

Alumina Layers Synthesized on Cemented Carbide Tools by MOCVD Method

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Abstract

This paper shows the results of investigation of a synthesis of pure aluminium oxide layers on cemented carbide cutting tools by the MOCVD (Metalorganic Chemical Vapour Deposition) method using $Al(O_2C_5H_7)_3$ as a precursor. The layers were deposited at 800°C in two stages. Initially, as carrier gases ammonia (99.95 % pure) and/or argon (99.995 % pure) were used. Then, a thin and continuous Al_2O_3+C layer was obtained. It was so-called the intermediate layer. In the second stage, air was added into a CVD reactor and then a thicker external carbon-free Al_2O_3 layer was synthesized. The average growth rate of the layers was about 5 µm/h. The obtained layers were additionally annealed in air at temperatures up to 1050°C, which caused formation of α - Al_2O_3 .

Structure and microstructure of the layers were examined. Microhardness tests were performed by Vickers method over a load of 1N. The average value of microhardness of the layers with no annealing was about 0.98 GPa. After annealing at 1050°C, the average value of the microhardness amounted to about 2.25 GPa. Adhesion of Al_2O_3 layers to the substrate of cemented carbides was examined by the scratch test. Estimated average value L_c for the not annealed Al_2O_3 layer of 5 µm thickness was 41 N. In the case of samples annealed at 1000°C this value reached even 85 N.

Keywords: Al₂O₃ layers, Cemented carbide tools, MOCVD method, Aluminium acetylacetonate, Microstructure

WARSTWY TLENKU GLINU SYNTEZOWANE METODĄ MOCVD NA NARZĘDZIACH Z WĘGLIKÓW SPIEKANYCH

Artykuł pokazuje wyniki badań nad syntezą warstw czystego tlenku glinu na narzędziach do obróbki skrawaniem wykonanych z węglików spiekanych. Syntezę wykonano za pomocą metody MOCVD przy wykorzystaniu $Al(O_2C_5H_7)_3$ jako prekursora. Warstwy osadzano dwuetapowo w 800°C. Najpierw wykorzystano gazy nośne w postaci amoniaku (o czystości 99.95 %) i/lub argonu (o czystości 99.955 %) do otrzymania cienkiej i ciągłej warstwy Al_2O_3+C . Była to tzw. warstwa pośrednia. W drugim etapie, do reaktora CVD wprowadzano powietrze w celu syntezowania grubszej, zewnętrznej warstwy Al_2O_3 , pozbawionej węgla. Średnia szybkość wzrostu wynosiła około 5 µm/h. Otrzymane warstwy były dodatkowo wygrzewane w powietrzu w temperaturach aż do 1050°C, co powodowało utworzenie się α -Al₂O₃.

Zbadano strukturę i mikrostrukturę warstw. Badania mikrotwardości przeprowadzono za pomocą metody Vickersa przy sile obciążającej wynoszącej 1N. Średnia wartość mikrotwardości warstw nie wygrzewanych wynosiła około 0.98 GPa. Po wygrzewaniu w 1050°C, średnia wartość mikrotwardości osiągnęła wartość około 2.25 GPa. Adhezję warstwy Al_2O_3 do podłoża z węglików spiekanych oznaczono za pomocą testu zarysowania (*scratch test*). Oszacowana średnia wartość L_c w przypadku nie wygrzewanej warstwy Al_2O_3 o grubości 5 µm wynosiła 41 N. W przypadku próbek wygrzanych w 1000°C wartość ta osiągnęła nawet 85 N.

Słowa kluczowe: warstwa Al₂O₃, narzędzia z węglików spiekanych, metoda MOCVD, acetyloacetonian glinu, mikrostruktura

1. Introduction

Aluminium oxide layers have been deposited onto cemented carbide cutting tools for a commercial scale since the 1970s. They have been formed from gas mixtures of AlCl₃ – $H_2 - CO_2$ [1] or AlCl₃ – $H_2O - CO_2$ [2] at temperatures above 1000°C on the surface of cemented carbides pre-coated by thin CVD layer of TiC or Ti(C, N). Such a high temperature of the synthesis favours a homogeneous nucleation process [3]. As a consequence of this process, in the gas phase porous powders of Al₂O₃ are formed. In order to obtain a dense product on the substrate surface, the process should be carried out using low reagents concentration. Therefore, the layer growth is slow (0.5–1 µm/h) [3]. High temperature of

the synthesis process also causes the growth of the rough layer (growth of crystallites of elongated shapes "needles"). It seems that using more reactive metalorganic compounds of aluminium should make possible a synthesis of Al_2O_3 layers at significantly lower temperatures. These layers should be also dense and smooth. This work shows the results of investigations of the synthesis of aluminium oxide layers on cemented carbides by MOCVD method using aluminium acetylacetonate ($Al(O_2C_5H_7)_3$) as a precursor.

2. Experimental

Aluminium oxide layers were synthesized on the commercial cemented carbide cutting tools S30S SNUN 120412

(Sandvik Baildonit) by MOCVD method. Aluminum acetylacetonate (contents of Al($O_2C_5H_7$)₃ - min. 98 %) was used as a precursor and argon (99.995 % pure) as a carrier gas. The first stage of the research comprised the deposition of a very thin Al₂O₃ layer, containing carbon straight on the cemented carbide surface. When this layer became continuous, the synthesis process was implemented, also with presence of air (second stage). Air (source of oxygen) was necessary for elimination of carbon, which was a solid by-product of aluminium acetylacetonate decomposition. This carbonfree layer was significantly thicker. The synthesis time of external layer was 15-120 min. The layers were synthesized at 800°C. The temperature of Al($O_2C_5H_7$)₃ evaporation was changed in the range of 140-170°C. Total gas pressure in the reactor attained values of $3.7 \cdot 10^2 - 1013.3 \cdot 10^2$ Pa. The parameters of the synthesis process were established in such a way that the extended Gr_x/Re_x^2 criterion [4] was less than 0.1 at both the inlet and the outlet of the reactor (Gr, Re - Grashof's and Reynold's numbers, respectively; x - adistance from the inflow point of gas onto the heated substrate). Selected samples were additionally annealed in air at the temperatures of 850-1050°C. The obtained samples were examined by scanning electron microscopy (Jeol 5400 with energy dispersive X-ray spectroscopy (EDS) LINK ISIS Seria 300 - Oxford Instruments) and X-ray diffraction (XRD-Seifert). Microhardness of the layers and their adhesion to the substrate were tested using Micro Combi Tester (CSEM Instruments). Microhardness tests of the obtained layers were performed by the Vickers method using a load of 1N. Adhesion of the layers to the substrate was examined by the scratch test using different loads of stylus. The tests of determination of the surface roughness were performed by profile measurement gauge TOPO 01K.

3. Results and discussion

The obtained layers were glossy. Their colour changed from black to grey. Black layers were obtained when the synthesis was carried out without the presence of air. When air was present during their growth, they became grey. Such layers were obtained when in the CVD reactor laminar flow of gases was kept ($Gr_x/Re_x^2 < 0.1$). Shiny grey layers were



Fig. 1. Surface of AI_2O_3 layer synthesized at 800°C. Synthesis time: 1 h. Synthesis time of the intermediate layer: 10 min. The layer thickness: about 4.5 μ m.

obtained also when an initially very thin continuous layer containing carbon was deposited onto the substrate surface and later (with the presence of air) the "right" carbon-free layer was synthesized. This external carbon-free layer was significantly thicker. Fig. 1 shows an example of surface of Al₂O₃ layer synthesized at 800°C during 1h. Synthesis time of the intermediate layer was 10 min.

A part of samples obtained at 800°C was additionally annealed. An example of the layer synthesized at 800°C additionally annealed at 1050°C is shown in Fig. 2 and its fracture with linear microanalysis EDS in Fig. 3.



Fig. 2. Surface of AI_2O_3 layer synthesized at 800°C (1 h) and additionally annealed at 1050°C (30 min). The layer thickness: about 5 μ m.

The results of visual observation and examinations performed using SEM indicate that the thin Al₂O₃+C layer (the intermediate layer with thickness of about 0.07 µm) is continuous and protects the working carbon-free Al₂O₃ layer against diffusion of cobalt from the substrate. This layer is also a barrier for diffusion of oxygen to the substrate during deposition of the external layer. Discontinuity and porosity of this layer would affect easy oxidation of substrate and formation of oxides of elements from the substrate. The presence of cobalt in the synthesized layer is its impurity and causes also its roughness (presence of cobalt in deposited Al₂O₃ layer causes the growth of crystallites of elongated shapes and, as a consequence, roughness of this layer). Therefore, the deposition of a continuous, well adhered to the substrate. dense and uniform in thickness intermediate layer assures purity and smoothness of the external (working) layer.

Also X-ray analysis (Fig. 4) confirms that the intermediate layer is tight and effectively protects both the substrate and the synthesized layer against undesirable processes.

Roughness of the obtained layers and substrate was also determined. Fig. 5 shows the results of tests for the specially ground and next polished surface of cemented carbides and Fig. 6 the results of tests for AI_2O_3 layer synthesized on ground substrate of cemented carbides at 800°C.

From Figs. 5 and 6 it results that the roughness of Al_2O_3 layer is only insensibly higher than the roughness of ground and polished surface of the substrate.

Additional annealing of layers synthesized at 800°C caused their crystallization and formation of α -Al₂O₃ (Fig. 4). It was expected that the occurrence of the crystallization process of the layer should influence their hardness. The results





Fig. 3. Fracture of the sample presented in Fig. 2 and linear microanalysis EDS along the marked line.



Fig. 4. X-ray diffraction pattern of the sample presented in Figs. 2 and 3 (α -Al₂O₃).



Fig. 5. Roughness of ground and polished surface of the cemented carbide substrate; $P_t = 1.146 \ \mu m \ (P_t - the maximum roughness height).$



Fig. 6. Roughness of Al_2O_3 layer synthesized on the ground surface of cemented carbide substrate at 800°C. Synthesis time: 1 h. Synthesis time of the intermediate layer: 10 min. $P_t = 2.237 \ \mu m \ (P_t - the maximum roughness height)$.



Fig. 7. Influence of annealing temperature of Al_2O_3 layers on their microhardness μHV (a load of 1 N).

of measurements of microhardness of Al_2O_3 layers performed by Vickers method using a load of 1 N allow the authors to ascertain that microhardness of the obtained layers increases with the increase of their annealing temperature (Fig. 7).

Analyzing also the results of adhesion tests of obtained layers to the substrate of cemented carbides, it is concluded that the increase of annealing temperature of the layers

Table 1. Results of scratch test for Al_2O_3 layers synthesized at temperature of 800°C with thickness of about 3.5 μ m. Samples not annealed and annealed at 1000°C.

Conditions of annealing	Max. load L [N]	Average value of scratch depth h₁[μm] under the load L.	Estimated average value of L_c [N] for the layer with thickness of h_2 = 5 µm
Not annealed	8	2.2	41
1000°C, 10 min	15	2.1	85
1000°C, 20 min	15	2.2	77
1000°C, 30 min	15	2.3	71



Fig. 8. Surface of Al_2O_3 layer synthesized at 800°C with thickness of about 3 μ m. Sample not annealed. Scratch test was made using a load of 15 N.



Fig. 9. Surface of Al_2O_3 layer synthesized at 800°C with thickness of about 3 μ m. Sample annealed at 1000°C (30 min.). Scratch test was made using a load of 15 N.

causes improvement of their adhesion to the substrate. Fig. 8 presents an example of Al_2O_3 layer synthesized at 800°C and Fig. 9 an example of Al_2O_3 layer additionally annealed at 1000°C during 30 min. after scratching using a load of 15 N. The thickness of the layers amounts to about 3 μ m. In the case of the layer presented in Fig. 9 only its surface is insignificantly damaged.

The load of the used stylus was too low to scratch the layer. Taking it into consideration and assuming that optimum thickness of the working layer amounts to 5 μ m calculated critical load L_c using formula [5]:

$$L_C = \frac{h_2^2}{h_1^2} \cdot L,$$

where h_{1} , h_{2} – scratch depth respectively over loads L and L_{c} . The results of the scratch test for Al₂O₃ layers synthesized at 800°C with thickness of about 3.5 µm annealed at 1000°C and not annealed are gathered in Table 1.

The estimated average value L_c for layer synthesized at 800°C with thickness of 5 µm not annealed amounts to 41 N. In the case of the layers additionally annealed this value increases even to 85 N.

4. Conclusions

Smooth, well adhered and carbon-free Al₂O₃ layers were obtained on the cemented carbides by MOCVD method using aluminium acetylacetonate as a precursor. The layers were deposited straight on the cemented carbide substrate (without intermediate layer of TiC or Ti(C,N)). They were synthesized at the high growth rate. Additional annealing of the layers deposited at 800°C caused their crystallization and formation of α -Al₂O₃. The obtained layers exhibit high microhardness µHV and good adhesion to the substrate. Annealing of the layers at 850–1050°C causes an increase both in their microhardness and adhesion to the substrate of cemented carbides.

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