensitivity to residual impurities within the deposition chamber cause an enlarged zone of repeated nucleation with only small grains [26]. Thus, for Al contents x higher than 0.7 the transition from the nano-crystalline to the competitive growth regime is hindered throughout the whole coating thickness unless a proper adatom arrangement is stimulated, e.g. by the addition of an adequate seed layer or the use of a capable substrate material.

5. Summary and conclusions

$(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ coatings with $x = 0.25, 0.5, 0.7$ and 0.85 were synthesised by cathodic arc evaporation at a substrate temperature of $\sim 550^\circ\text{C}$ and studied with respect to their crystal structure and growth morphology. In general, a predominant corundum-type crystal structure was observed up to an Al content of $x = 0.7$ if the coatings were grown as single layers. Prior to the development of the columnar coating microstructure, a fine grained nucleation zone exists. Its thickness strongly depends on the chemical composition as it increases with increasing Al content and its microstructure is dominated by grains exposing low surface energy facets, e.g. (012), (104) and (116). With the transition to the competitive growth regime, a preferred (110) orientation develops that is still present at high coating thickness. Factors that facilitate the formation of this columnar microstructure are high Cr_2O_3 contents and energetic ion bombardment. In the latter case, a reduction of the fine grained nucleation zone by 50% as well as an enhancement of the predominant (110) texture was obtained after increasing the substrate bias from 60 to 160 V. These changes are attributed to increased adatom mobility, enhanced subsurface rearrangements as well as removal of surface impurities.

Apart from variations in the deposition parameters, the application of an appropriate seed layer strongly affects the coating's microstructure. $(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_3$ seed layers with $x = 0.25$ and 0.5 can trigger the growth of crystalline top layers with $x = 0.7$ and 0.85 if the columnar growth regime was reached before switching to the deposition of the top layer. Overcoming the nucleation zone with small grains was found to be crucial in order to allow for localized epitaxy and thus promote the propagation of a structural template effect. By this means the synthesis of crystalline corundum-type coatings up to an Al content of $x = 0.85$ was feasible. In addition, a strongly oriented seed layer can be used as an instrument to control the top layer's texture in a dual layer coating arrangement without significant modifications in its stress state.

In summary, the application of a low Al containing $(\text{Al,Cr})_2\text{O}_3$ seed layer which is isostructural to the top layer is beneficial for the growth of a crystalline high Al containing top layer and is able to stimulate the development of a corundum-type crystal structure. Thus, such well selected multilayer coating arrangements might be the basis for the commercial application of wear resistant cathodic arc evaporated $(\text{Al,Cr})_2\text{O}_3$ coatings with a stable corundum-type crystal structure.

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