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# Correlation between target surface and layer nucleation in the synthesis of Al–Cr–O coatings deposited by reactive cathodic arc evaporation

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ABSTRACT

The deposition parameters of reactive cathodic arc are correlated with processes at the surface of the composite Al–Cr targets and the nucleation and phase formation of the synthesized Al–Cr–O layers. The oxygen pressure and the pulsed operation of the arc current influence the formation of intermetallic phases and solid solutions at the target surface. The nucleation of the ternary oxide coatings at the substrate site appears to be, to some extent, controllable by the intermetallics or solid solutions formed at the target surface. A specific nucleation process at the substrate site can therefore be induced by the free choice of target composition in combination with the oxygen pressure and a pulsed arc operation. It also allows the control over the oxide island growth at the target surface which occurs occasionally at higher oxygen pressure. This hypothesis is supported by the X-ray diffraction analysis of the layers as well as of the target surface, and the layer analysis by cross-sectional scanning electron microscopy and Rutherford backscattering spectroscopy.

## 1. Introduction

There have been efforts for many years to establish cathodic arc evaporation for oxide deposition. Issues associated with process stability and droplet formation prevented the utilization of this technology on a large scale in production and initiated the development of the filtered arc evaporation which produces oxide coatings for optical and other dedicated applications. Oxide coatings obtained by this technology were investigated extensively by a number of groups and are reviewed by Tay and co-workers [1]. Although cathodic arc evaporation is well understood and the dominant technology in the PVD tool coating for conductive layer materials, only little attention was paid to the deposition of oxide coatings utilizing non-filtered arc evaporation. This was due to the undesirable droplet formation during the evaporation process and due to the difficulties to stabilize the arc evaporation in oxygen atmosphere. The issue of process stability in batch-type deposition systems for wear resistant coatings has only recently been solved by the development of a production technology (P3e™) [2]. It allows the arc operation in pure oxygen gas with a variation of the oxygen pressure up to 10 Pa. The direct exposure of the substrates to the targets in this non-filtered arc evaporation results in similar high deposition rates as obtained in conventional arc evaporation of the metal nitrides. The problem of droplet formation, however, still exists.

Oxide coatings synthesized by reactive non-filtered cathodic arc evaporation have been already investigated for different applications. CuO was produced for radiation cooling layers [3,4], yttria-stabilized zirconia for thermal barrier coatings [5], Cr doped $TiO_2$ for photocatalysis [6] and Al–Cr–O films for hydrogen diffusion barriers [7]. Wear resistant $Cr_2O_3$/CrN duplex layers were examined for aluminum die casting [8] and multi layers of Zr–O/Al–O were synthesized for cutting tool applications [9]. Al–Cr–O coatings are of distinctive interest for wear protective coatings and were synthesized by molecular beam epitaxy [10], sputtering [11–13] and arc evaporation [2,14] because they can be synthesized as Al–Cr–O solid solution in corundum-type structure. In arc evaporation, their synthesis is based on the utilization of composite targets. The targets are produced from elemental powders which are densified at high pressure and temperature or produced by similar methods. These methods of production allow a nearly free choice of the target composition and, therefore, the synthesis of specific ternary oxide coatings.

It has been reported that during arc evaporation in nitrogen a compound layer is formed at the target surface [15–21]. Recently, this compound layer has been investigated in more detail for Ti–Al powder metallurgical targets utilized for the deposition of $Ti_{0.5}Al_{0.5}$ N coatings [22] and for $Ti_{1-x}Si_x$ ($x = 0, 0.1, 0.2$) alloyed cathodes for the synthesis of Ti–Si–N coatings [23,24]. It was found that, in addition to a nitridation of the surface layer, the phase composition of the

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uppermost target surface changed and a formation of intermetallic phases occurred to a depth of a few micrometers.

In our work, a first approach has been made to correlate the surface of powder metallurgical composite Al–Cr targets with the nucleation and phase formation of Al–Cr–O layers at the substrate surface if the arc is operated in pure oxygen.

## 2. Experimental

The experiments were performed in an INNOVA batch-type production system of OC Oerlikon Balzers AG which is routinely used to coat cutting tools. The operation of the targets during oxide deposition usually takes place in a pure oxygen atmosphere. In the experiments, the oxygen flow was controlled by a flow controller. The arc sources were operated with DC as well as with pulsed arc current. For the pulsed operation the pulse parameters (pulse width 0.5 ms, pulse height 420 A, frequency 666 Hz) were chosen so that the time average of the pulsed arc current was 200 A and equal to DC operation. The substrates were mounted on substrate holders with two-fold rotation and in line-of-sight to the arc source and target surface. New targets were utilized in each process to exclude the influence of target surface cleaning. Powder metallurgical produced Al–Cr targets (PLANSEE Composite Materials GmbH) with a composition of 70 at.% Al and 30 at.% Cr and a density 3.746 g/cm$^3$ (99.5% of the theoretical density) were utilized for the experiments. The mean grain size of the powders was <80 µm. The substrates, pieces of (100) silicon wafers and polished cemented carbide inserts (WIDIA SPGN 120308, 94 wt.% WC/6 wt.% Co), were wet-chemically cleaned before deposition. After evacuation of the process chamber below $10^{-3}$ Pa, the substrates were heated to deposition temperature and an argon ion etch was performed to ensure a good layer adhesion to the substrate. For the deposition of the samples in the experiments, only one arc source with 150 mm diameter was utilized and the samples were positioned at the height of the source. For all depositions, a substrate temperature of 550 °C and a substrate bias of −60 V were selected. The symmetric bipolar bias voltage had a frequency of 25 kHz with a negative pulse length of 36 µs and 4 µs positive pulse length. The deposition parameters are summarized in Table 1. In all experiments, the inner chamber wall of the deposition system and the substrate holder were covered by oxide layers from previous runs. This reduces gettering of oxygen by these surfaces. The stable total (oxygen) pressure was obtained within about 3 min as it can be estimated comparing the pressure values obtained for the deposition of sample A and B from Table 1 with the longer deposition runs. A more detailed description of the deposition process and the P3e™ approach is given elsewhere [2].

The analysis of the target surfaces was performed in a LEO 1530 scanning electron microscope (SEM). Elastically back-scattered electrons were utilized to enhance the material contrast and to visualize the existence of materials with different atomic number before and after arc operation. The thicknesses of the deposited layers were obtained from fracture cross-sections (X-SEM) of the coated cemented carbide inserts. EDX compositional analysis was performed on the integrated EDAX (Phoenix) system with a UTW-Si(Li) detector (active area of 10 mm$^2$) and an energy resolution ≤ 133 eV for the MnKα line at 100 µs.

The crystal structures at the target surface and on the coated silicon samples were studied by X-ray diffraction. The measurements were performed on a PANalytical X'Pert MRD PRO instrument using Cu Kα-radiation in the ω/2θ mode for all target samples and in the grazing incident mode (2θ scan, ω = 1°) for all layer samples. The grazing incident technique was applied in order to get more information from the coated layer. The ICDD-data base [25] was used to identify the crystallographic phases being present at the target surface and in the coatings. The grain sizes were estimated using the Scherrer Formula [26] applying a form factor of K = 0.90. The reflection at 25.3° 2Theta [corundum (012)] using its Full Width at Half Maximum (FWHM) has been chosen for the calculation. A correction has been done for the instrumental peak broadening using a reference silicon powder.

The layer composition was analyzed by Rutherford Backscattering Spectrometry (RBS) [27] at the 6 MeV tandem accelerator of the Federal Institute of Technology in Zurich. The measurements were performed using a 2 MeV, $^4$He beam and a silicon surface barrier detector under 165°. The collected data were evaluated using the RUMP program [28].

## 3. Observation of oxide island growth

The arc operation of Al–Cr composite targets in pure oxygen gas results in a modification of the target surface and, occasionally, in the formation of oxide islands at the target. Fig. 1 shows the surface of an unused Al–Cr target with the nominal composition of 70 at.% Al and 30 at.% Cr visualized by elastically back-scattered electrons in the SEM. The dark regions at the target surface stem from elemental aluminum, the light regions with the higher intensity from chromium. In Fig. 2, a target surface is shown which was obtained after a deposition process. In this specific process, two Al–Cr targets with the same composition were utilized and operated at 200 A DC with an oxygen flow of 300 sccm for a time of 75 min. A distinctive modification of the target surface is visible. The contrast between the elemental Al and Cr regions from Fig. 1 changed to regions with less contrast. It is evident that the change in the contrast in Fig. 2 could be attributed to intermixing of the elemental target constituents. An additional aspect not observed for nitrogen reactive gas in [22–24] is illustrated in Fig. 3. In this experiment, again two targets were operated at 200 A for 75 min, but with the much higher oxygen flow of 1000 sccm resulting in a total pressure of 3.0 Pa. Comparing with the unused target surface, the contrast is also changed and regions of different intensities similar to Fig. 2 are visible. In addition to this, three-dimensional island growth can be recognized. The islands are not uniformly distributed over the target surface and show different sizes with diameters up to 200 µm. An EDX mapping of the islands and the surrounding surface suggests a compound consisting mainly of aluminum and oxygen. The islands are charging in the electron beam of the SEM which indicates an insulating material. The XRD pattern (not shown here) obtained by grazing incident measurements proves the formation of α-$Al_2O_3$ in accordance with PDF No. 00-046-1212 as the main crystalline component of the islands. We never

**Table 1**
Parameters utilized for the operation of the Al–Cr composite targets and for synthesis of the samples in the processes A, B, C, D, E and F.

| Process (target/sample) | Target Al/Cr [at.%] | Arc current [A] | Oxygen flow [sccm] | Total pressure [Pa] | Operation time [min] | Layer thickness [µm] |
|---|---|---|---|---|---|---|
| A | Al/Cr (70/30) | 200 (DC) | 300 | 0.6 | 3 | 0.1 |
| B | Al/Cr (70/30) | 200 (DC) | 800 | 2.2 | 3 | 0.1 |
| C | Al/Cr (70/30) | 200 (DC) | 300 | 0.9 | 30 | 0.9 |
| D | Al/Cr (70/30) | 200 (DC) | 800 | 2.5 | 30 | 0.6 |
| E | Al/Cr (70/30) | 200 (470/50 pulsed) | 300 | 0.8 | 30 | 1.3 |
| F | Al/Cr (70/30) | 200 (470/50 pulsed) | 800 | 2.3 | 30 | 1.0 |