MICROSTRUCTURE OF CVD - Al2O3
C. Chatfield, J. Lindström, M. Sjöstrand

To cite this version:

HAL Id: jpa-00229568
https://hal.archives-ouvertes.fr/jpa-00229568
Submitted on 1 Jan 1989

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Résumé - Les mécanismes de la réaction de CVD-\(\text{Al}_2\text{O}_3\) sont brièvement examinés. Deux chemins de réaction indépendants existent, un, dont la limitation de vitesse dépend d'une réaction volumétrique et un dépendant d'une réaction superficielle.

\(\text{Al}_2\text{O}_3\) cristallise sous plusieurs formes différentes. Le corindon de \(\alpha\)-\(\text{Al}_2\text{O}_3\) est la phase stable à la température de dépôt normale (950-1050°C). La phase métastable \(\omega\) est la seconde phase la plus commune. On montre que \(\omega\) - et \(\Theta\) - \(\text{Al}_2\text{O}_3\), se forment sur les facettes de TiC (111) pur avec une relation d'orientation de réseaux bien définie entre ceux de TiC et \(\text{Al}_2\text{O}_3\). Au contraire, aucune relation épitaxiale existe entre TiC et \(\omega\) - \(\text{Al}_2\text{O}_3\) et la région de contact entre ceux-ci est d'une très grande porosité. La différence de propriété de la région de contact est vue par l'adhésion entre TiC et \(\text{Al}_2\text{O}_3\).

On conclut que la formation résultant en \(\omega\) - \(\text{Al}_2\text{O}_3\) ne se produit pas sur TiC mais sur une couche mince intermédiaire d'oxyde de titane, par exemple \(\text{Ti}_2\text{O}_3\) ou \(\text{Ti}_3\text{O}_5\), qui se décompose pendant la croissance de \(\text{Al}_2\text{O}_3\).

Abstract - The reaction mechanisms of CVD-\(\text{Al}_2\text{O}_3\) are briefly reviewed. Two independent reaction paths exist; one of which is rate limited by a volume reaction and the second one by a surface reaction.

\(\text{Al}_2\text{O}_3\) crystallizes in several different phases. The \(\alpha\) - structure is the stable phase at normal deposition temperature (950-1050°C). The metastable \(\omega\) - phase is the second most commonly occurring phase. It is shown that \(\omega\) - and \(\Theta\) - \(\text{Al}_2\text{O}_3\) nucleate on pure TiC (111) facets with well defined lattice orientation-relationships between TiC and \(\text{Al}_2\text{O}_3\). In contrast, no epitaxial relationship between TiC and \(\omega\) - \(\text{Al}_2\text{O}_3\) is found and the latter interface contains a considerable amount of porosity. The difference in the interface properties is reflected in the adhesion between TiC and \(\text{Al}_2\text{O}_3\).

It is concluded that the nucleation resulting in \(\omega\) - \(\text{Al}_2\text{O}_3\) does not occur on TiC but on an intermediate thin layer of titanium oxide e.g. \(\text{Ti}_2\text{O}_3\) or \(\text{Ti}_3\text{O}_5\), which is dissolved during the subsequent \(\text{Al}_2\text{O}_3\) growth.

1 - INTRODUCTION

Chemical Vapor Deposition of alumina on cemented carbide cutting tools has been industrial praxis for more than ten years and the wear properties of \(\text{Al}_2\text{O}_3\) as well as of TiC and TiN have been discussed intensively in the literature (1-4).

The CVD technique has also been used to produce coatings of other metal oxides, carbides and nitrides with the metal either selected from the transition metals of the groups IV, V and VI of the Periodic Table or from silicon, boron and aluminum. Many of these compounds have found practical applications as wear resistant or protective coatings, but few have received as much attention as TiC, TiN and \(\text{Al}_2\text{O}_3\) which have by far been the objects for most of the studies undertaken.

Initially coated tools were intended for turning applications, but today, tools designed for milling as well as drilling applications, are coated.
Improvements of the bonding to the substrate and between different coating materials have resulted in a plurality of coating combinations with double, triple or multi-layer structures.

The reaction mechanisms occurring during the CVD of Al₂O₃ have been analysed on several occasions (5-10), little however, has been mentioned about the stability and microstructure of the deposited alumina phases and how the formation of these phases depends on the deposition process.

Alumina crystallizes in several different phases of which the \( \alpha \)-structure (Corundum) is the stable phase at typical deposition temperatures (950-1050°C). The metastable \( \delta \)-phase is the second most commonly occurring alumina modification in CVD-Al₂O₃. Other infrequently occurring types are \( \theta \), \( \gamma \) and \( \delta \).

The purpose of the work presented here is to elucidate the crystallography, microstructure and morphology of the \( \alpha \)- and the \( \delta \)-phase of CVD-Al₂O₃ and how the conditions in the nucleation stage determine which one of these phases or a mixture thereof grows. Since for commercial tools alumina is deposited on TiC coated cemented carbides, the interface reactions on the TiC surface are of special importance and will be discussed here.

2 - THE ALUMINA DEPOSITION PROCESS

Alumina deposition is usually carried out employing AlCl₃, CO₂, and H₂. AlCl₃ exists at normal temperatures as a powder and is very hygroscopic. For this reason AlCl₃ is preferably generated within the deposition system through chlorination of Al metal with HCl. Besides AlCl₃, other halides notably AlBr₃ and AlI₃, have also been investigated as Al-donors. However, the influence of the type of halide seems to be of less importance when H₂ is used as carrier gas (6).

It has experimentally been shown that there exist two independent contributions or reaction paths to the Al₂O₃ deposition (8) one of which is rate limited by the kinetics of the homogeneous water gas shift reaction (5):

\[
H₂ + CO₂ \rightarrow H₂O + CO
\]

The second reaction path is a surface reaction which may be rate controlled by the heterogeneous decomposition of CO₂ or possibly by the direct reaction between the halide (AlCl₃) and CO₂. The exact nature of this surface contribution is not very well understood and, in particular, the role of hydrogen is unclear.

The relative contribution from the rate limited volume- and surface reactions is naturally dependent on the ratio of free gas volume-to-substrate surface area (V/A). The homogeneous water gas shift reaction is extremely slow. The reaction rate has been determined by Tingey (11) and a comparison of the calculated deposition rate based on Tingey's kinetic equation with the experimentally determined deposition rate as a function of volume-to-surface ratio is illustrated in Fig. 1 (6,8). It is assumed that all water vapor produced in the free gas volume is consumed in the hydrolysis reaction with AlCl₃.

The results in Fig. 1 show that the difference between the experimentally determined deposition rates and the calculated ones is constant over the volume-to-surface ratios investigated (0.3-2.0 cm). This difference is interpreted as the surface controlled contribution to the Al₂O₃ deposition. The experimental curve in Fig. 1 will naturally deviate from linearity for larger V/A ratios since the effects of both forced convection and diffusion are not included in the model. However, for V/A ratios less than 2 these effects can be neglected.
3 - MORPHOLOGY AND MICROSTRUCTURE OF ALUMINA COATINGS AND THE TiC/Al2O3 INTERFACE

Morphology

A typical surface structure of a CVD-Al2O3 coating containing both the \( \alpha \)- and the \( \delta \)-phase is illustrated in Fig. 2a. The micrograph shows a coarse-grained \( \alpha \)-Al2O3 area marked C, surrounded by a much more fine-grained \( \delta \)-area, marked B2 and A. Areas A and B2 are separated by a crack pattern, see arrows in Fig. 2a. Another crack pattern has developed inside the \( \alpha \)-Al2O3 area. In Fig. 2b it can also be seen how the coarse-grained \( \alpha \)-area protrudes above the surrounding \( \delta \)-area.

Generally, the \( \alpha / \delta \) ratio varies over a wide range, however, a larger ratio is obtained for longer coating process times and for additional heat treatments. This is illustrated in Fig. 3 where the percentage of \( \delta \)-Al2O3 measured by XRD is plotted versus post-coating heat treatment time at 1030°C in \( \text{H}_2 \) at ambient pressure. It is seen from the time dependence that essentially all the metastable \( \delta \)-Al2O3 is transformed into the stable \( \alpha \)-Al2O3 phase after 3 h of heat treatment. It is also interesting to notice that the \( \delta \rightarrow \alpha \) transformation occurs without any greater changes in the surface morphology. Fig. 4 shows the \( \alpha \) and \( \delta \) pattern before and after the heat treatment. The surface morphology looks essentially the same.

The crack pattern seen in Fig. 2a could be a result of the thermal contraction occurring upon cooling from deposition temperature to room temperature and possibly also from the \( \delta \rightarrow \alpha \) transformation due to the difference in density (\( \rho_{\delta} = 3.99 \text{ g/cm}^3 \), \( \rho_{\alpha} = 3.77 \text{ g/cm}^3 \)) (12).

Microstructure of the alumina coating

The internal microstructure of a 100% \( \alpha \)-Al2O3 coating is illustrated in Fig. 5a. What is characteristic for such a 1 \( \mu \text{m} \) thick coating is its grain size, 0.5–1.0 \( \mu \text{m} \), and the existence of porosity. The latter seems to exist in two forms: (i) as individual isolated pores in grains and at grain boundaries, (ii) as pore channels often extending along grain boundaries as indicated in Fig. 5a. Similar types of porosity are observed in electro-deposited metal films (13) and are probably due to reactant gases being trapped in the film during growth. \( \alpha \)-Al2O3 in CVD films also contains a number of dislocations.

In contrast, \( \delta \)-Al2O3 is essentially pore-free and exhibits a much smaller grain-size, \( \leq 0.1 \mu \text{m} \). The \( \delta \)-Al2O3 also contains a varying degree of internal defects, probably twins, arrowed in Fig. 5b. Electron diffraction confirms that the \( \delta \)-Al2O3 has a hexagonal crystal structure with \( a = 0.963 \text{ nm} \) and \( c = 0.904 \text{ nm} \) in agreement with reference (12).

Al2O3 coatings occasionally contain a number of inclusions which may be outgrowths from the underlaying TiC surface. The inclusion types that have been found are e.g. faceted cobalt particles, see Fig. 6, TiC coated Co, see Fig. 7. An important observation is that in no case has a rational lattice orientation-relationship been found between these TiC coated inclusions and the Al2O3 phase they are in contact with.

Microstructure of the TiC/Al2O3 interface

The TiC/Al2O3 coatings chosen for this investigation exhibited a mediocre and a good adhesion between the TiC and the Al2O3 coating respectively. The TEM investigations of the interfaces reveal very clearly why one Al2O3 coating adheres and the other one does not.

In Fig. 8 is illustrated the TiC/Al2O3 interface for the poorly adhering coating. As is readily seen a considerable amount of porosity exists at and in the vicinity of the interface. The alumina phase is identified as
the α-structure. The physical contact between TiC and α-Al₂O₃ is poor. Electron diffraction shows that the crystal planes making up the surface of the TiC coating are, in all cases, the close-packed (111) planes.

In contrast, the TiC/Al₂O₃ interface in the specimen with good adhesion between TiC/Al₂O₃ is pore-free, see Fig. 9. Moreover, the Al₂O₃ phase in contact with TiC is very rarely α-Al₂O₃, but rather θ- or, occasionally, θ'-Al₂O₃. As seen from the micrographs of these phases nucleate on each TiC facet. Furthermore, as in the sample with poor TiC/Al₂O₃ adhesion, the TiC surface is composed only of (111) facets.

For both the α- and the θ-phase in contact with TiC well defined lattice orientation-relationships are found between TiC and Al₂O₃. For TiC/α-Al₂O₃ this is:

(111) TiC // (0001) α-Al₂O₃
[110] TiC // [1010] α-Al₂O₃

and for TiC/θ-Al₂O₃ this is:

(111) TiC // (310) θ-Al₂O₃
[110] TiC // [001] θ-Al₂O₃

For the various stable and metastable modifications of Al₂O₃, the common feature is that they can all be imagined as being composed of close-packed sheets of oxygen atoms between which can be found the Al atoms. In the case of α-Al₂O₃, the hexagonal unit cell can be visualized as being composed of a stack of six planes with an ABAC stacking sequence. Thus the interface between TiC and α-Al₂O₃ is composed of parallel close-packed planes in both structures. From the lattice orientation-relationship given above, the positioning of the atoms in the two phases at the interface can be visualized as in Fig. 10. Here it is seen that the smaller Ti atoms in the TiC lattice are located in the "holes" in the close-packed oxygen plane of the α-Al₂O₃ lattice. Such an atomic arrangement can be expected to give strong bonding across the interface and the maximum adhesion.

The lattice arrangement between TiC and θ-Al₂O₃ seems to be more complex, however, this arrangement is the same as that found by Katz et al (14) for MgAl₂O₄/θ-Ga₂O₃. MgAl₂O₄ is a spinel phase with a fcc close-packed structure as TiC, while θ-Ga₂O₃ and θ'-Al₂O₃ are isomorphs. In θ-Ga₂O₃ the (310) plane was identified as the close-packed oxygen plane (14). Thus, at the TiC/θ-Al₂O₃ interface there is a close-packed oxygen plane parallel to a close-packed TiC plane and the same type of local atomic arrangement as is found in Fig. 10 is expected.

Although no lattice orientation relationship between TiC and θ-Al₂O₃ has been found in the two specimens investigated, these results must not necessarily be interpreted as indicating that such does not exist. For instance in a TiN/Al₂O₃ coating interface the following lattice orientation-relationship has been found:

(111) TiN // (0001) θ-Al₂O₃
[110] TiN // [1010] θ-Al₂O₃

This is identical to that between α-Al₂O₃ and TiC and can be interpreted according to Fig. 10.

4 - INTERFACE REACTIONS IN THE TiC/AL₂O₃ SYSTEM

From the results of the TEM investigations of the TiC/Al₂O₃ interface described above, it is clear that the process conditions during the early
nucleation stage of $\text{Al}_2\text{O}_3$ on TiC are of uttermost importance in order to obtain not only good bonding but also for the subsequent growth of the coating. Accordingly, an interesting question is what factor encourages a high density of $\alpha$-Al$_2$O$_3$ nuclei to form or, on the other hand, $\gamma$-Al$_2$O$_3$ nuclei to form. In general a high supersaturation will result in a high density of nuclei.

There is a very strong indirect evidence that the oxidation state(s) of the TiC surface is imperative for the type of nuclei being formed. Experimentally, it can easily be shown that when deliberately oxidizing the TiC surface prior to Al$_2$O$_3$ deposition, $\alpha$-Al$_2$O$_3$ is always obtained and very rarely $\gamma$-Al$_2$O$_3$. Simple thermodynamic calculations (SOLGASMIX) show e.g. that the presence of H$_2$O in H$_2$ has a drastic effect on the TiC surface. Oxidation of TiC to Ti$_3$O$_5$ is thermodynamically possible for as little as 5 ppm H$_2$O in H$_2$ at a temperature 1000°C and a pressure 50 mbar. For H$_2$O > 25 ppm in H$_2$ the calculations show an oxidation of TiC predominantly to Ti$_3$O$_5$. It should be pointed out here that a transformation of TiC to Ti$_2$O$_3$ or Ti$_3$O$_5$ is concomitant with a 25-30 % volume expansion (3).

The water gas concentration in the reactor during the Al$_2$O$_3$ deposition is very small and all H$_2$O is consumed in the hydrolysis reaction with AlCl$_3$. For instance, in a reactor containing a multispecimen batch with a characteristic distance between objects to be coated of approximately 2 mm, the H$_2$O concentration can be calculated to be of the order 0.01-0.1 ppm. However, during the nucleation stage long before full coverage of nuclei on the surfaces has been accomplished locally and over the entire reactor volume, the H$_2$O concentration may fluctuate heavily and can reach maximum values of 1000-2000 ppm. Hence, conditions for oxidizing the TiC surface exists according to thermodynamics.

A second contribution to the oxidation of the TiC surface may originate from the heterogeneous decomposition of CO$_2$:

$$\text{CO}_2 \rightarrow \text{CO} + \text{O}$$

where the surface-adsorbed monatomic oxygen readily oxidizes the TiC surface.

The above hypothesis is very tentative. However, it has been shown in studies on the kinetics of CO$_2$ on metal surfaces that certain metals, notably Co and Fe, catalyze the above decomposition reaction (15). Cobalt in small amounts originating from the cemented carbide substrate, is usually unevenly distributed over the TiC surface. Furthermore, it has clearly been shown in experiments where the surface of a TiC coated sample has been "smeared" with Co (or Ni) metal and subsequently been heat treated in a gas atmosphere of 2 % CO$_2$ in H$_2$ at 1000°C and at 55 mbar, that the presence of Co on the surface catalyzes the oxidation of TiC into Ti$_3$O$_5$. The strongly reducing H$_2$ atmosphere prevents Co from being oxidized.

5 - DISCUSSION

The results from the TEM investigation showed that no well-defined lattice orientation-relationship could be found between TiC and $\alpha$-Al$_2$O$_3$. Furthermore, the interface exhibited large amounts of porosity. To rationalize these findings with the above analyses of the kinetics of the surface oxidation of TiC, one has to conclude that it is very plausible that the nucleation resulting in $\alpha$-Al$_2$O$_3$ does not occur on TiC but rather on a very thin titanium oxide film, e.g. Ti$_2$O$_3$ or Ti$_3$O$_5$ (16), and hence, makes it impossible to develop epitaxial relationship with the underlaying TiC facet. However, since there is no evidence from the TEM investigations of any trigonal (Ti$_2$O$_3$) or monoclinic (Ti$_3$O$_5$) titanium oxide interfacing TiC with Al$_2$O$_3$, it must be assumed that a transformation back to the fcc TiO or TiCO phases has occurred during the fairly long deposition period. The volume contraction (25-30 %) accompanying the phase transformations would then explain the observed interface porosity.
In contrast, δ- or Θ-Al₂O₃ nucleate directly on non-oxidized TiC facets which results in an epitaxial relationship between TiC/Al₂O₃ and the absence of interface porosity. The subsequent kinetics behind the phase transformation of the metastable δ- to Θ-Al₂O₃ is not clear. It is possible that small changes in the composition of the coating, or the influence of impurities, alter the phase stabilities. It should be pointed out, however, that only small rearrangements of the close-packed oxygen layers are needed to convert δ-Al₂O₃ to Θ-Al₂O₃.

6 - ACKNOWLEDGEMENT

We thank Marian Mikus for providing us with SEM micrographs of δ/Θ specimens.

REFERENCES


/6/ Colombier, C., Lindström, J. and Lux, B., 8th Int. Conf. on Vacuum Metallurgy, Linz, Austria (1985) 162.


Fig 1. Comparison of the calculated and experimentally determined deposition rates of $\text{Al}_2\text{O}_3$ as a function of volume-to-surface ratio (6,8).

Fig. 2a and Fig. 2b

Fig. 2. Morphology of $\alpha$- and $\omega$-$\text{Al}_2\text{O}_3$ coatings.

A coarse grained area is imaged in Fig. 2a in the absorbed-electron mode which readily reveals the crack pattern around (marked) and through the coarse-grained area C.

Another coarse grained area is imaged in Fig. 2b using secondary electrons and it can be seen how it protrudes above the fine-grained $\omega$-$\text{Al}_2\text{O}_3$. 
Fig. 3.
Percentage of α-Al₂O₃ measured by XRD versus postcoating heat treatment time at 1030°C in H₂ at 1 atm pressure.

Fig. 4.
SEM photomicrographs illustrating the lack of any microstructural changes of the surface morphology in the Al₂O₃ coating after 4 h heat-treatment at 1030°C in H₂. Photo A was taken before and photo B after the heat-treatment.
Fig. 5. TEM micrographs illustrating the microstructure of two different Al₂O₃ coatings. Fig. 5a is from a 100% α-Al₂O₃ coating and in this porosity within the grains and pores "channels" at grain boundaries (arrowed) can be seen. In contrast a δ-Al₂O₃ containing coating is pore-free and has a much smaller grain size. Linear defects, probably microtwins, are seen in the δ grains, Fig. 5b.
Fig. 6. TEM micrograph showing a faceted Co particle in $\alpha$-$\text{Al}_2\text{O}_3$.

Fig. 7. TEM micrograph showing a TiC coated cobalt inclusion in $\alpha$-$\text{Al}_2\text{O}_3$.

Fig. 8. TEM micrograph of the TiC/$\alpha$-$\text{Al}_2\text{O}_3$ interface. The traces of the $\{111\}$ TiC planes are marked. The porosity at the TiC/$\text{Al}_2\text{O}_3$ interface and in the $\text{Al}_2\text{O}_3$ grain is very visible.
Fig. 9. TEM micrograph of the TiC/δ-Al₂O₃ interface. The traces of the {111} TiC planes are marked. No porosity is visible at this interface and a well-defined orientation-relationship exists between δ-Al₂O₃ and TiC.

Fig. 10. The atomic relationship between TiC (111) and δ-Al₂O₃ (0001). Spheres marked C represent the close-packed oxygen atoms and spheres marked A and B represent the Ti-atoms in the close-packed (111) plane.