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MODEL RESEARCH ON SYNTHESIS OF Al$_2$O$_3$-C LAYERS BY MOCVD

BADANIA MODELOWE NAD SYNTEZĄ WARSTW Al$_2$O$_3$-C METODĄ MOCVD

These are model studies whose aim is to obtain information that would allow development of new technology for synthesizing monolayers of Al$_2$O$_3$-C with adjusted microstructure on cemented carbides. The Al$_2$O$_3$-C layer will constitute an intermediate layer on which the outer layer of Al$_2$O$_3$ without carbon is synthesized. The purpose of the intermediate layer is to block the cobalt diffusion to the synthesized outer layer of Al$_2$O$_3$ and to stop the diffusion of air oxygen to the substrate during the synthesis of the outer layer. This layer should be thin, continuous, dense and uniform in thickness.

Al$_2$O$_3$-C layers were synthesized from aluminum acetylacetonate by the CVD method on quartz glass heated in an induction furnace in the temperature range 800-1000°C using argon as a carrier for the reactants. The layers were prepared also at low temperatures and were then subjected to crystallization at higher temperatures. The resulting layers prepared at temperatures above 900°C were nanocrystalline (including the α-Al$_2$O$_3$ phase). Due to the fact that crystallization can be controlled, we may have a greater influence on the structure and thus the properties of the layer compared to direct synthesis at high temperature.

Keywords: MOCVD method, cutting tools, composite layers Al$_2$O$_3$-C/Al$_2$O$_3$

Celem prowadzonych modelowych badań nad syntezą warstw Al$_2$O$_3$ metodą MOCVD jest uzyskanie informacji przydatnych do opracowania nowej technologii nanoszenia tych warstw na podłoża z węglików spiekanych. Warstwa Al$_2$O$_3$-C będzie stanowić pośrednią warstwę, na której będzie syntezowana zewnętrzna warstwa Al$_2$O$_3$ nie zawierająca węgla. Zadaniem warstwy pośredniej jest blokowanie dyfuzji kobaltu do syntezowanej zewnętrznej warstwy Al$_2$O$_3$ oraz ochrona podłoża przed utlenianiem podczas syntezy zewnętrznej warstwy. Warstwa ta powinna być cienka, ciągła, gęsta i mało zróżnicowana w grubości.

Warstwy Al$_2$O$_3$-C syntezowano z acetyloacetonianu glinu metodą CVD na szkle kwarcowym. Podłoże ogrzewano indukcyjnie w zakresie temperatur 800-1000°C. Gazem nośnym był argon. Warstwy syntezowane w niższych temperaturach były poddawane krystalizacji w wyższych temperaturach. Otrzymane warstwy w temperaturach powyżej 900°C były nanokrystaliczne (zawierały fazę α-Al$_2$O$_3$). Z uwagi na to, że proces krystalizacji warstw może być kontrolowany, można wpływać na strukturę oraz właściwości warstw.

1. Introduction

Al$_2$O$_3$ layers synthesized by CVD from the following reactants AlCl$_3$-CO$_2$-H$_2$ or the AlCl$_3$-H$_2$O (steam) – CO [1] are applied to the preparation of cemented carbide cutting tools used in machining alloys with very precise composition (about 0.0001%). These tools are used to prepare metal parts of devices, such as robots. Mounting tapes with mounted robots must work flawlessly for several years. Therefore, the robots must be reliable at this time. Reliability is achieved by very strict observance of the chemical composition of the alloys from which they are made and also their structure and microstructure. In view of the above-mentioned fact that metal elements are largely obtained in the machining process, it is important that they are not contaminated during the process by materials coming from the cutting tools which the blade during the cutting process can heat up to a temperature of 800°C or more. For this reason, it is important that the layers adhere well to the substrate, and were very pure and smooth, so that they can work longer.

These layers with a optimal thickness of about 5 microns as monolayers or multilayers of existing technology are synthesized for several hours on a previously deposited layer of TiN, TiC or Ti(C, N) [2] at a temperature above 1000°C. The purpose of the intermediate layer is to prevent the diffusion of cobalt from the substrate to the layer of synthesized Al$_2$O$_3$. The presence of cobalt in the layers at such high temperatures of the substrate promotes the synthesis of a layer with excessively long crystallites of α-Al$_2$O$_3$ phase [3, 4]. The as-synthesized Al$_2$O$_3$ layers contain the κ-Al$_2$O$_3$ and / or α-Al$_2$O$_3$ phase. K-Al$_2$O$_3$ phase is metastable and with relatively soft and small grains. In the layers constituting the multilayers they may have a size of the order of nanometers. α-Al$_2$O$_3$ phase is durable, tough and has a large grain size (order of microns) [5]. It should be noted that the κ-Al$_2$O$_3$

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phase grows directly on the intermediate layer of TiC, TiN and Ti (C, N) [4]. This phase may also grow on the α-Al_2O_3 phase [5, 7].

In contrast, the layer containing the α phase is formed on the κ-Al_2O_3 layer or intermediate layer, where it is partially oxidized such as when the surface is coated with a thin layer of titanium oxide [8].

Furthermore, it should be noted that the smaller the grains are in the material, as well as in the layers, the greater its strength (exponential dependence). Fine-grained layers are also smoother, which is important especially in the case when the tools with the layer are used for rapid cutting. High-speed cutting can increase the efficiency of the process and allows to obtain high smoothness of the machined surfaces. Afterwards additional treatment of these surfaces by sanding and polishing is required.

High speed cutting causes rapid heating of the blade at temperatures above 800°C. The layers are rougher, the process of heating the tool edge is intense. For this reason, it would seem that the layers on indexable carbide should only contain κ-Al_2O_3 phase grains as small as possible, which is possible to achieve when there is a lot of layers in multilayer. It is therefore possible that an increase in multilayer subsequent layers is not carried out continuously. When the synthesized layer reaches the desired thickness, the synthesis is terminated. The growth of a new layer growth is carried out from the beginning, that is, the pre-nucleation occurs, then the grain growth [9]. Thus, the layers are thinner, and the grain size may be smaller. Due to the fact that the κ-Al_2O_3 phase is unstable and there is the conversion of the α-Al_2O_3 phase, because during the operation of the tool at the interface micro-fractures are formed between the phases. This is a result of the κ phase molar volume being about 8% lower than the α-phase Al_2O_3. In monolayers the micro-fractures are larger and distributed randomly throughout their volume. However, in the case of multilayers they are smaller and occur mainly at the interfaces between layers, mainly because the process of this transformation begins there. As a consequence, it accelerates the wear of the edges in the multilayer due to delamination (peeling of) the individual layers [10]. It should be noted that currently there is no known method of blocking this negative transformation.

From the above, it is concluded that, although the monolayer can be more durable, they are very rough and the multilayers are smoother, but the layers constituting them are easily peeled during the cutting process, eg [13]). Presently, it appears that it is not possible to obtain greater forward progress in the modification of existing solutions.

Taking the above into account, we are conducting research to develop a new method for the preparation of the Al_2O_3 layer, which would allow to obtain smooth and thick monolayers containing stable α-Al_2O_3 phase grains with very small diameters (of the order of nanometers) with a high rate of growth using the MOCVD method with the use of organometallic reagents.

The preliminary studies on this subject [14, 15] indicate that such a layer on a cemented carbide tools should consist of two layers: an intermediate layer of Al_2O_3-C with small thickness synthesized by using ammonia or argon carrier gas, and a thick outer layer of Al_2O_3 synthesized in the presence of air. The outer layer (without carbon) was synthesized using air as a reagent. After annealing, the obtained layers were characterized by a nanocrystalline microstructure comprised of the α-Al_2O_3 phase. The κ-Al_2O_3 phase was not identified. The microhardness of these layers was about 2.2 GPa at a load of 1 N, while the adhesion of the L_C layer with a thickness of 5 μm was approximately 80 N. This high value of the L_C layer is evidence of their good adhesion [14].

The purpose of carbon in the intermediate layer is to block cobalt diffusion towards the Al_2O_3 layer of the substrate during its synthesis (the presence of cobalt in the layer would be pollution, and could cause crystallite growth of an α-Al_2O_3 phase with elongated shapes), and to block oxygen diffusion during the synthesis of the layer without carbon towards the substrate.

2. Materials and methods

The present work was carried out modeling studies on the synthesis of the intermediate layer of Al_2O_3-C on quartz glass in the form of plates with dimensions similar to the dimensions of indexable carbide using argon as the carrier gas. The use of quartz glass instead of cemented carbides was due to the following reasons: it does not react with Al_2O_3 below a temperature of 1100°C, it is well transparent, and therefore allows for a very quick visual assessment of the obtained layer thickness i.e., thickness distribution, and also very easy to determine whether during a given synthesis unfavorable homogeneous nucleation process occurred. In the process porous powders formed in the gas phase, which can be deposited on a synthesized layer causing porosity, thereby lowering the transparency, and its mechanical strength and adhesion. This process promotes high temperature synthesis, high concentrations of the reactants, and their turbulent flow.

The use of highly reactive organometallic aluminum reagents considerably reduces the temperature of the synthesis of layers. Therefore, the growth rate of the layers can be increased by the increase in the concentration of reactants. The relatively low temperature of such a process should not favor homogeneous nucleation, despite higher concentrations of the reactants. The synthesis conditions of aluminum oxide layers are shown in TABLE 1.

TABLE 1

Synthesis conditions of Al_2O_3-C layers on quartz glass by MOCVD method

Parameter	Conditions of synthesis
Summary gas pressure in the CVD reactor [Pa]	$1-70 \times 10^2$
Flow rate of Ar [Nl/h]	0,03-30
The temperature of the carrier gas [°C]	150-220
The temperature of evaporator [°C]	140-180
The temperature of substrate [°C]	800-1000
Synthesis time [min.]	10-20
Weight of Al(acac)$_3$ [g]	0,1
The value of the developed criterion Gr_x/Re_x^2 [4]	<0,1

The obtained samples were subjected to a preliminary visual analysis. Selected samples were tested using the scanning

electron microscope (SEM NANO NOVA 200 from FEI EU-ROPE COMPANY cooperating with the analyzer EDAX EDS company), and X-ray analysis (X-ray diffractometer X'Pert Pro Philips).

3. Results and discussion

Obtained samples were assessed visually, which allowed for determining whether during the synthesis of layers powders were formed. Their presence would cause turbidity of layers. When parameters of the synthesis process were appropriately selected the layers were transparent This analysis also allowed for determining whether there were differences in the distribution of layer thicknesses. When there are differences in the thickness of the layers, different interference colors are visible. The layers obtained under the conditions presented in TABLE 1 do not show this differentiation. The layers are slightly "tinted", which is result of the presence of these atoms in the form of rings, similar to the carbon black, in addition to σ bonds there are π-type bonds. This influences the absorption of visible light and consequently causes black carbon color [3, 15]. Tests were carried out on selected samples using scanning electron microscopy and X-ray diffraction.

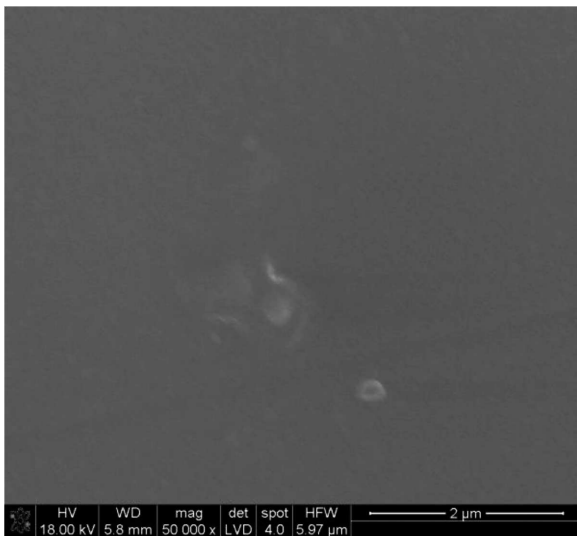Figure 1 shows the surface layer of Al_2O_3-C synthesized at 800°C.

Fig. 1. Surface of Al_2O_3-C layer on quartz glass. Layer was synthesized at 800°C. Synthesis time: about 20 min

X-ray studies indicate that layers synthesized at this temperature have on amorphous microstructure. However, Figure 1 shows however that the layer contains nanocrystalline aggregates, probably low-temperature Al_2O_3 variations, but number of them is small and therefore they are not detected by X-ray diffraction. Maximum size of crystallites is about 300 nm.

Figure 2 shows the surface of the Al_2O_3 layer synthesized at a temperature of 900°C.

The crystallites in Fig. 2 are much larger and more diverse in the size than those in Fig. 1, although the size is of the order of nano. Maximum crystallites size is about 400 nm. The layers are not porous.
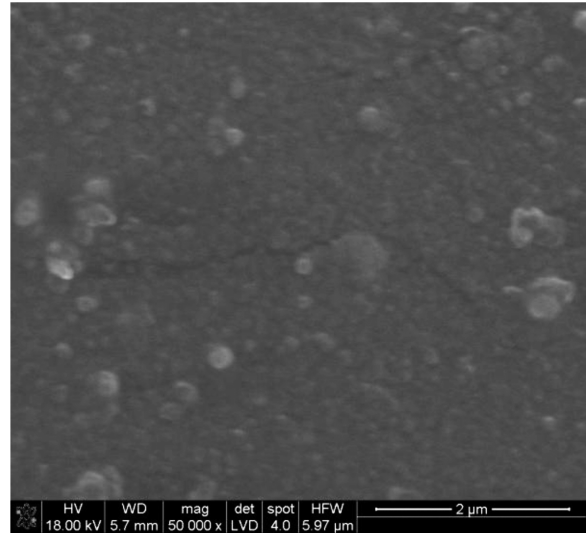

Fig. 2. Surface of Al_2O_3-C layer on quartz glass. Layer was synthesized at 900°C. Synthesis time: about 20 min
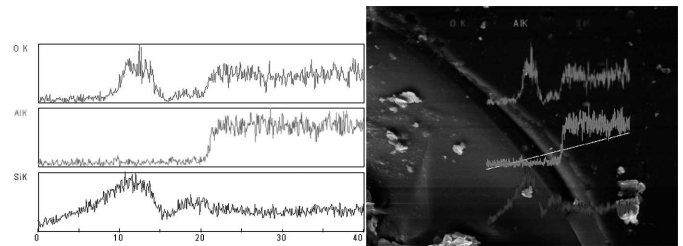

Fig. 3. Fracture of Al_2O_3-C layer synthesized at 950°C on quartz glass and linear EDAX analysis. Synthesis time: about 20 min

Figure 3 shows the fracture surface of the layer of Al_2O_3-C synthesized at 950°C and a linear analysis of the fracture. The layer is continuous, smooth, non-porous, uniform in thickness and well adherent to the substrate. It is clear that the layer broke away together with a fragment of the glass surface, which means that the mechanical strength of the layer and the layer-to-glass connections are greater than the mechanical strength of the glass. We have observed a similar phenomenon in the case of the synthesis of amorphous Si_3N_4 layer doped with C on quartz glass [15]. Si_3N_4-C layers, in which the coal was in the form of aggregates with dimensions up to approximately 100 nm, showed a much higher tensile strength than the layers that do not contain carbon. The increase in the strength of the fragile layers of Si_3N_4-C is the result of the presence of these C particles of lesser strength than Si_3N_4, on which the block followed by an increase in the radius fracture cracks on the particle. This is called dispersion strengthening particles of brittle materials with less strength than the matrix. According to the mechanism of brittle materials cracking (Cook-Gordon mechanism) [16], in this case, it leads to a reduction in tensile stress at the end of the slot due to the increase in the size of the particle radius.

Figure 4 shows the diffraction pattern of the surface of sample No. 3. From this figure it can be seen that the layer contains the α-Al_2O_3 phase.
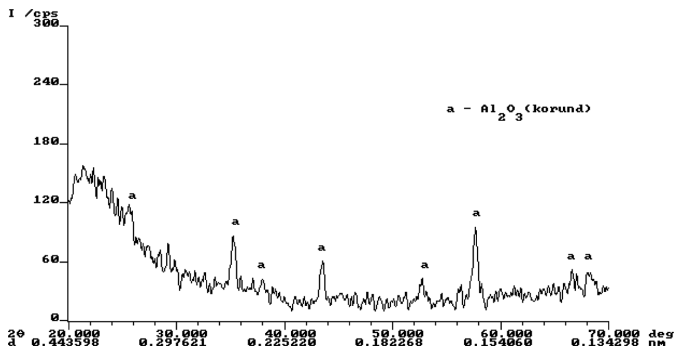
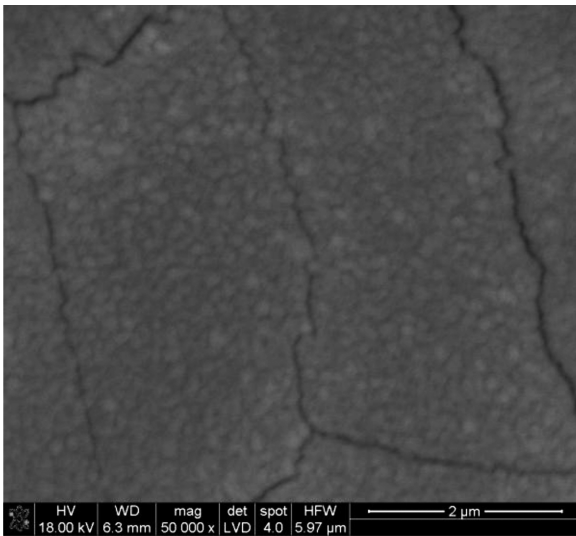Fig. 4. X-ray pattern of sample with Al$_2$O$_3$ layer synthesized at 950°C

Fig. 5. Surface of Al$_2$O$_3$-C layer on quartz glass. Layer was synthesized at 1000°C (synthesis time: 15 min)

Figure 5 shows the surface layer of Al$_2$O$_3$-C. Visible crystallites are large (about 400 nm). Cracking of the surface layer was formed during the breaking of the sample. From Figure 5 it can be concluded that the amount of α-Al$_2$O$_3$ phase in the layer is much larger than in the case of the sample shown in Figure 3. For this reason hardness of the layer presented in fig. 5 is significantly higher than hardness of the layer in Figure 3 and therefore undergo easy cracking during breaking of the samples.

4. Conclusion

The study shows that the layers of Al$_2$O$_3$-C synthesized in the temperature range 800-1000°C are dense, non-porous, smooth, and well adherent to the substrate.

They have dark color. It's characteristic of carbon with π binding. This indicates, that carbon is present in the layer in the form not of individual atoms but aggregates causing dispersion strengthening of the Al$_2$O$_3$-C layer. The layers have a nanocrystalline microstructure. The temperature increase causes an increase in the synthesis of crystallite size and the appearance of α-Al$_2$O$_3$ phase. Homogeneous nucleation process does not occur during the synthesis of layers.

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