



Regular article

Impact of Si and B on the phase stability of cathodic arc evaporated $\text{Al}_{0.70}\text{Cr}_{0.30}$ -based oxidesC.M. Koller^{a,b,*}, V. Dalbauer^a, A. Kirnbauer^a, M. Sauer^c, S. Kolozsvári^d, J. Ramm^e, P.H. Mayrhofer^{a,b}^a Christian Doppler Laboratory for Application Oriented Coating Development at the Institute of Materials Science and Technology, TU Wien, Vienna, Austria^b Institute of Materials Science and Technology, TU Wien, Vienna, Austria^c Analytical Instrumentation Center, TU Wien, Vienna, Austria^d Plansee Composite Materials GmbH, Lechbruck am See, Germany^e Oerlikon Balzers, Oerlikon Surface Solutions AG, Balzers, Liechtenstein

ARTICLE INFO

Article history:

Received 22 March 2018

Received in revised form 12 April 2018

Accepted 12 April 2018

Available online xxxxx

Keywords:

Cathodic arc evaporation, $(\text{Al,Cr})_2\text{O}_3$

Thermal stability

Corundum structure

Oxides

ABSTRACT

$\text{Al}_{0.70}\text{Cr}_{0.30}$ -, $\text{Al}_{0.665}\text{Cr}_{0.285}\text{B}_{0.05}$ -, and $\text{Al}_{0.665}\text{Cr}_{0.285}\text{Si}_{0.05}$ -based cathodic arc evaporated oxides were investigated with respect to their structural evolution during vacuum annealing. Unalloyed $(\text{Al}_{0.69}\text{Cr}_{0.31})_2\text{O}_3$ crystallises with a mixed phase microstructure composed of corundum (α) and metastable cubic and γ -/ θ -type phases. Alloying 5 at.% of B or Si to the cathodes results in significant grain refinement of the coatings and the suppression of the α -phase in as-deposited state. In addition, the thermally-induced phase transition from metastable into single-phased α -structured coatings is effectively shifted from ~ 900 °C to 950 °C or 1150 °C, respectively.

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Al_2O_3 and Al_2O_3 -based coatings are highly interesting for protective application due to their mechanical properties and chemical integrity. However, their polymorphic nature [1,2] is a significant drawback when being exposed to elevated temperature, and therefore strong efforts are made to enhancing their thermal and mechanical properties by alloying. There are basically two strategies, which current research activities pursue: Stabilisation of the thermodynamically-stable corundum (α) phase at unfavourable growth conditions (i.e., low deposition temperatures or high Al contents), or a shift of the phase transformation into the corundum phase to temperatures beyond what can be expected during applications.

The most successful method in stabilising the α -phase even at relatively low deposition temperatures is the alloying of Al_2O_3 with Cr to form a hexagonal-structured α - $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ solid solution [3,4]. The correlation between Cr-content, attainable phase fractions and therewith associated mechanical properties has been investigated by several research groups [5–7], indicating that Cr contents of approximately 50 at.% or more are necessary for α -dominated coatings prepared by industrially-relevant deposition techniques (neglecting architectural coating concepts such as seed-layers [6,8]). However, as α - Al_2O_3 , for instance, exhibits a significant lower ion diffusion than α - Cr_2O_3 [9–14], an

Al content as high as possible is desired. Therefore, currently the highest research interest is devoted to compositions close to $(\text{Al}_{0.70}\text{Cr}_{0.30})_2\text{O}_3$ -based coatings, which typically exhibit a mixed phase composition of α and metastable cubic phase fractions [6,15,16].

The other concept of shifting relevant phase stabilities in Al_2O_3 was recently addressed by *ab initio* calculations [17,18] and experiments (sputter deposition-based techniques or filtered cathodic arc) [19,20]. Although γ - or α - $(\text{Al,Si})_2\text{O}_3$ solid solutions apparently tend to decompose into Al_2O_3 and SiO_2 from an energetically point of view, their stabilisation by means of physical vapour deposition characterised by limited kinetics is likely, and a γ -type $(\text{Al,Si})_2\text{O}_3$ structure indicates a higher stability than the corundum-type counterpart. Si and apparently B also favour a θ - $(\text{Al,X})_2\text{O}_3$ structure rather than α [21]. Experimentally, a stabilisation of both amorphous and metastable crystalline Al_2O_3 phases to temperatures of 200 °C above those obtained for unalloyed Al_2O_3 was reported for reactively sputtered [19] and filtered arc evaporated [20] alumina films.

From this point of view, the alloying of $\text{Al}_{1-x}\text{Cr}_x$ cathodes (where Cr is alloyed to promote the α -phase) with Si or B (to stabilise metastable phase) might appear counterintuitive, but a reasonable explanation can be given when bearing the inherent differences of sputter deposition and (non-filtered) cathodic arc evaporation in mind. Obtaining high quality coatings by arc evaporation of pure Al is quite difficult due to its relatively low melting point. Especially for oxygen containing processes, the cathode erosion is high and the droplet generation is often unacceptable for applications. The alloying of elements which

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form higher melting intermetallic compounds with Al is a suitable way to homogenise the arc evaporation of oxides (so to speak cathode design) and by this obtain better coating qualities. Thus, a certain amount of Cr can be considered necessary, even when studying coating compositions which ought to be predominately metastable cubic.

We here investigate the impact of 5 at.% Si or B with respect to phase formation, mechanical properties, and phase stability upon annealing in vacuum.

The coatings investigated, were prepared in an industrially-scaled unfiltered arc facility Oerlikon Balzers Innova using $\text{Al}_{0.70}\text{Cr}_{0.30}$, $\text{Al}_{0.665}\text{Cr}_{0.285}\text{B}_{0.05}$ or $\text{Al}_{0.665}\text{Cr}_{0.285}\text{Si}_{0.05}$ cathodes (powder-metallurgically produced by Plansee Composite Materials GmbH). To guarantee for stoichiometric sesquioxides, the deposition conditions were: arc current of 180 A, bipolar-pulsed substrate bias of -120 V (Oerlikon Balzers P3e™ [4] technology; one pulse period consists of a $38\ \mu\text{s}$ negative pulse, followed by a $2\ \mu\text{s}$ positive pulse and a $10\ \mu\text{s}$ pause [16,22]), deposition temperature of $550\ ^\circ\text{C}$, and $1000\ \text{sccm}\ \text{O}_2$ flow (using 4 active cathodes, i.e. $250\ \text{sccm}\ \text{O}_2$ per active source). A Tecnai F20 transmission electron microscope (TEM) was used for microstructural analyses in addition to an XPERT III PANalytical XPert Pro diffractometer (Cu- $\text{K}\alpha$ radiation in Bragg-Brentano arrangement). The powered coating material (removed from the low-alloy steel foil substrates by chemically dissolving the steel foil with diluted hydrochloric acid) and coated sapphire substrates were annealed in a Centorr LF 22-2000 vacuum furnace (heating rate of $20\ \text{K}/\text{min}$, holding time of either 1 or 6 h, and passive cooling to room temperature). Hardness measurements were carried out using a UMIS II Nanoindentation system equipped with a Berkovich indenter, applying normal loads between 10 and 25 mN (surface pre-treated by mechanical polishing; evaluation according to Oliver and Pharr [23]). X-ray photoelectron spectroscopy (XPS) was carried out on a custom-built SPECS spectrometer equipped with a monochromatized Al-K α X-ray source (uFocus 350) and a hemispherical analyser (WAL 150). The spectra were evaluated using CASA XPS software employing Shirley backgrounds [24], Scofield sensitivity parameters [25] and Gaussian-Lorentzian [GL(30)] peak shapes for deconvolution of spectra. All measurements were corrected in binding energy to show the main C component (carbon) at $284.8\ \text{eV}$.

The effect of B and Si on the synthesis process is remarkable, as the formation of unfavourable, non-conductive oxide islands at the cathode surfaces are in both cases prevented. Although the reasons for the beneficial effect of Si [26] have been ascribed to the formation of intermetallic Cr-Si phases (shifting the average Al-composition) as well as metastable Si-O oxides [27], no such information is available for $\text{Al}_{0.665}\text{Cr}_{0.285}\text{B}_{0.05}$ cathodes and an throughout explanation would require further studies. The positive effect of Si on the oxide island formation appears to be related to the cathode surface roughness, where a larger number of surface asperities also lead to an increased number of oxide islands. Growth rates of coatings prepared from $\text{Al}_{0.665}\text{Cr}_{0.285}\text{B}_{0.05}$ and $\text{Al}_{0.665}\text{Cr}_{0.285}\text{Si}_{0.05}$ cathodes are ~ 11.0 and $15.7\ \text{nm}/\text{min}$ per source, respectively, and thus below the $\text{Al}_{0.70}\text{Cr}_{0.30}$ reference ($\sim 17\ \text{nm}/\text{min}$).

Cross-section TEM bright field (BF) images of the $\text{Al}_{0.665}\text{Cr}_{0.285}\text{B}_{0.05}$ -based coating on (100) Si substrates shown in Fig. 1a (aligned in growth direction) reveal a relatively compact and fine-grained microstructure containing large fractions of dark-contrasted regions (indicated by solid white lines) and a minor fraction of underdense, bright-appearing column boundaries (indicated by dashed white lines). The parallel streak pattern suggests for the formation of stacking faults and/or twins and was not observed in such numbers within $\text{Al}_{0.70}\text{Cr}_{0.30}$ -based coatings which were subject of previous studies [22,28,29]. Cubic lattice parameters calculated from d_{hkl} values agree with literature data [30], although, d_{hkl} of higher-indexed lattice planes indicate a minor deviation from an ideal cubic unit cell.

The microstructure of the Si-containing film is dominated by faceted grains with underdense grain boundaries, see Fig. 1b. The number of flat-shaped macroparticles embedded in the $\text{Al}_{0.665}\text{Cr}_{0.285}\text{Si}_{0.05}$ -based coating, revealed by Z-contrast STEM imaging (small inset

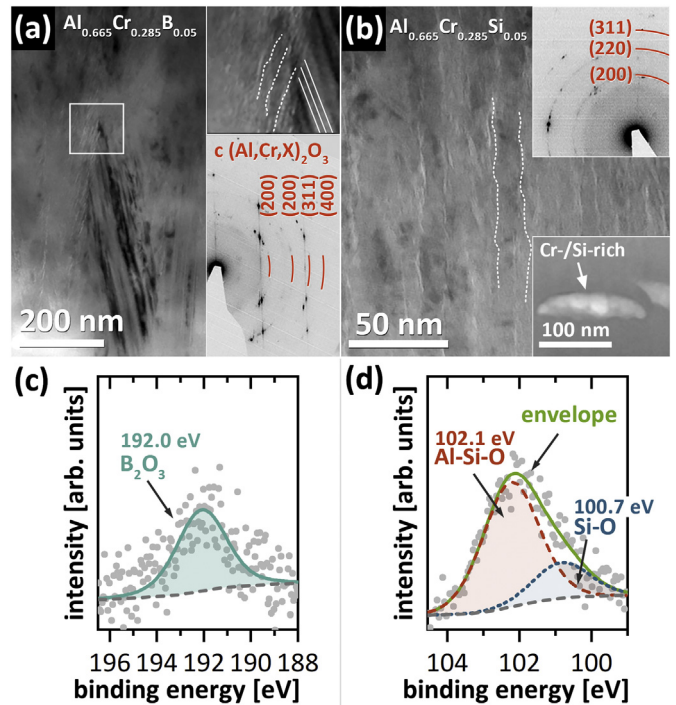


Fig. 1. (a) Cross-section TEM BF image of the $\text{Al}_{0.665}\text{Cr}_{0.285}\text{B}_{0.05}$ -based coating on (100) Si substrates in as-deposited state. Crystalline areas are detectable next to underdense grains (small inset). (b) TEM BF image of the $\text{Al}_{0.665}\text{Cr}_{0.285}\text{Si}_{0.05}$ -based coating, showing a bright seam at column boundaries. The corresponding SAED pattern in (a and b) indicates metastable cubic $(\text{Al,Cr,X})_2\text{O}_3$. (c) and (d) represent XPS data of the $\text{Al}_{0.665}\text{Cr}_{0.285}\text{B}_{0.05}$ - and $\text{Al}_{0.665}\text{Cr}_{0.285}\text{Si}_{0.05}$ -based coating, respectively, which indicate B_2O_3 or Si-O and Al-Si-O bonds.

Fig. 1b), exceeds those in chemically-similar coatings [7,31]. These particles are Cr- and Si-rich, whereas the few spherical droplets contain mostly Al and Cr. The presence of higher-melting Cr- and Si-rich intermetallic phases (with respect to the major cathode constituent Al) formed at the cathode surface (which are eventually incorporated into the growing film) agrees with the binary Cr-Si phase diagram [32]. The SAED pattern shown in the small inset in Fig. 1b also indicates polycrystalline metastable cubic $(\text{Al,Cr})_2\text{O}_3$, yet the crystallite size is obviously decreased as the diffraction rings are almost continuous with no larger diffraction spots. Hexagonal phase fractions cannot be identified.

For comparison with the $\text{Al}_{0.70}\text{Cr}_{0.30}$ -based coating we refer the reader to our previous publication in which identical deposition parameters were used [22]. Generally, their coating morphology is more compact and both metastable cubic and hexagonal phases are present. Voided and underdense grain boundary regions, such as those visible in Fig. 1b for Al-Cr-Si-O, are only present in those $\text{Al}_{0.70}\text{Cr}_{0.30}$ -based coatings when droplets interrupted the film growth.

XPS measurements of the $\text{Al}_{0.665}\text{Cr}_{0.285}\text{B}_{0.05}$ -based coating (Fig. 1c) reveal B-O bonds matching B_2O_3 . Although B-Al-O or B-Cr-O bonds, which would indicate a B incorporation to $(\text{Al,Cr})_2\text{O}_3$, are not clearly detectable, reports suggest for a strong interaction between B and Al in $\gamma\text{-Al}_2\text{O}_3$ catalysts [33]. However, the signal suggests only for a small amount of incorporated B.

In agreement with Ref. [20], Si-O and Si-Al-O bonds can be found within the $\text{Al}_{0.665}\text{Cr}_{0.285}\text{Si}_{0.05}$ -based coating. However, compared to Si-alloyed Al_2O_3 coatings prepared by filtered cathodic arc, the increased Si-Al-O peak intensity is higher than that of Si-O, which in turn strongly suggests that the fraction of SiO_2 formed is lower. We can thus expect a certain amount of Si to be incorporated into the alumina structure forming $(\text{Al,Cr,Si})_2\text{O}_3$, whereas a smaller fraction of SiO_2 is formed and presumably accumulated at grain boundaries as also suggested by TEM.

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