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Structural and mechanical properties of corundum and cubic $(Al_xCr_{1-x})_{2+y}O_{3-y}$ coatings grown by reactive cathodic arc evaporation in as-deposited and annealed states

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Abstract

Coatings of $(Al_xCr_{1-x})_{2+y}O_{3-y}$ with $0.51 \leqslant x \leqslant 0.84$ and $0.1 \leqslant y \leqslant 0.5$ were deposited on hard cemented carbide substrates in an industrial cathodic arc evaporation system from powder-metallurgy-prepared Cr/Al targets in pure O_2 and $O_2 + N_2$ atmospheres. The substrate temperature and bias in all the deposition runs were 575 °C and −120 V, respectively. The composition of the coatings measured by energy dispersive X-ray spectroscopy and elastic recoil detection analysis differed from that of the facing targets by up to 11%. Microstructure analyses performed by symmetrical X-ray diffraction and transmission electron microscopy showed that corundum, cubic or mixed-phase coatings formed, depending on the Cr/Al ratio of the coatings and O_2 flow per active target during deposition. The corundum phase was promoted by high Cr content and high O_2 flow per target, while the cubic phase was observed mostly for high Al content and low O_2 flow per active target. *In-situ* annealing of the cubic coatings resulted in phase transformation from cubic to corundum, completed in the temperature range of 900–1100 °C, while corundum coatings retained their structure in the same range of annealing temperatures. Nanoindentation hardness of the coatings with Cr/Al ratio <0.4 was 26–28 GPa, regardless of the structure. Increasing the Cr content of the coatings resulted in increased hardness of 28–30 GPa for corundum coatings. Wear resistance testing in a turning operation showed that coatings of Al–Cr–O have improved resistance to crater wear at the cost of flank wear compared with TiAlN coatings.

Keywords: Physical vapor deposition; Ternary alloys; Alumina; Solid solution; Al–Cr–O alloys

1. Introduction

Alumina (Al_2O_3) is a widely used material in industry. High hardness, chemical inertness, and wear and corrosion resistance motivate the use of Al_2O_3 coatings in thermal and diffusion barrier [1,2], semiconductor [3] and tooling [4,5] applications. Al_2O_3 exists in several different polymorphs, of which only α-Al_2O_3 (also known as corundum) is thermodynamically stable [6,7] in the conditions applicable to the above. Synthesis of α-Al_2O_3 is typically performed by chemical vapor deposition (CVD) at temperatures of 1000 °C and above [8]. Conventional CVD is, however, not a preferred method for a variety of substrate types, which cannot tolerate such high process temperature. Several attempts have thus been performed to optimize the CVD process to decrease the temperature in deposition of α-Al_2O_3 coatings; e.g., using bombardment of the growing coating by energetic particles in plasma-assisted CVD to deposit α-Al_2O_3 at temperatures of 500–600 °C [9–11].

Interest has also developed in depositing α-Al_2O_3 coatings at lower temperatures by physical vapor deposition (PVD) methods, magnetron sputtering [11–16] and cathodic arc evaporation [17–19] at substrate temperatures of ~500–700 °C. In this regard, chromia (Cr_2O_3) has been

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used as a facilitator for the lower-temperature deposition of corundum phase. This is because Cr_2O_3 is isostructural with α-Al_2O_3: both have corundum structure (crystallographic space group $R\bar{3}c$). The two oxides are close in their lattice parameters by 4% and 4.7% for their a and c axes, respectively [20,21]. Also, Cr_2O_3 coatings can be deposited by PVD methods at much lower substrate temperatures compared with α-Al_2O_3. Cr_2O_3 can thus be used as a template for nucleation of α-Al_2O_3 or in an $(Al_xCr_{1-x})_2O_3$ solid solution synthesized by deposition from elemental/alloyed Al and Cr targets. Employing the former approach has enabled the deposition temperature of α-Al_2O_3 to be decreased to 280–450 °C [20–24]. In the latter approach, formation of $(Al_xCr_{1-x})_2O_3$ solid solutions was performed by Ramm et al. [25,26], Vieira et al. [27] and Pohler et al. [28] using cathodic arc evaporation, and Diechle et al. [29], and Pedersen et al. [30] using magnetron sputtering. These works reported the formation of the corundum phase at substrate temperatures of 500–600 °C. A cubic-$(Al_xCr_{1-x})_2O_3$ solid solution deposited by radiofrequency magnetron sputtering at a substrate temperature of 400 °C is also reported (see Refs. [31,32]), and was recently confirmed by Najafi et al. [33] and Edlmayr et al. [34].

The experimental parameters affecting the formation of cubic structure in Al–Cr–O solid solution coatings are still unknown. Therefore, the purpose of this work is to investigate the parameters that favor the deposition of cubic-structure coatings in comparison with the known corundum ones, using an industrial scale cathodic arc evaporation system equipped with Al/Cr alloyed targets in O_2 and $O_2 + N_2$ atmospheres. The mechanical properties of the coatings, including hardness and cutting performance, are then discussed with respect to the composition and structure.

2. Experimental details

Coatings of $(Al_xCr_{1-x})_{2+y}O_{3-y}$ with $0.51 \leqslant x \leqslant 0.84$ and $0.1 \leqslant y \leqslant 0.5$ were deposited on 12 × 12 × 5 mm substrates (Sandvik SNMA-120408-KR, WC–10 wt.% Co) and turning inserts (Sandvik CNMG-120408-MM, WC–10 wt.% Co) using an industrial-scale Oerlikon Balzers Innova cathodic arc evaporation system. The platform can be equipped with up to six 16-cm-diameter circular targets, three in two different levels. They were operated in pairs (one up and one down) to cover the full height of the substrate table. Two process parameters are in focus in this study: the Cr/Al ratio and the oxygen flow per active target. Choosing a combinatorial approach, the Cr/Al targets had different compositions in up and down positions. The following combinations were used: Cr/Al:30/70 (up) and Cr/Al:15/85 (down) for runs A, B, D and E; Cr/Al:50/50 (up) and Cr/Al:30/70 (down) for run C. To vary the oxygen flow per active targets significantly, one (runs C, D and E) or two (runs A and B) Cr/Al target pairs were used. The remaining pairs were equipped with Ti/Al:50/50 targets. The target disposition and compositions employed

Table 1
Target disposition and composition during the functional oxide step.

Run	Targets in use (see Fig. 1)	Cr/Al ratio (at.%) in target (see Fig. 1)			
		1	2	3	4
A	1, 2, 3, 4	30/70	15/85	30/70	15/85
B	1, 2, 3, 4	30/70	15/85	30/70	15/85
C	1, 2	50/50	30/70	–	–
D	1, 2	30/70	15/85	–	–
E	1, 2	30/70	15/85	–	–

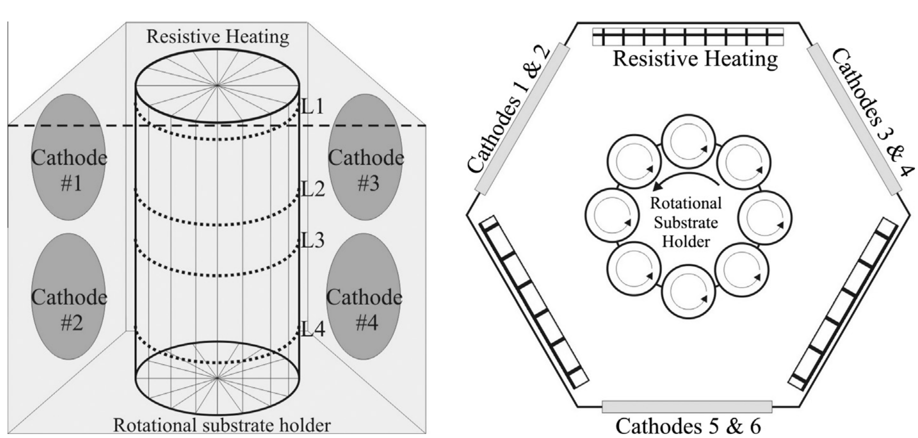

Fig. 1. Schematic drawing of the side (left) and top (right) views of the deposition chamber. L1–L4 represent the levels (~10–15 cm separated) on which the substrates are placed during the arc evaporation process. The top-view drawing shows the threefold rotation of the substrate holder.