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Pulse enhanced electron emission (P3e™) arc evaporation and the synthesis of wear resistant Al–Cr–O coatings in corundum structure

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Abstract

Pulse enhanced electron emission (P3e™) is a new approach in PVD technology for the deposition of metal oxides. The process is dedicated to the formation of alumina-based and other metallic oxide layers and comprises high current pulse technique for the arc sources. The method allows a deposition of hard alumina-based coatings at substrate temperatures below 600 °C.

Different oxide layers and layer combinations were prepared with this new technique illustrating the enormous potential for the design of wear resistant coatings. The layers were characterized with respect to hardness, stress, composition, crystal structure, and thermal stability. Solid solutions of $(Al_{1-x}Cr_x)_2O_3$ could be synthesized for a composition range of $0.3 \leq x < 1$. The growth of the solid solutions has also been demonstrated at TiCN and TiAlN interfaces.

Keywords: Cathodic arc; Metal oxide; Solid solution; Corundum; Thermal stability

1. Introduction

Wear resistant coatings for cutting tools are produced either by chemical vapor deposition (CVD) or physical vapor deposition (PVD). 40 years ago, CVD production started with TiC and TiN coatings and changed since 30 years the focus successively to layer combinations of Ti–C–N and α-alumina (corundum). These coatings show outstanding properties for high temperature machining due to the hardness and chemical inertness at elevated temperatures of α-alumina [1], the only thermodynamical stable phase in the alumina material system.

The main disadvantage of the CVD approach is the high deposition temperature necessary to synthesize α-alumina. It restricts the free selection of tool materials and is the reason for tensile stress due to thermal mismatch between layer and tool material which may limit its utilization for interrupted cutting or milling applications. Therefore, the low temperature deposition of α-alumina has been the background for many developments in the past.

PVD has several advantages over CVD technology. The deposition temperature can be reduced to 500 °C and below. This reduces undesired diffusion processes or reactions between substrate and coating and makes it compatible with high speed steel substrates. PVD nitride coatings like TiN and TiAlN show usually compressive stress which is known to be an advantage for interrupted cutting. Therefore it is comprehensible that since decades there are efforts in PVD to achieve α-alumina at reduced temperatures and develop a production technique which can compete for this material with the established CVD technology.

Reactive sputtering has been investigated in detail to control the alumina phases at low temperatures. Zywitzki et al. [2] utilized reactive dual magnetron sputtering and showed that the deposition temperature for α-alumina could be lowered to 750 °C. Schneider et al. [3,4] used reactive ionized magnetron sputtering to deposit orthorhombic κ-alumina and monoclinic θ-alumina at substrate temperatures as low as 430 °C and 472 °C, respectively. In this approach, an additional ionization for Ar as well as for the sputtered Al and the O reactive gas was utilized in combination with pulsed DC substrate bias. The deposition was performed at stainless steel coated silicon wafers. Astrand et al. [5] demonstrated in a production system

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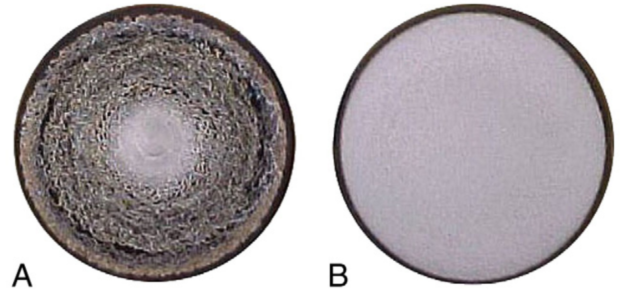

Fig. 1. Comparison of the surface erosion profiles of Al/Cr alloy targets for the operation under identical process conditions for a standard source configuration (A) in comparison with a source under P3e™ conditions (B).

the growth of γ-alumina at deposition temperatures of 700 °C at TiN and TiAlN interfaces utilizing reactive bipolar pulsed dual magnetron sputtering.

Filtered arc deposition of alumina was another approach investigated to control the phases of alumina. Yamada et al. [6] showed that α-alumina can be grown at substrate temperatures as low as 460 °C on vanadium substrates and Brill et al. [7] verified the formation of α-alumina on Inconel substrates at substrate temperatures of about 600 °C utilizing substrate bias. The effect of the ion energy on the structure and composition in filtered arc deposition of alumina was carefully investigated by Rosén et al. [8] for depositions on stainless steel substrates. The phase formation to α-alumina started at substrate temperatures of about 600 °C.

Besides PVD, also CVD technology moves towards lower substrate temperatures. Ruppi and Larsson [9] reported the formation of γ-alumina at 800 °C. Kyrylov et al. [10] studied the effect of ion irradiation during the deposition of alumina by plasma assisted CVD and it has been shown that α-alumina could be deposited at 580 °C in a bipolar pulsed plasma with a cathode power density of 6.6 W/cm^2.

In addition to the search for the most suitable technology, the utilization of templates for the formation of α-alumina was another field of investigation. These approaches were mainly focused upon escolaite chromia which is isostructural to corundum and can be synthesized below 500 °C. Ashenford et al. [11] showed in basic experiments that homoepitaxial growth of α-alumina on sapphire substrates could be achieved by molecular beam epitaxy (MBE) in combination with a reactive oxygen source for substrate temperatures as low as 430 °C. Towards lower temperatures, the layer-by-layer growth was more and more replaced by the three-dimensional growth. The direct deposition of α-alumina on steel was not successful. However, it was demonstrated that escolaite chromia could be grown on steel in the temperature range between 300 °C and 500 °C. Utilizing chromia as template, alloy growth of Al_2O_3/Cr_2O_3 in corundum structure could be achieved up to an alumina concentration of 35%. During the deposition of these alloys with higher alumina concentrations and for pure alumina the growth mode reverts back from corundum structure to amorphous within a few nanometers.

The template approach was also investigated for radio frequency (RF) sputtering of oxide targets. Jin et al. [12] succeeded to grow α-alumina on escolaite chromia templates at temperatures as low as 400 °C. Andersson et al. [13] were able to decrease the deposition temperature for this non-reactive RF sputtering approach to 280 °C in UHV environment. It was shown that the utilization of high energetic bombardment of the substrate surface initiates the phase transition to α-alumina.

For reactive sputtering the template approach was explored by Kohara et al. [14]. They showed that this technique can be used in production batch systems to deposit α-alumina on CrN pre-coated cemented carbide substrates at 750 °C under the condition that the CrN layer was plasma oxidized before alumina deposition. Finally, Andersson et al. [15] demonstrated the growth of α-alumina utilizing high energetic bombardment during deposition at temperatures of 500 °C.

Another interesting approach to synthesize and stabilize the corundum structure of alumina at lower temperatures could be based on the utilization of additives discussed by Wallin et al. [16].

In summary, there have been many efforts to produce α-alumina coatings and other alumina phases at low temperatures and tremendous progress has been achieved during the last decade in this field. Although it was proven that α-alumina could be synthesized at low temperatures, until now a production technique for this material at deposition temperatures below 600 °C does still not exist. The present work intends to contribute to this development and discusses the possibility to deposit metal oxides below 600 °C utilizing a new approach of cathodic arc evaporation with a wide process window. More specifically, it will be shown

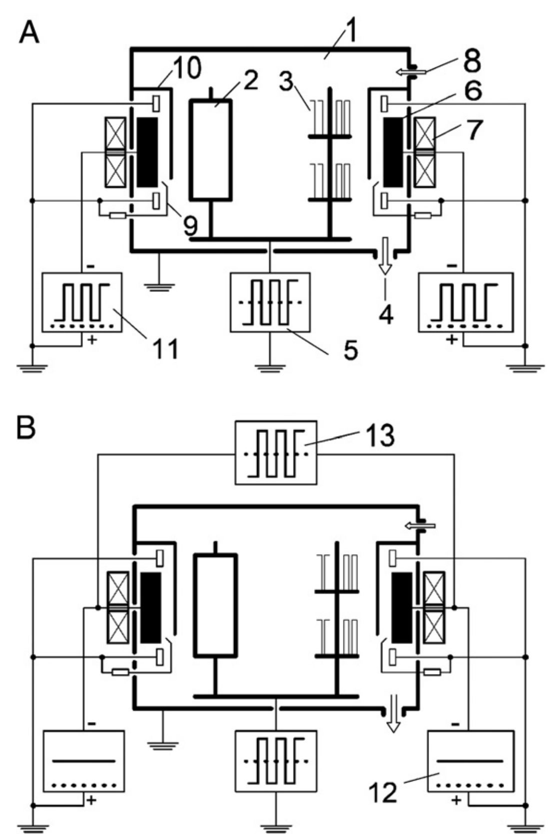

Fig. 2. (A) Schematic for the configuration of P3e™ for which each arc source is operated with a pulsed power supply. (B) Schematic for the configuration of P3e™ for which one bipolar power supply is operated between two DC arc sources.