Formation of cubic structured \((Al_{1-x}Cr_x)_2O_3\) and its dynamic transition to corundum phase during cathodic arc evaporation

H. Najafi a,⁎, A. Karimi a, P. Dessarzin b, M. Morstein b

a Institute of Condensed Matter Physics (ICMP), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland
b PAITIT AG, Advanced Coating Systems, CH-2545 Seltzach, Switzerland

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A B S T R A C T
Mixed aluminum–chromium oxide coatings in the form of \((Al_{1-x}Cr_x)_2O_3\) solid solutions have attracted extensive research interest during the past years due to their successful use for challenging wear applications and the comparative ease of their moderate-temperature deposition by physical vapor deposition techniques. During our research into the reactive cathodic arc deposition of this type of coating, we found a previously unobserved transition between two crystalline aluminum–chromium oxide structures. During the early growth stage, films arc-deposited from \(Al_{65.5}Cr_{0.45}\) targets form a first zone, that was found to contain exclusively the metastable cubic \(fcc-(Al_{1-x}Cr_x)_2O_3\) phase. This kinetically favored phase is reproducibly followed by the growth of a second zone made of the initially expected corundum phase, \(α-(Al_{1-x}Cr_x)_2O_3\), as observed by TEM. This dynamic transition has a significant effect on the film properties. XPS studies and structural data show that the formation of \(fcc-(Al_{1-x}Cr_x)_2O_3\) with a \((200)\) preferred orientation arises from the initial presence of a metastable monoxide \((M_1-O)\) film, which is stabilized by the incorporation of metal vacancies. Moreover, as the thickness of coating increases, the thermodynamic aspect becomes more important as compared to kinetics and leads to a loss of structural stability in the cubic layer, which is a kinetically favored phase. As a result, the system will transform into the metastable corundum \(α-(Al_{1-x}Cr_x)_2O_3\), which is thermodynamically more stable than the cubic phase. In this paper, formation of \(fcc-(Al_{1-x}Cr_x)_2O_3\) and its transformation to corundum phase are discussed in detail with respect to the structural and electronic properties of the different phases.

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1. Introduction

Due to their pronounced capability for providing integrity and environmental protection between 650 and 1000 °C, \((Al_{1-x}Cr_x)_2O_3\) solid solution coatings grown by physical vapor deposition (PVD) have found an intense interest [1–6]. The thermodynamically metastable corundum structure of this ternary oxide at an energetically preferred level has been reported to originate from the stable binary oxides, \(α-Al_2O_3\) (corundum) and \(α-Cr_2O_3\) (eskolaite) at temperatures as high as 1200 °C [7]. Further research efforts were lately directed to establish corundum phase formation by PVD methods at low temperatures (i.e., below 700 °C) under non-equilibrium conditions [1,2]. Ramm et al. [8] and Pohler et al. [9] have carried out a comprehensive investigation on the formation of \((AlCr)_2O_3\) coatings deposited by reactive cathodic arc evaporation, relating the phase formation to the target surface state on the one hand and substrate surface processes on the other hand. Considering the equilibrium diagram, the only known cubic phase reflections present in this system are assigned to the spinel-structure of \(γ\)-alumina [10]. It should be emphasized that a metastable \(fcc\) phase of \((Al_{1-x}Cr_x)_2O_3\) has never been synthesized by equilibrium methods within the \(Al_2O_3-Cr_2O_3\) ternary system. However, recently Khatibi et al. [11,12] reported the PVD deposition of a face-centered cubic \((fcc\) \((AlCr)_2O_3\) solid solution thin films with 33% vacancies on the metal sites and its transformation to corundum phase during annealing temperatures of 900 °C and above. Moreover, Kurapov [13] has also claimed an industrial synthesis of cubic \((AlCr)_2O_3\) films deposited by cathodic arc evaporation. Furthermore, Stüber et al. [14] described the formation of AlCr-based oxynitride coatings in both corundum and \(fcc\) structures as a function of elemental compositions. In our previous work on AlCr-based oxynitride films [15], we have furthermore observed the formation of \(fcc-(AlCr)_2O_3\) at temperature despite the large proportion of oxygen (i.e. \(O/(O+N)≈97\%) and the high content of metal vacancies.

In this work, using fixed, stable deposition conditions such as arc current, oxygen flow, process temperature and a high substrate bias, we found that the growth of oxide coating reproducibly starts by the formation of \(fcc-(Al_{1-x}Cr_x)_2O_3\) at an early stage of deposition, which at a certain point (thickness; 2 μm) reverts to corundum structure \(α-(Al_{1-x}Cr_x)_2O_3\), as schematically illustrated by Fig. 1. Interestingly, there is an extremely fast transition from cubic to corundum growth for which no information is available. Due to the similar
crystal structure and lattice parameter, first, a cubic nitride interlayer (B1-structured CrN, a = 4.13 Å) used for promoting adhesion of the oxide coating had been suspected to generate pseudomorphic growth of fcc-(Al1−xCr)x2O3. In order to refute this hypothesis, an interlayer with hexagonal structure, i.e. (Al0.97Si0.03)N,1 was deposited and, according to our results, the same growth behavior has been observed. The possible causes for this dynamic transition from cubic phase to c-Rutile structure growth are discussed in the following, with respect to both kinetic and thermodynamic aspects.

2. Experimental details

The solid solution Al−Cr−O coatings were deposited using a Platit P300 rotating cathodes arc system from powder metallurgical Al−Cr targets (PLANSEE) with a composition of 55 at.% Al and 45 at.% Cr. The mean grain size of the powders was <80 μm. In the experiments, the residual base pressure was below 10−3 Pa and the oxygen flow was controlled by a flow controller at a total working pressure of 2–3 Pa. The arc sources were operated with an arc current of up to 200 A. Polished WC-10% Co disks (Extramet, grade EMT210) with a diameter of 32 mm were used as substrates for coating deposition. The substrate holders had two-fold rotation and were positioned in line-of-sight to the arc sources (with diameter of 150 mm) and target surface. The substrate temperature was set to 550 °C ± 10, and the total coating thickness was kept at around 3 μm. For all deposition, a high multi-frequency pulsed substrate bias was selected. The stable total pressure was obtained within 2–3 min. The ion current density at the substrate was in the range of 10–50 mA cm−2 and ions have a directed kinetic energy of 20–30 eV. The coatings were deposited with a deposition rate of around 2 μm/h. In order to improve the adhesion of the oxide coating on the substrate, a thin nitride buffer layer with a thickness (t) of 100–200 nm was deposited. To investigate any potential epitaxial effect of this layer, both cubic (CrN) and hexagonal (Al0.97Si0.03)N nitride buffer layers were applied in situ, immediately prior to oxide deposition using metallic Cr and Al0.97Si0.03 targets and a nitrogen-containing plasma. The chemical composition of the films was quantitatively analyzed by Electron Probe Micro Analysis (EPMA) as well as energy dispersive X-ray (EDX) microanalysis in the TEM. The architecture of the investigated coatings and their chemical composition are presented in Table 1. The crystal structure was determined by X-ray diffraction (XRD) using a Rigaku X-ray diffractometer (Cu Kα radiation, 40 kV, 30 mA) operating in either Bragg–Brentano or grazing incidence (α = 4°) geometries. The obtained coating diffraction patterns were Rietveld refined by Jana-crystallographic computing system [16], which allows investigating the crystallographic details for all present phases such as unit cell constants, atomic positions and site occupancies.

To explore the chemical environment on the atomic scale, X-ray photoelectron spectroscopy (XPS) was employed (Kratos analytical, Manchester, UK). The system was operated using monochromatized Al Kα X-ray source (1486.6 eV). The electronic properties in terms of core-level electron binding energy (BE) and valence band (VB) electronic structure were considered. In order to remove possible surface contaminations, sputter-cleaning was employed solely for 1 min using 4 keV Ar+ ions. The binding energy scale was referenced to the C 1s peak position at 284.8 eV to be independent of any possible electrostatic sample charging effects. The microstructure of samples was observed by means of transmission electron microscopy (TEM), using a Philips CM-20 equipment working at 200 kV. To prepare TEM foils, the coated specimens were first cut by a diamond wire saw to obtain slices with thickness of around 600 μm. The slices were subsequently thinned using mechanical polishing on diamond

![Figure 1](image1.png) A schematic view of the growth of (AlCr)2O3 coating on the WC-Co substrate.

![Figure 2](image2.png) Bragg–Brentano and grazing incidence XRD patterns of a) sample A with cubic buffer layer and b) sample B with a hexagonal buffer layer. The symbols ■, ▲ and ▼ correspond to fcc-(AlCr)2O3, α-(AlCr)2O3 and AlCn4, respectively, and ● refers to the substrate (WC).

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Interlayer</th>
<th>Target Composition [at.%]</th>
<th>Al/ Cr</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CrN</td>
<td>Al0.97Cr0.03</td>
<td>22.5</td>
<td>20</td>
</tr>
<tr>
<td>B</td>
<td>(Al0.97Si0.03)N</td>
<td>Al0.97Cr0.03</td>
<td>23</td>
<td>18.5</td>
</tr>
</tbody>
</table>

1 Wurtzite structure.
pads up to ≃40 μm, followed by ion milling for final thinning up to transparency to the electron beam.

3. Results

3.1. Film structure

The elemental composition of the investigated coatings obtained from the surface by EPMA is presented in Table 1. The coatings A and B displayed a cation/anion ratio (Al + Cr)/O of 0.74 and 0.71, respectively. Considering the systematic error (0.03), it is slightly higher than the expected 0.66 of stoichiometric oxide, which can also be attributed to the presence of metallic droplets (AlCr$_{ss}$, Al$_4$Cr, Al$_8$Cr$_5$) in the film. Moreover, since EPMA has a typical measurement depth of around 1 μm, these results thus are referred to the corundum type phase as a top layer. Fig. 2 illustrates the XRD patterns of coating A (Fig. 2a) described in Table 1 in comparison to coating B (Fig. 2b), that had been deposited using a hexagonal buffer layer instead of the cubic applied for A, at both Bragg–Brentano and grazing incidence (α = 4°) geometries. The coatings exhibit pronounced peaks corresponding to the (012), (104), (110), (024), and (116) reflections of the α-(Al$_{1-x}$Cr$_x$)$_2$ + δO$_3$ corundum phase$^2$ as well as an additional peak at 43.5°. At this stage we were not able to identify this peak; however, by employing selected area electron diffraction (SAED) in the TEM (presented in the following) this peak was assigned to the (200) plane of the cubic (Al$_{1-x}$Cr$_x$)$_2$ + δO$_3$ with fcc structure. The d-value of the assigned (200) is 2.055 Å which is in a good agreement with XRD results. Moreover, the Bragg–Brentano pattern reveals the strong reflection of the (200) crystal plane in the fcc structure more clearly than the grazing incidence geometry diffractogram. This can be explained by a preferred crystallographic orientation with the lattice planes parallel to the layer surface, whereas in grazing incidence geometry the lattice planes are oriented with an angle of (θ − α) to layer surface and therefore the intensity is lower for a pronounced texture (i.e. (200)). In addition, in each pattern there is a peak at around 45°, which may suggest the co-existence of another fcc phase with different lattice parameters; however, in small quantities. This may be attributed to an AlCr intermetallic phase incorporated into the film in the form of droplets, as has been previously observed by Ramm et al.[8].

Cross-sectional TEM images obtained from sample A with a cubic buffer layer are displayed in Fig. 3. The observations confirm that the Al–Cr–O coating is made up of two layers; at first growth starts in the near-substrate region in the form of a cubic layer with columnar microstructure and its thickness is around 2 μm. Selected area electron diffraction (SAED) reflections found in this region can be assigned to the (200) and (220) crystal planes of the fcc structure. The d-value of the assigned (200) is 2.055 Å which is in a good agreement with XRD results. In addition, the column size of the cubic layer is around 100 ± 10 nm. The second layer consists of a finer microstructure and the SAED pattern exhibits mainly the (012), (104), (110), (113), (024), and (116) crystal orientations of the corundum structure, which are not visible in the near-substrate region. Moreover, the electron diffraction pattern shows diffuse rings with a low intensity indicating the presence of small fractions of an amorphous phase. TEM-EDX data (see Table 2) for both layers indicate the existence of a compositional difference between the two layers. This matter can also be revealed

\footnote{pdf no. 046-1212 and 038-1479, [17].}
from the bright and dark contrasts in the TEM images of the layers related to variation of the mass density in the sample. The corundum layer (spectrum 2) shows the expected lower values of cation/anion (0.64) ratio, compared to the cubic layer (0.69, spectrum 1). Systematically lower values of the cation/anion ratio detected by TEM-EDX in comparison with the EPMA method (0.74) might be assigned to two main causes: At first in EPMA the value of chemical composition is derived from the average of a much larger volume of sample as compared to EDX analysis. This can be of importance considering the incorporated metallic droplets. The second reason can be related to higher uncertainty of oxygen detection in EDX. In addition, the Al/Cr ratio is higher for the top layer corundum phase, where the thermodynamic aspect is dominant. This can be explained by the fact that aluminum has an extremely strong affinity for oxygen compared to chromium with heats of formation $\Delta H_f = -1621$ kJ/mol and $-1135$ kJ/mol, respectively [18]. As a consequence aluminum acts as a getter for oxygen, and this greater affinity of Al (in comparison with Cr) to form species with oxygen is a significant driving force for the preferential combination of Al-O within the corundum layer. Considering the target area, the higher Al/Cr ratio can also be related to complex poisoning and phase formation processes at the surface of the powder-metallurgical arc target. Similar processes have been previously observed by Ramam et al. [8], where they recognized that high oxygen flow results in the formation of three dimensional oxide islands at the Al-Cr composite targets which are not uniformly distributed over the target surface. Chemical mapping of the islands suggests a compound consisting of aluminum and oxygen which leads to higher participation of Al in the coating during deposition.

As mentioned earlier, a cubic nitride buffer layer was initially suspected to have nucleated epitaxial growth of cubic oxide film. Fig. 4 shows cross-sectional TEM images which were obtained from sample B with a hexagonal buffer layer confirmed by SAED (shown in the inset). Again, a cubic layer of fcc-(Al$1_x$Cr$y$,O$z$)$_2$ in the near-substrate region and a corundum phase $\alpha$-(Al$1_x$Cr$y$,O$z$)$_2$ in the near-surface region are observed, where the column size is decreased drastically to 50±10 nm. Therefore, it is evident that the type of buffer layer does not significantly influence the phase formation by way of nucleation of either oxide phase.

In order to obtain important crystallographic details, the Bragg pattern of sample A was studied in detail and refined using the Rietveld method. Background of pattern, zero shifts, lattice constants as well as profile parameters (using Gaussian peak-shape function) have been refined at the initial stage of refinement. Then, at the next stage atomic positions, site occupancy, and ODF texture values were refined. Besides the plot of experimental spectrum and the fit Fig. 5 shows as insets the respective unit cells of cubic and corundum aluminum–chromium oxide phases. To achieve better clarity, substrate peaks were previously subtracted. The refinement converged with $R_p = 3.85$, $R_{wp} = 4.22$. ($R_p = \sum \alpha y_i - y_i \text{Y}_{\text{O}}$: intensity observed at step $i$, $y_i$: sum of contributions from neighboring Bragg peaks and background noise, $R_{wp} = \sqrt{\frac{\sum w_i(y_i - \bar{y})^2}{\sum w_i y_i^2}}$: $w_i$ represents standard deviation of peaks and background [19]). Table 3 reveals the Rietveld refinement details for corundum $\alpha$-(Al$1_x$Cr$y$,O$z$)$_2$ phase. During the refinement of the corundum phase, it was found that the metal site is split into two positions that are equally occupied, thus, one cannot decide which site is preferred. However, only one oxygen position has been found. The two Al/Cr positions are separated by 0.07 Å and the metal-oxygen distances range from 1.757 Å to 1.802 Å. This is probably related to the fact that Cr–O distance is always larger than the Al–O distance, suggesting that the bonding in the Cr–O neighbors may be weaker than that in Al–O neighbors, being in accordance with the thermodynamic prediction of their bonding energy [20]. Comparing these results allows suggesting that the octahedral metal coordination is not regular and a distortion of the metal octahedron occurs, which is not observed in the pure $\alpha$-Al$_2$O$_3$/Cr$_2$O$_3$ structure. Moreover, refining the occupancies confirms that probably metal sites have more deficiencies as compared to oxygen sites. The ODF texture index of 1.09 shows that there is a small texture effect in the structure.

Since the most observed fcc phase with B1 structure in this material system (Al–Cr–O) is related to CrO, the CrO model was applied for the Rietveld refinement of the cubic structure. The Al atoms were inserted as a replacement of Cr in the chemical composition of the compound (Al/(Al + Cr) = 0.53). However, as previously observed, cubic phase shows solely one diffraction peak in the XRD (i.e., (200) plane). This can cause an expected unreliability during structural refinement of this phase. Therefore, only the unit cell parameter could be refined. The results of the refinement suggest that the cubic phase has the Fm-3m space group with a lattice parameter of $a = 4.11$ Å. In comparison, for CrO with a relaxed lattice parameter of $a = 4.16$ Å [21], the decrease of lattice parameter might be attributed to a decrease of the average ionic radius on the Cr site, caused by participation of smaller Al$^{3+}$ ions and metal vacancies (31%) in the structure, as derived from the metal deficiency in the chemical composition of the compound. The role of vacancies in the structural stability of this fcc phase will be addressed in more detail in the Discussion section.

### Table 2
Elemental composition of the layers estimated by TEM/EDX.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elemental composition (at%)</th>
<th>(Al/Cr)</th>
<th>Al (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Cr</td>
<td>O</td>
</tr>
<tr>
<td>Cubic</td>
<td>21.9</td>
<td>19.1</td>
<td>59</td>
</tr>
<tr>
<td>Corundum</td>
<td>22.5</td>
<td>16.5</td>
<td>61</td>
</tr>
</tbody>
</table>

3.2 XPS analysis

In order to provide information on the chemical environment of the involved phases, XPS investigations in the respective coating regions were performed. A separate single-phase film, which is made up of only a cubic layer was used for the XPS analysis of cubic phase. To obtain solely a cubic phase during film growth, the deposition process was stopped at a certain point before the cubic-to-corundum transition. As for corundum phase, coating A which consists of the corundum phase as a top layer was employed for the XPS analysis.

The core level spectra of Al 2p, Cr 2p and O 1s are shown in Fig. 6. The increase of binding energy (BE) during the transition from cubic to corundum structure reflects variations in the chemical environment of the investigated elements. It is evident that the full width at half maximum (FWHM) of the peaks in the cubic phase is larger than that of the corundum phase due to the overlapping of several chemical states. The value of the Cr 2p binding energy for the cubic (fcc) phase is close to that of CrO (576.1 eV) [22] and then reaches the value typical for Cr$_2$O$_3$ (576.7 eV) [23] for the corundum phase. It should be noted that the variations of both binding energy (BE) and FWHM for the Cr 2p peak are higher compared to the Al 2p signal. This can be attributed to the fact that contrary to the main group metal aluminum, the transition metal chromium shows a high flexibility in its oxidation states (Cr$^{+2}$, Cr$^{+3}$, Cr$^{+4}$, Cr$^{+6}$). The capability of chromium to change its oxidation state easily could explain the change of chromium concentration from the cubic to the corundum phases. Similarly, a chemical shift of the O 1s peak at 530.5 eV toward larger BE (531 eV) is observed when the structure changes from cubic (B1) to corundum. This is consistent with the shift of the main peaks and the valence band edge (VBE) toward higher BE from cubic (B1) to corundum structure as can be seen in Fig. 6d. The VBE, estimated from the XPS valence band curves, shifts
from about $-1.3 \text{ eV}$ to $-0.10 \text{ eV}$ with the transition from cubic to corundum phase. The energy difference between the VBE and the Fermi energy level is attributed to the free electron concentration and thus to the conductivity of the system [24]. Therefore, the shift of the VBE toward lower values implies an increased resistance of the corundum phase. Furthermore, valence band (VB) electronic structure clearly shows an increase in the anti-bonding character of Cr 3d orbitals for cubic phase as compared to corundum structure, which plays a key role in the phase and structural stability [20].

Comparison of Cr 2p$_{3/2}$ and Cr 2p$_{1/2}$ splitting provides further information about the electronic structure since the magnitude of splitting is a consequence of the spin–orbit coupling, which in turn depends on the oxidation state and the chemical environment of Cr. The measured $\Delta BE$ values between the Cr 2p$_{3/2}$ and the Cr 2p$_{1/2}$ peaks for cubic (B1) phase correspond to those found for CrO ($9.6 \text{ eV}$) and increase to $9.9 \text{ eV}$ for the corundum phase, approaching the value observed for Cr$_2$O$_3$ [22,23].

**Table 3**

<table>
<thead>
<tr>
<th>Phase</th>
<th>(Al$<em>{0.57}$Cr$</em>{0.43}$)$_2$O$_3$ Corundum</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>4.8691</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.3006</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>273.1</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>4.691</td>
</tr>
<tr>
<td>Al/Cr</td>
<td></td>
</tr>
<tr>
<td>x, y, z</td>
<td>(0, 0, 0.3494)</td>
</tr>
<tr>
<td>Site occupancy</td>
<td>0.92</td>
</tr>
<tr>
<td>O x, y, z</td>
<td>(0, 0, 0.3569)</td>
</tr>
<tr>
<td>Site occupancy</td>
<td>0.95</td>
</tr>
<tr>
<td>Texture index</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Fig. 4. Cross-sectional TEM micrographs depicting the microstructure and diffraction patterns of coating B consisting of a cubic adhesion layer followed by a hexagonal buffer layer, an fcc-(Al$_{1-x}$Cr$_x$)$_2$O$_3$ in the near-substrate region and a corundum layer α-(Al$_{1-x}$Cr$_x$)$_2$O$_3$ in the near-surface region.

Fig. 5. Rietveld refinement of the X-ray powder diffraction data of the coating A. The observed intensities, calculated profile and difference curve are shown. The inset shows the models of the cubic (fcc) and corundum structures (α).
To summarize, the XPS results, in accordance with the structural data, indicate that this material system behaves electronically like a monoxide \((\text{Al,Cr})_2\mathrm{O}_3\) for the cubic phase regime which is stabilized by the presence of vacancy defects [12] and adopts \((\text{Al,Cr})_2\mathrm{O}_3\) for the corundum phase regime.

4. Discussion

While corundum-structured \((\text{Al,Cr})_2\mathrm{O}_3\) is the most frequently observed phase in the Al–Cr–O system, we have observed the appearance of another metastable phase, \(\text{fcc}(\text{Al}_1 – \text{Cr}_x)_{2 + \delta}\mathrm{O}_3\) under cathodic arc deposition. This metastable phase transforms to corundum \((\text{Al}_1 – \text{Cr}_x)_{2 + \delta}\mathrm{O}_3\) at higher film thickness beyond 2 \(\mu\)m. It is a well-recognized fact that the appearance of \(\alpha\) phase at the relatively low deposition temperature of 550 °C is favored by the presence of esolalate \(\text{Cr}_2\mathrm{O}_3\), which is isostructural with corundum [1]. These observations raise two main questions: what are the mechanisms behind the formation of cubic \((\text{Al,Cr})_2\mathrm{O}_3\), and what is the driving force for the transition of cubic to corundum phase at higher thicknesses?

According to the structural data and electronic structure it was found in this study that the cubic phase behaves as a monoxide \((\text{Al, Cr})_1 – x\mathrm{O}\) with a defective \(\text{fcc}\) (B1) structure (31% metal deficiency) and same chemical environment. While from the thermodynamic point of view such monoxides are unstable and hence it is not possible to obtain them in the bulk form, being able to deposit them by PVD demonstrates the capability of thin-film technology to form non-equilibrium solid structures. A remarkable feature of these monoxides is the occurrence of a high percentage of vacancies in the lattice as reported by several research groups (up to 25% in NbO, 15% in TiO and VO, 20–30% in CrO) [25,26]. How the presence of vacancies in the lattice produces a stabilization of a crystal system has been dealt with by numerous theoretical and experimental works. In their contributions, Schmid et al. [27] and Eichler and Hafner [28] reported that CrO monolayers with B1 structure are stabilized by vacancies due to the reduced bond energy in the basal planes. Goodenough [29] proposed for TiO that the loss of Madelung energy originated by vacancy formation would be compensated for by an increase of the electron density in the anion holes \((h^+\)\) and by a depletion of the electron density at the cation holes \((h^-)\).

An alternative mechanism has been suggested by Burdett andHughbanks [30], who postulated that the reinforcement of the metal-metal bond across the vacancy would be the main contribution to the stabilization of the monoxide phase. Du et al. [31] showed that metastable thin CrO films with a B1 structure, can be deposited while 20–30% of the metal positions in lattice are vacant. In our case as can be seen from the XPS results, out of the variety of possible chromium oxidation states, \(\text{Cr}^{±2}\) and \(\text{Cr}^{±3}\) are the dominant states for this monoxide system. In addition, at an aluminum content in the film of over 50 at.\%, the presence of \(\text{Al}^{±3}\) as the replacement of \(\text{Cr}^{±2}\) can lead to vacancy defects in order to maintain electroneutrality of the network \((2\text{Al}^{3+} = 3\text{Cr}^{2+})\). Moreover, an electronic effect can be the driving force of the vacancy formation as suggested by Eichler and Hafner [28] indicating that the reduced bond strength induced by the occupation of anti-bonding d orbitals facilitates the formation of vacancies as can also be observed for Cr 3d orbitals in the cubic phase within this work (see Fig. 6d).

Additionally, the vacancies can also be generated during high-energy ion deposition, a common feature in PVD thin films [32]. In general, point defects created during deposition are related to a variety of types such as vacancies, interstitial and point defect clusters. This allows suggesting that vacancies in the structure can consist of an intrinsic part resulting from growth defects as well as an electronic part caused by the changes of chemical environment of the compound as mentioned above. Considering these points, it can be suggested that the cubic layer formed at the early stage of deposition obeys to the same mechanisms of formation and is stabilized by the occurrence of vacancies.

However, as the thickness of coating increases up to around 2 \(\mu\)m a cubic-to-corundum transition occurs and the system will transform into the metastable corundum \((\text{Al}_1 – x\text{Cr}_x)_{2 + \delta}\mathrm{O}_3\), which is thermodynamically more stable than the cubic phase. It is a point of interest how this transition can occur in spite of very stable deposition conditions? This indicates that the coating growth is faced by
the thickness-dependent or time-dependent phenomenon, which may be understood in term of the correlation between target surface modification, variation of chemical composition along the film thickness, and coating conductivity changes during the growth. As previously mentioned, Ramm et al. [8] showed the transformation of the elemental target constituents to intermetallic and solid solution compounds for Al-Cr composite targets. With this regard, oxygen incorporation has a considerable influence on this phase modification. This means that a constant oxygen pressure, there is a non-stationary state at the target surface during deposition up to a fully oxidized state is achieved. Furthermore, we have shown that there is a composition change along the thickness; the bright and dark contrast of the TEM images are interpreted as variations of the mass density in the layers as also confirmed by TEM-EDX. Similar observations have been previously reported by Sjöld et al. [33] for Ti-Al–O–N films. Moreover, valence band spectra of the layers revealed an increasing electrical resistance when the coating becomes thicker which in turn can result in the reduced ion-induced collisions and kinetic effects. Indeed as also [33] indicated, we infer that the initial cubic layer ($\text{fcc-}$(Al$_{1-x}$Cr$_x$)$_2$+$\alpha$O$_3$) can be formed in the coating by the arc deposition process due to the kinetic effects and recoil mixing during ion impingements. However, by target surface modification and consequently variation of chemical composition along the film thickness as well as change in coating conductivity, the thermodynamic effects can become dominant until, ultimately, the transition occurs and $\alpha$-(Al$_{1-x}$Cr$_x$)$_2$+$\alpha$O$_3$ is formed.

In other words, in films deposited by a highly non-equilibrium process, such as arc evaporation PVD, the formation of metastable defective structures has to be considered. Under non-equilibrium conditions coating growth can be determined by kinetic aspects rather than by thermodynamic. In this kinetic–thermodynamic competition, kinetics initially dominate as the films crystallize in a defective cubic (B1) structure. Then, after the target surface modification and changes in film composition as well as coating conductivity, thermodynamic effects become dominant and corundum phase is formed. It may be concluded that those deposition parameters (such as substrate temperature, oxygen pressure), which strengthen the thermodynamic aspect (annihilation of growth defects), can result in an increasing corundum phase formation. In contrast, process factors that support kinetic effects and induce a high level of defect density, such as high substrate bias or growth rate, may favor the development of cubic phase.

5. Summary

The growth and phase development of aluminum–chromium oxide coatings deposited by rotating cathodes arc PVD together with a high substrate bias were examined. Results show that the films crystallize in the B1 structure at the early stage of deposition and then a cubic-to-corundum transformation occurs at a certain point (thickness=2 μm) and the film adopts a thermodynamically more stable structure, i.e. corundum $\alpha$-(Al$_{1-x}$Cr$_x$)$_2$+$\alpha$O$_3$. Transmission electron microscope, XRD and XPS results alongside indicate that the cubic (B1) layer acquires the properties of a metastable monoxide, which is kinetically stabilized by occurrence of metal vacancies (31%). The thickness-dependent transition from cubic to corundum phase can be correlated to alterations of the target surface state, film composition and coating conductivity during film growth. This suggests that the deposition conditions such as temperature on the formation of aluminum–chromium oxide layer structures, which should be taken into account for the process design of related oxide systems.

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References