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MICROSTRUCTURE OF CVD - $\text{Al}_2\text{O}_3$

C. CHATFIELD, J.N. LINDSTRÖM and M.E. SJÖSTRAND

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 $\alpha$-$\text{Al}_2\text{O}_3$ 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. Ti$_2$O$_3$ or Ti$_3$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 \( \epsilon \)-phase is the second most commonly occurring alumina modification in CVD-Al₂O₃. Other infrequently occurring types are \( \gamma \), \( \delta \) and \( \theta \).

The purpose of the work presented here is to elucidate the crystallography, microstructure and morphology of the \( \alpha \)- and the \( \epsilon \)-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 AlBr₂ and AlI₂, 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):

\[
H_2 + CO_2 \rightarrow H_2O + CO
\]

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.
The internal microstructure of a 100% α-Al₂O₃ coating is illustrated in Fig. 5a. What is characteristic for such a 1 μm thick coating is its grain size, 0.5-1.0 μm, 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. α-Al₂O₃ in CVD films also contains a number of dislocations.

In contrast, δ-Al₂O₃ is essentially pore-free and exhibits a much smaller grain-size, see Fig. 5b. The δ-Al₂O₃ also contains a varying degree of internal defects, probably twins; arrowed in Fig. 5b. Electron diffraction confirms that the δ-Al₂O₃ has a hexagonal crystal structure with a = 0.963 nm and c = 0.904 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. facetted 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 free, see Fig. 9. Moreover, the Al₂O₃ phase in contact with TiC is very rarely α-Al₂O₃ but rather θ-Al₂O₃. As seen from the microstructure of this phase, 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/θ-Al₂O₃ this is:

\[(1\bar{1}1) \text{ TiC }// (0001) \theta-Al₂O₃\]
\n\[\{110\} \text{ TiC }// \{10\bar{1}0\} \theta-Al₂O₃\]

and for TiC/θ-Al₂O₃ this is:

\[(1\bar{1}1) \text{ TiC }// (310) \theta-Al₂O₃\]
\n\[\{\bar{1}\bar{1}0\} \text{ TiC }// \{001\} \theta-Al₂O₃\]

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 θ-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 θ-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 θ-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 MgAl₂O₃/θ-Ga₂O₃. MgAl₂O₃ 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 α-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:

\[(1\bar{1}1) \text{ TiN }// (0001) \alpha-Al₂O₃\]
\n\[\{110\} \text{ TiN }// \{10\bar{1}0\} \alpha-Al₂O₃\]

This is identical to that between θ-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 $\bullet$ (or $\bigcirc$) nuclei to form or, on the other hand, $\alpha$-$\text{Al}_2\text{O}_3$ 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 $\text{Al}_2\text{O}_3$ deposition, $\alpha$-$\text{Al}_2\text{O}_3$ is always obtained and very rarely $\bigcirc$-$\text{Al}_2\text{O}_3$. Simple thermodynamic calculations (SOLGAS/MIX) show e.g. that the presence of $\text{H}_2\text{O}$ in $\text{H}_2$ has a drastic effect on the TiC surface. Oxidation of TiC to TiO$_2$ is thermodynamically possible for as little as 5 ppm $\text{H}_2\text{O}$ in $\text{H}_2$ at a temperature 1000°C and a pressure 50 mbar. For $\text{H}_2\text{O} > 25$ ppm in $\text{H}_2$ the calculations show an oxidation of TiC predominantly to TiO$_2$. 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.

The water gas concentration in the reactor during the $\text{Al}_2\text{O}_3$ deposition is very small and all $\text{H}_2\text{O}$ is consumed in the hydrolysis reaction with $\text{AlCl}_3$. For instance, in a reactor containing a multispecimen batch with a characteristic distance between objects to be coated of approximately 2 mm, the $\text{H}_2\text{O}$ 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 $\text{H}_2\text{O}$ 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 $\text{CO}_2$:

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

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 $\text{CO}_2$ 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 % $\text{CO}_2$ in $\text{H}_2$ at 1000°C and at 55 mbar, that the presence of Co on the surface catalyzes the oxidation of TiC into TiO$_2$. The strongly reducing $\text{H}_2$ 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 $\alpha$-$\text{Al}_2\text{O}_3$. 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 $\alpha$-$\text{Al}_2\text{O}_3$ does not occur on TiC but rather on a very thin titanium oxide film, e.g. TiO$_2$ 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 $\text{Al}_2\text{O}_3$, it must be assumed that a transformation back to the fcc TiO or TiO$_2$ 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 \(\delta\)-Al\(_2\)O\(_3\) nucleate directly on non-oxidized TiC facets which results in an epitaxial relationship between TiC/Al\(_2\)O\(_3\) and the absence of interface porosity. The subsequent kinetics behind the phase transformation of the metastable δ to \(\alpha\)-Al\(_2\)O\(_3\) 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 \(\delta\)-Al\(_2\)O\(_3\) to \(\alpha\)-Al\(_2\)O\(_3\).

6 - ACKNOWLEDGEMENT

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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 ($\delta, \theta$).

Fig. 2. Morphology of $\alpha$- and $\delta$-$\text{Al}_2\text{O}_3$ 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 $\delta$-$\text{Al}_2\text{O}_3$. 
Fig. 3.
Percentage of \( \alpha - \text{Al}_2\text{O}_3 \) measured by XRD versus postcoating heat treatment time at 1030°C in \( \text{H}_2 \) at 1 atm pressure.

Fig. 4.
SEM photomicrographs illustrating the lack of any microstructural changes of the surface morphology in the \( \text{Al}_2\text{O}_3 \) coating after 4 h heat-treatment at 1030°C in \( \text{H}_2 \). 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 pore "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/\(\alpha\)-\(\text{Al}_2\text{O}_3\) 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 \(\alpha\)-\(\text{Al}_2\text{O}_3\) and TiC.

Fig. 10. The atomic relationship between TiC (\(\{111\}\)) and \(\alpha\)-\(\text{Al}_2\text{O}_3\) (0001). Spheres marked C represent the close-packed oxygen atoms and spheres marked A and B represent the Ti-atoms in the close-packed (\(1\overline{1}1\)) plane.