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## MODEL RESEARCH ON DEPOSITION OF PURE ALUMINIUM OXIDE LAYERS BY MOCVD METHOD

### MODELOWE BADANIA NA SYNTEZĄ CZYSTYCH WARSTW TLENKU GLINU METODĄ CVD

The purpose of this research is to develop an optimal method for synthesizing of nanocrystalline  $\text{Al}_2\text{O}_3$  monolayers at high growth rates on cemented carbides coated with an intermediate layer of pre- $\text{Al}_2\text{O}_3\text{-C}$  (composite layers  $\text{Al}_2\text{O}_3\text{-C}/\text{Al}_2\text{O}_3$ ). The use of quartz glass substrate allows for obtaining information about the quality of the layers such the thickness and density, because of its high transparency. The  $\text{Al}_2\text{O}_3$  layers that do not containing carbon were synthesized on quartz glass by MOCVD using aluminum acetylacetonate and air as the reactants at temperatures of 700-1000°C. Argon was also a carrier gas. The resulting layers were transparent, as homogeneous nucleation did not occur during the synthesis process. The layers synthesized at lower temperatures were subjected to a crystallization process at temperatures above 900°C. The crystallization process was studied as a function of time and temperature. The obtained layers were characterized by their nanocrystalline microstructure.

*Keywords:* MOCVD method, composite layers  $\text{Al}_2\text{O}_3\text{-C}/\text{Al}_2\text{O}_3$ , cutting tools

Celem badań jest opracowanie metody otrzymywania nanokrystalicznych monowarstw  $\text{Al}_2\text{O}_3$  z dużą szybkością wzrostu na węglkach spiekanych pokrywanych warstwą pośrednią  $\text{Al}_2\text{O}_3\text{-C}$  (warstwy kompozytowe  $\text{Al}_2\text{O}_3\text{-C}/\text{Al}_2\text{O}_3$ ). Użycie podłoża ze szkła kwarcowego z uwagi na jego przezroczystość pozwoli uzyskać informacje dotyczące jakości otrzymanych warstw, np.: ich grubości, gęstości.

Warstwy  $\text{Al}_2\text{O}_3$  nie zawierające węgla syntezowano na szkłe kwarcowym metodą MOCVD z użyciem acetyloacetonianu glinu oraz powietrza jako reagentów w temperaturach 700-1000°C. Gazem nośnym był argon, a także powietrze. Otrzymane warstwy były przezroczyste, co świadczyło o tym, że w trakcie wzrostu warstw nie występował proces nukleacji homogenicznej. Warstwy syntezowane w niższych temperaturach były poddawane krystalizacji w temperaturach powyżej 900°C. Badano przebieg procesu krystalizacji w funkcji czasu i temperatury. Otrzymane warstwy charakteryzowały się nanokrystaliczną budową.

### 1. Introduction

Cutting tools made of cemented carbides initially coated with an intermediate layer of TiN, TiC or Ti (C, N), and then a pure aluminum oxide layer as monolayers, or multilayers consisting of a number of thin layers with a total thickness of such a monolayer are currently the best cutting tools used to manufacture by rapid machining (as high as 600m/min) metal parts (of precision chemical composition) of equipment such as robots.  $\text{Al}_2\text{O}_3$  layers on an industrial scale are obtained by CVD using  $\text{AlCl}_3$  as the main reagent at a temperature of about 1000-1050°C. The layers synthesized by this method are polycrystalline, and have lower or higher amounts of metastable  $\kappa\text{-Al}_2\text{O}_3$  phase with fine-grain and stable  $\alpha\text{-Al}_2\text{O}_3$  phase with larger grains. The thicker the layers the larger the grains of these phases are. The larger grains in the layer, the greater its surface roughness. In the case of multilayers the  $\kappa$  – phase is formed as a very thin layer at the beginning of the synthesis of the individual layers. The roughness of the monolayer is greater than that of the multilayer. The more layers in multilayer, the smoother it becomes. During high-speed cutting,

the coated edge of the tool with such layers heats up to 800°C and above. The heating is more intense in the case of rough layers. At these temperatures, with the participation of stresses caused by machining, there is a detrimental phase transformation of  $\kappa\text{-Al}_2\text{O}_3$  phase to  $\alpha\text{-Al}_2\text{O}_3$ . As a result of this change at the interface micro-fractures are formed between these phases. This is a result of a smaller molar volume (about 8%) of the  $\alpha\text{-Al}_2\text{O}_3$  phase with respect to the molar volume of the  $\kappa\text{-Al}_2\text{O}_3$  phase [1]. Micro-fracturing of the monolayer is greater than that of the multilayer and are statistically distributed in the entire volume, while micro-fracturing in the multilayer focuses mainly on the contact layer comprising it. This leads to peeling (delamination) of the multilayer during tool operation and consequently to rapid wear of the edge. The thinner the layers in the multilayer are, the more intense the process of their peeling is. The cutting tools are coated with multilayers in order to obtain a very smooth metal surfaces as a result of cutting, without any additional treatment, such as grinding and polishing [2, 3].

The authors are conducting research on obtaining  $\text{Al}_2\text{O}_3$  layers by MOCVD. In the present work modeling studies on

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obtaining the composite layers  $\text{Al}_2\text{O}_3\text{-C}/\text{Al}_2\text{O}_3$  using quartz glass in the form of tubes and flat were carried out. A pure  $\text{Al}_2\text{O}_3$  layer is synthesized on an intermediate layer of  $\text{Al}_2\text{O}_3\text{-C}$  applied directly on quartz glass. This layer is obtained by MOCVD from  $\text{Al}(\text{acac})_3$  with the use of argon as a carrier gas. The outer layer was synthesized with the participation of air. Results of these studies on the synthesis of the intermediate layer are shown in [4] and the results of the studies on composite layers are presented in this work.

## 2. Materials and methods

A diagram of the apparatus used for the synthesis of the composite layers is shown in [5]. The synthesis conditions of the composite layers are presented in TABLE 1.

TABLE 1  
Conditions for the synthesis of composite layers  $\text{Al}_2\text{O}_3\text{-C}/\text{Al}_2\text{O}_3$  by MOCVD method

Parameter	Synthesis conditions
Summary gas pressure in the CVD reactor [Pa]	$3,7\text{-}1013,3 \times 10^2$
Flow rate [NI/h]	
Ar	0-30
Air	0-100
$\text{NH}_3$	0-3
The temperature of the carrier gases [°C]	140-200
The temperature of evaporator [°C]	140-170
The temperature of substrate [°C]	700-1050
Synthesis time of $\text{Al}_2\text{O}_3\text{-C}$ layer [min.]	2
Synthesis time of $\text{Al}_2\text{O}_3$ layer [min.]	20
Weight of $\text{Al}(\text{O}_2\text{C}_5\text{H}_7)_3$ [g]	0,2
The temperature of annealing of layers synthesized at 800°C [°C]	900-1050
Annealing time [min.]	10-30
The value of the developed criterion $\text{Gr}_x/\text{Re}_x^2$	<0,1

Initially, the intermediate layer of  $\text{Al}_2\text{O}_3\text{-C}$  was synthesized with the participation of argon and then air was introduced instead of argon. In this manner, the outer layer does not contain carbon. Samples obtained at 800°C were annealed further. For selected samples tests were performed using scanning electron microscopy (SEM NANO NOVA 200 from FEI EUROPE COMPANY cooperating with the analyzer EDAX EDS company), and a X-ray diffractometer (X'Pert Pro Philips).

## 3. Results and discussion

Figure 1 shows the surface of the composite layer synthesized at a temperature of 800°C without annealing (intermediate layer synthesis time: 2 min., outer: 15 min.).

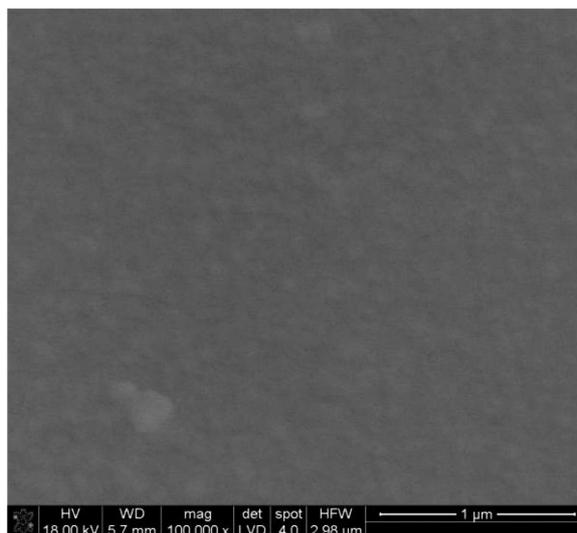


Fig. 1. Surface of composite layer  $\text{Al}_2\text{O}_3\text{-C}/\text{Al}_2\text{O}_3$  synthesized at 800°C. Without heating. Intermediate layer synthesis time: 2 min., outer: 15 min

From Fig. 1 it is clear that on the surface of the layer very numerous white spots of various sizes are visible, the largest of which are about 250 nm in size. You can expect that these are crystallites of low-temperature  $\text{Al}_2\text{O}_3$  varieties.

At the surface of the composite layer synthesized at 900°C (Fig. 2) numerous crystallites are visible (possibly low temperature modifications of  $\text{Al}_2\text{O}_3$ ). These crystallites have of larger sizes and they are more numerous than those observed in the case of the sample synthesized at 800°C. Maximum size of these crystallites is about 300 nm. The layer is very smooth and non-porous.

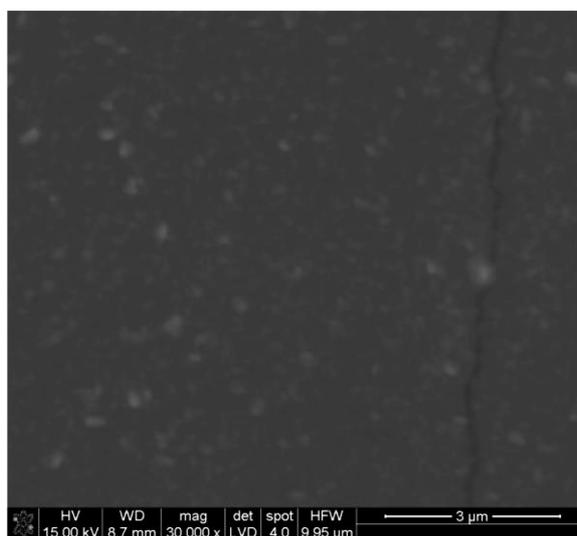


Fig. 2. The surface of the composite layer  $\text{Al}_2\text{O}_3\text{-C}/\text{Al}_2\text{O}_3$  synthesized at 900°C. Without heating. Intermediate layer synthesis time: 2 min., outer 15 min

Figure 3 shows the surface of a composite layer synthesized at 900°C and further heated at 950°C for 30 min. In the case of the sample presented in Figure 3 maximum crystallites size is about 380 nm and they are significantly numerous than those in Figure 2. Their shapes are oval.

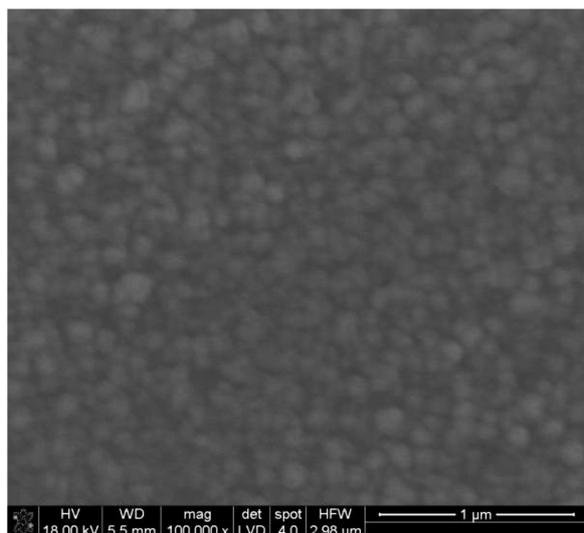


Fig. 3. Surface of composite layer  $\text{Al}_2\text{O}_3\text{-C}/\text{Al}_2\text{O}_3$  synthesized at  $900^\circ\text{C}$ . Additionally, heated at  $950^\circ\text{C}$  for 30 min. Intermediate layer synthesis time: 2 min., outer 15 min

Figure 4 shows the X-ray diffraction analysis from the surface of the layer of Figure 3. The layer contains  $\alpha\text{-Al}_2\text{O}_3$ .

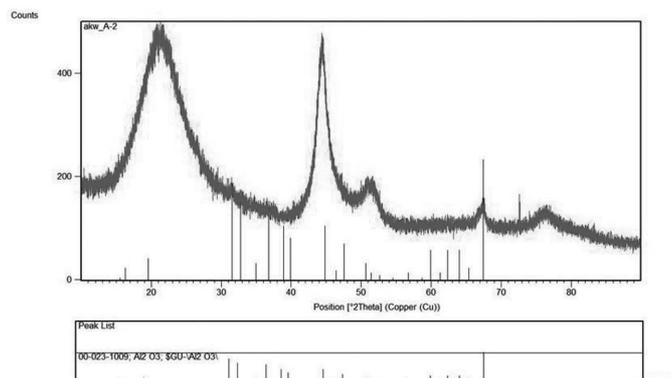


Fig. 4. XRD pattern of composite layer synthesized at a temperature of  $900^\circ\text{C}$ . Additionally, heated at  $950^\circ\text{C}$  for 30 min

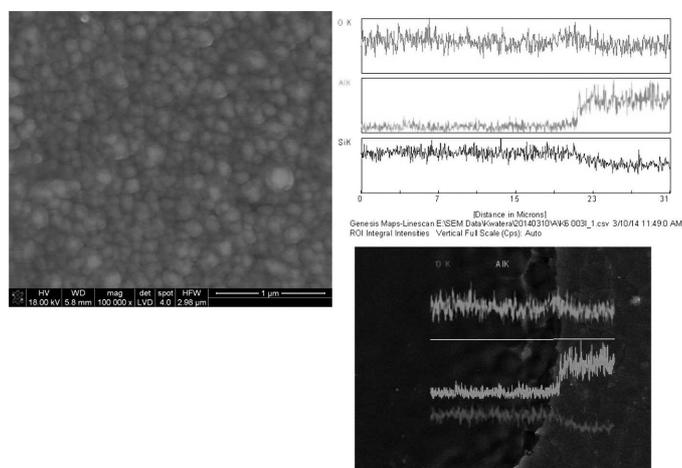


Fig. 5. Surface of composite layer  $\text{Al}_2\text{O}_3\text{-C}/\text{Al}_2\text{O}_3$  synthesized at  $800^\circ\text{C}$ , its fracture with EDAX analysis. Additionally, annealed at  $1000^\circ\text{C}$  for 30 min. Intermediate layer synthesis time: 2 min., outer: 15 min

Among them in Figure 3 quite large darker areas are visible (probably amorphous or low-temperature varieties of  $\text{Al}_2\text{O}_3$ ). The composite layer obtained at  $900^\circ\text{C}$ , and annealed at a  $950^\circ\text{C}$  is smooth, non-porous and brittle (visible crack in Figure 3), which further confirms the presence of the  $\alpha\text{-Al}_2\text{O}_3$  phase.

Figure 5 contains the surface of a composite sample synthesized at  $800^\circ\text{C}$  and further annealed for 30 min. at  $1000^\circ\text{C}$ .

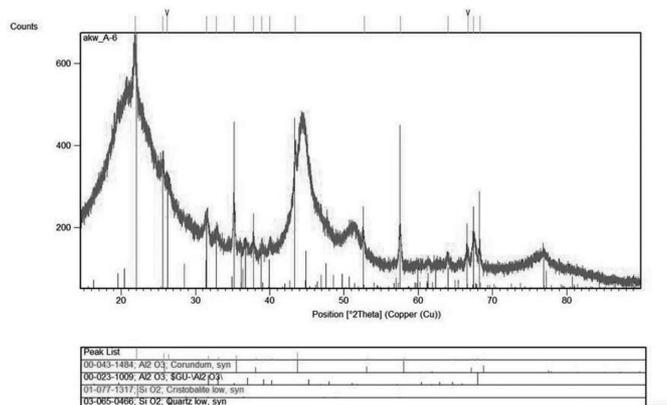


Fig. 6. XRD pattern of the sample synthesized at  $800^\circ\text{C}$  and annealed at  $1000^\circ\text{C}$  for 30 min

From Figures 5 and 6 we can conclude that the obtained layer is crystalline and contains the  $\alpha\text{-Al}_2\text{O}_3$  phase. The size of the grains at the layer surface are in the range of 70-500 nm. The layer is smooth and non-porous. The darker areas are less numerous than in the case of the sample shown in Figure 3.

Figure 7 shows the surface of the composite layer synthesized at  $1000^\circ\text{C}$ , while Figure 8 shows its diffraction pattern. The sample was not further annealed.

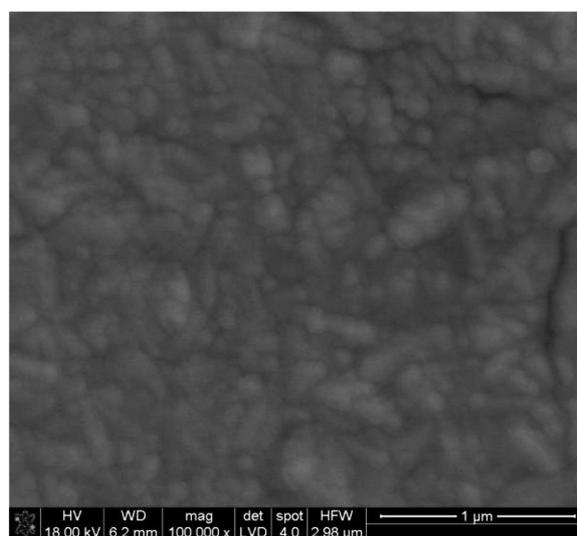


Fig. 7. Surface of composite layer  $\text{Al}_2\text{O}_3\text{-C}/\text{Al}_2\text{O}_3$  synthesized at  $1000^\circ\text{C}$ . Intermediate layer synthesis time: 2 min., outer: 15 min

Figures 7 and 8 show that the layer is crystalline and includes the  $\alpha\text{-Al}_2\text{O}_3$  phase in a larger amount than the sample shown in Fig. 5. Grains at the layer surface are also larger than in the case of a sample presented in Fig. 5. They have elongated shapes. Grains size ranges from 80-750 nm. The

layer is smooth and non-porous. In this case cracks of the layer also formed during breaking of the sample.

For comparison, Figure 9 shows the surface of the  $\text{Al}_2\text{O}_3$  layer synthesized using the traditional method of  $\text{AlCl}_3$  on the surface of cemented carbides (Sandvik Coromant).

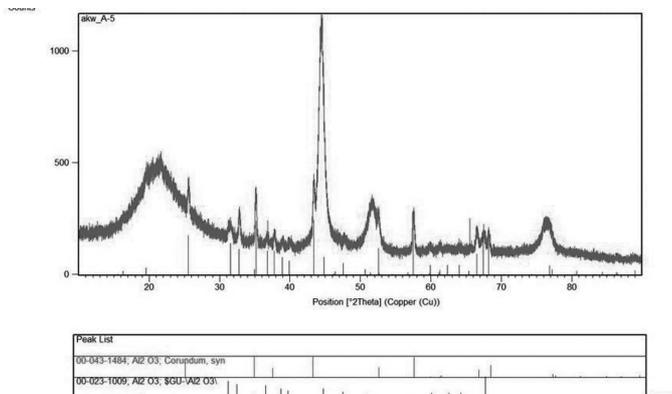


Fig. 8. XRD pattern of the sample synthesized at 1000°C (without heating)

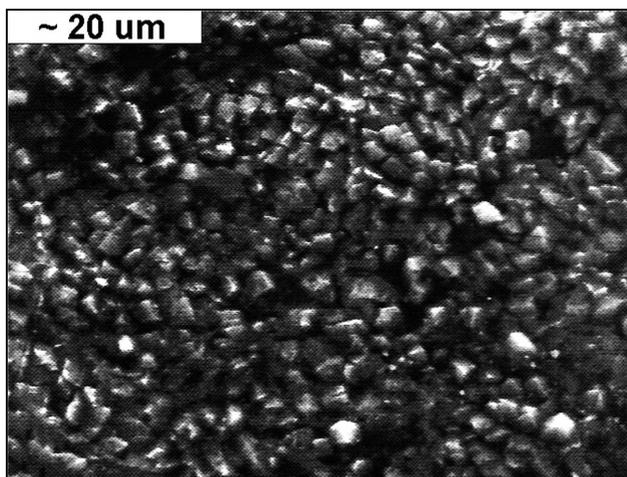


Fig. 9. Surface of  $\text{Al}_2\text{O}_3$  layer with a thickness of approximately 0.5 microns synthesized by traditional method on cemented carbides (Sandvik Coromant)

The layer thickness is around 0.5  $\mu\text{m}$ , and grains size: 2-4  $\mu\text{m}$ . From the above it results that probably the layer forms flattened grains of approx. 0.5  $\mu\text{m}$  height.

The surface of the layer shown in Fig. 9 is very rough, because the grains have sharp-edged shapes.

#### 4. Conclusions

The study showed that:

1. An  $\text{Al}_2\text{O}_3$  layer with high transparency and good adhesion to the substrate can be obtained with a high growth rate using the MOCVD method.
2. The resulting layers at temperatures of 800-900°C are amorphous or contain low temperature modifications of  $\text{Al}_2\text{O}_3$ .
3. Additionally, their annealing at temperatures above 950°C causes the formation of the  $\alpha$ - $\text{Al}_2\text{O}_3$  phase.
4. The transparent layers containing the  $\alpha$ - $\text{Al}_2\text{O}_3$  phase can also be obtained at a high speed of growth by direct synthesis at temperatures of about 1000°C.
5. The grains size of  $\alpha$ - $\text{Al}_2\text{O}_3$  phase in annealed layers may be controlled by the time and temperature of annealing.
6. Grains of sizes up to several hundred nanometers are oval and the layer surface is smooth.
7. Grains at the  $\text{Al}_2\text{O}_3$  layers synthesized using the traditional CVD method have sharp-edged shapes. The size of the grains is about 1 row larger than those synthesized by MOCVD.

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