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M. Danzinger, R. Haubner, B. Lux. INFLUENCE OF ETCHING THE TiC UNDERLAYER WITH CH₄/AlCl₃/H₂ ON THE CVD FORMATION OF KAPPA-Al₂O₃. Journal de Physique IV Proceedings, 1991, 02 (C2), pp.C2-579-C2-586. 10.1051/jp4:1991269 . jpa-00249859

HAL Id: jpa-00249859

<https://hal.science/jpa-00249859>

Submitted on 1 Jan 1991

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INFLUENCE OF ETCHING THE TiC UNDERLAYER WITH $\text{CH}_4/\text{AlCl}_3/\text{H}_2$ ON THE CVD FORMATION OF KAPPA- Al_2O_3

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Abstract: Al_2O_3 coatings deposited by CVD on cemented carbide inserts precoated with TiC did not lead to kappa- Al_2O_3 formation under laboratory conditions. An "etching treatment" with $\text{CH}_4/\text{AlCl}_3/\text{H}_2$ gas mixtures prior to Al_2O_3 deposition did however promote kappa- Al_2O_3 growth. A pronounced dependence of the amount of kappa- Al_2O_3 on the etching time and on the CH_4 concentration during the etching procedure was observed. A decrease in the deposition temperature increased the amount of the kappa- Al_2O_3 . The alpha:kappa- Al_2O_3 ratio was also influenced by the Co content in the cemented carbide inserts. Higher percentages of kappa- Al_2O_3 were observed for inserts with the lower Co concentrations than with the higher Co concentrations. However, no kappa- Al_2O_3 was deposited when CH_4 was added during Al_2O_3 deposition. Only the pure and undoped $\text{AlCl}_3/\text{CO}_2/\text{H}_2$ system led to the kappa- Al_2O_3 formation.

INTRODUCTION

Aluminum oxide exhibits different allotropic modifications /1/. Around 1000°C the alpha-modification is the stable phase, the second most commonly occurring phase is kappa- Al_2O_3 , which is less stable than the alpha phase. At temperatures above 1000°C , kappa- Al_2O_3 transforms to the alpha modification /2-5/.

Recent TEM investigations by C.Chatfield /5/ showed an epitaxial relationship between TiC and kappa- Al_2O_3 , which is supposed to improve the coating adhesion. Furthermore kappa- Al_2O_3 has a finer grain structure than the alpha-modification /3,7/. Kappa- Al_2O_3 formation and epitaxy occurred only on a clean, unoxidized TiC underlayer. If Ti_2O_3 or Ti_3O_5 was present, only the alpha- Al_2O_3 phase was obtained, and no epitaxy could be found in this case /5/.

CH_4 addition in an $\text{AlCl}_3/\text{H}_2/\text{CO}_2$ environment stabilized the kappa- Al_2O_3 /6/, which was deposited on a WC-Co substrate even without a TiC underlayer. Other investigations showed that Co, which is usually unevenly distributed over the TiC surface, acts as a catalyst for the heterogeneous decomposition of CO_2 to CO and monoatomic oxygen. This monoatomic oxygen can be responsible for the oxidation of TiC /5/. Also substrates, which were exposed to normal air and humidity for weeks oxidize. On such substrates under laboratory conditions always alpha- Al_2O_3 was obtained but never kappa- Al_2O_3 /6,8/.

The purpose of the present work was to study the influence of an "etching treatment" with $\text{AlCl}_3/\text{H}_2/\text{CH}_4$ gas mixtures, prior to the Al_2O_3 deposition, of the oxidized TiC underlayers on the formation of kappa- Al_2O_3 .

2 EXPERIMENTAL PROCEDURE

Both etching treatment of the TiC underlayers and the Al_2O_3 deposition were carried out in a hot-wall CVD reactor as described elsewhere /6/. The $\text{AlCl}_3/\text{CO}_2/\text{H}_2$ system was used for the Al_2O_3 deposition.

The substrates used were:

- SPUN GC 1025*: 76 % WC, 15 % (Nb,Ta,Ti)C, 8,5 % Co
8 μm CVD-TiC; denoted "WC 8,5 % Co"
- SPKN 1203 ED R*: 92 % WC, 2 % (Nb,Ta)C, 6 % Co
8 μm CVD-TiC; denoted "WC 6 % Co"

*: Grade SANDVIK COROMANT

2.1 Etching procedure for the TiC underlayers

Different gas flow sequences were studied (Fig. 1). These gas flow cycles and the parameters were varied as summarized in Table 1 and Fig.1.

Table 1: Investigated parameters of the predeposition etching treatment of TiC layers with $\text{AlCl}_3/\text{H}_2/\text{CH}_4$ gas mixtures

gas flow cycles	TiC etching	Al_2O_3 deposition gas
1	no treatment	$\text{AlCl}_3/\text{CO}_2/\text{H}_2$
2	$\text{AlCl}_3/\text{CH}_4/\text{H}_2$	$\text{AlCl}_3/\text{CO}_2/\text{H}_2$
3	$\text{AlCl}_3/\text{CH}_4/\text{H}_2$	$\text{AlCl}_3/\text{CO}_2/\text{H}_2 + \text{CH}_4$

Investigated etching parameters:

CH_4 concentration: 3, 6 mol%

Gas phase: 2 mol% AlCl_3 ; 94 mol% H_2

Etching time: 1, 3, 5, 7, 10 min

Etching temperature: 950, 1030°C

Co concentrations of the: 6, 8.5 %
substrates

2.2 Al_2O_3 deposition

For the Al_2O_3 deposition following the TiC etching treatment, the parameters listed in Table 2, were kept constant.

Table 2: Constant Al_2O_3 deposition parameters

Pressure: 50 torr

Temperature: 950, 1030°C

Gas mixture: 2 mol% AlCl_3 (purity: 99,99%)

4 mol% CO_2 (purity: 99,996%)

94 mol% H_2 (purity: 99,999%)

Deposition time: 60 min

Leakage rate: $< 5 \cdot 10^{-4}$ torr/l.s

Up-stream reactor: 20 mm diameter

Distance between substrates: 3 mm

2.3 Characterization of the Al_2O_3 coatings

Growth rates were calculated from the weight increases (weights measured before and after deposition).

Al_2O_3 modification was determined by X-Ray diffraction.

Al_2O_3 morphology and grain size were examined by SEM without sputtering a thin gold layer. This procedure allowed the identification of differences in contrast, which are characteristic for the alpha(white) and kappa(dark) Al_2O_3 /7/.

The incorporation of impurities, e.g. solid carbon, in the Al_2O_3 coatings can also lead to changes in the electrical conductivity and therefore misleadingly simulate alpha- and kappa- Al_2O_3 . In such cases only X-Ray diffraction clearly indicates the true Al_2O_3 modifications present.

Fig.1: Schematic illustration of the investigated gas flow cycles of the TiC etching treatment and Al_2O_3 deposition

3 RESULTS OF THE Al_2O_3 DEPOSITION

3.1 Normal Al_2O_3 deposition on a TiC underlayer: gas flow cycle 1

Al_2O_3 coatings deposited by gas flow cycle 1 always consisted of pure alpha- Al_2O_3 and were used as reference samples. These coatings were uniform and the sizes of well faceted crystals were in the range of 0.5 - 3.0 μm .

3.2 CH_4 treatment of the TiC prior to the Al_2O_3 deposition

without CH_4 during Al_2O_3 deposition: gas flow cycle 2

- temperature: 950°C

No influence on the Al_2O_3 growth rates was observed for either of the investigated substrates (Table 3). Kappa- Al_2O_3 was deposited only after etching the TiC underlayers with 6 vol% CH_4 for 1 min. The Co content of the substrates strongly influenced the alpha:kappa ratio. On the substrates with 6% Co the kappa- Al_2O_3 percentage was 100%, on the substrates with 8.5% Co it was about 24% (Table 3, Fig.2).

- temperature: 1030°C

The TiC underlayers etched at 1030°C for 1 to 7 min showed no changes in the Al_2O_3 growth rates; a decrease occurred on those etched for 10 min (Table 4).

Kappa- Al_2O_3 was deposited only after etching the TiC layers for 5 min with 3% CH_4 at 1030°C (Fig.3). All the other investigated etching parameters led to the formation of alpha- Al_2O_3 (Table 4). This can be explained by the influence of the deposited carbon on the TiC underlayer and by Co removal due to the formation of volatile CoCl_2 .

In all experiments compact and uniform Al_2O_3 coatings, consisting of well faceted crystals, were observed. The grain sizes (range of 0.5 - 3.0 μm) are the same as those in the coatings deposited without a TiC etching treatment (gas flow cycle 1).

Table 3: TiC etch treatment: Al_2O_3 modification and growth rate
no CH_4 during Al_2O_3 deposition: gas flow cycle 2
substrate: WC 6% Co; WC 8.5% Co; T=950°C;

TiC etch treatment CH_4 [mol%] time [min]		growth rate [$\mu\text{m}/\text{h}$]	Al_2O_3 modification alpha kappa [%]	
Substrate: WC 6% Co				
3	3	1.0±0.0	100	0
3	7	1.0±0.0	100	0
6	1	1.1±0.0	0	100
Substrate: WC 8.5% Co				
3	3	1.05±0.05	100	0
3	7	1.0 ±0.0	100	0
6	1	1.15±0.05	76	24

Table 4: TiC etching treatment: Al_2O_3 modification and growth rate
no CH_4 during Al_2O_3 deposition: gas flow cycle 2
substrate: WC 8.5% Co; T = 1030°C

TiC etch treatment CH_4 [mol%] time [min]		growth rate [$\mu\text{m}/\text{h}$]	Al_2O_3 modification alpha kappa [%]	
3	1	1.65±0.05	100	0
3	3	1.55±0.05	100	0
3	5	1.6 ±0.0	58	42
3	7	1.65±0.05	100	0
3	10	0.75±0.05	100	0
6	1	1.65±0.05	100	0
6	3	1.65±0.05	100	0
6	10	0.6 ±0.05	100	0

3.3 CH₄ treatment of the TiC prior to the Al₂O₃ deposition with CH₄ during Al₂O₃ deposition: gas flow cycle 3

The etching parameters and the addition of 3 and 6% CH₄ during Al₂O₃ deposition led to a strong decrease in the Al₂O₃ growth rate (Table 5). In the investigated range the addition of CH₄ during the Al₂O₃ deposition led to the formation of alpha-Al₂O₃ only. No kappa-Al₂O₃ was detected (Table 5).

Table 5: Influence of the TiC etch treatment and CH₄ addition during Al₂O₃ deposition on the Al₂O₃ modification and growth rate: gas flow cycle 3; substrate: WC 8.5 % Co; T=1030 °C;

TiC etch treatment		CH ₄ [mol%]	Al ₂ O ₃ deposition		
CH ₄ [mol%]	time [min]		growth rate [μm/h]	Al ₂ O ₃ modification alpha	kappa [%]
3	5	3	0.6 ± 0.05	100	0
3	10	3	0.60 ± 0.1	100	0
6	5	6	0.7 ± 0.05	100	0
6	10	6	0.55 ± 0.05	100	0

"White spots" on the Al₂O₃ surface, caused by differences in the conductivity, were found. These changes seemed to be caused by the incorporation of carbon. X-Ray diffraction showed only alpha-Al₂O₃. Al₂O₃ coatings with grain sizes from 0.05 to 0.50 μm were obtained. These coatings were much finer grained than the Al₂O₃ coatings deposited without CH₄ addition /8/.

Fig.2: Influence of the Co content in WC-Co on the Al₂O₃ deposition: TiC etch treatment: 6 mol% CH₄/1min (gas flow cycle 2) Temp.: 950 °C

Fig.3: Al₂O₃ coating morphology; TiC etch treatment: 3 mol% CH₄/5 min substrate: WC 8,5 % Co, Temp.: 1030 °C (gas flow cycle 2)

4 DISCUSSION OF THE RESULTS

As known from the literature a clean TiC underlayer is necessary to deposit kappa-Al₂O₃. Cobalt and oxygen prevent the deposition of kappa-Al₂O₃. During the TiC etching treatment with AlCl₃/CH₄/H₂, impurities are removed from the TiC surface, making the deposition of kappa-Al₂O₃ possible (Table 6). These "cleaning procedures" can be described by the following reactions:

Table 6: Stable phases formed thermodynamically under experimental conditions during the TiC etching

conditions: 2 mol% AlCl₃; 3, 6 mol% CH₄, 96 mol% H₂
0.1 mol% Ti₂O₃; 0.1 mol% Co

950°C

condensed phases

CH ₄	C(s)	Co	CoAl	TiC	Al ₂ O ₃
3	2.72	0.05	0.04	0.2	0.09
6	5.71	0.04	0.06	0.2	0.99

gaseous phases

CH ₄	CoCl ₂	AlCl ₃	AlCl ₂	AlCl	TiCl ₃
3	2.6·10 ⁻⁵	1.65	0.08	0.025	2.3·10 ⁻⁵
6	2.6·10 ⁻⁵	1.64	0.08	0.03	2.3·10 ⁻⁵

1030°C

condensed phases

CH ₄	C(s)	Co	CoAl	TiC	Al ₂ O ₃
3	2.7	-	0.09	0.2	0.09
6	5.7	-	0.09	0.2	0.09

gaseous phases

CH ₄	CoCl ₂	AlCl ₃	AlCl ₂	AlCl	TiCl ₃
3	3·10 ⁻⁵	0.22	0.04	0.39	8·10 ⁻⁶
6	8·10 ⁻⁵	1.45	0.16	0.1	3.4·10 ⁻⁵

These calculations indicate that Ti₂O₃ should react completely. Two different reactions are possible, one being the reduction and carburization of Ti₂O₃ to TiC by the CH₄ addition (reaction 2) and the other one the reaction between Ti₂O₃ and AlCl₃ to form Al₂O₃ (reactions 1). The deposition of solid carbon is thermodynamically possible at all CH₄ concentrations (reaction 4).

Two different Co reactions are predicted by thermodynamics, a CoAl alloy and the volatile CoCl₂. Since the CoAl alloy should have formed under all etching conditions, it apparently has no influence on the Al₂O₃ modification (reaction 3).

The etching parameters CH₄ concentration, etching time, temperature and Co concentrations strongly influenced the formation of kappa-Al₂O₃. The experimentally observed relationships are reflected by the calculations given in Table 7. Fig.4 summarizes these results.

Table 7: Influence of the TiC etching time and CH_4 concentration on the Al_2O_3 modification: no CH_4 during Al_2O_3 deposition

etching time	CH_4 concentration	Al_2O_3 modification
short	low	alpha
short	high	alpha-kappa
long	low	alpha-kappa
long	high	alpha

This dependence of the kappa- Al_2O_3 formation on the etching time and CH_4 concentration can be explained as follows:

Etching with high CH_4 concentrations for short periods, or with low CH_4 concentrations for longer periods, totally removes oxygen from the surface and no carbon is deposited. Kappa- Al_2O_3 formation becomes possible on these cleaned surfaces because of the epitaxy of TiC.

Etching times which are too long and CH_4 concentrations which are too high cause the deposition of carbon, which disturbs the epitaxial nucleation of kappa- Al_2O_3 on TiC. On the other hand etching times which are too short do not remove all the Ti_xO_y .

Summarized, the etching parameters must be precisely controlled in order to remove all of the oxygen from the TiC underlayers but without permitting any solid carbon deposition.

Fig.4: Influence of the CH_4 concentrations and etching times on the kappa- Al_2O_3 formation

5 CONCLUSION

TiC coatings are oxidized by air and humidity if removed after coating from the reaction chamber. In a subsequent Al_2O_3 deposition on such substrates no kappa- Al_2O_3 was formed.

The experimental results from etching the TiC underlayers with different $\text{CH}_4/\text{AlCl}_3/\text{H}_2$ gas mixtures followed by the Al_2O_3 deposition without CH_4 indicated different parameters which permit the preparation of an oxygen-free TiC underlayer.

The etching parameters which influenced the alpha:kappa- Al_2O_3 ratio are:

- the lower CH_4 concentration during TiC etching caused longer etching times for the deposition of kappa- Al_2O_3 ,
- the amount of kappa- Al_2O_3 could be increased by decreasing the etching and deposition temperature,

- the lower Co concentration led to a higher amount of $\kappa\text{-Al}_2\text{O}_3$.

For industrial application it is important that CO_2 be added at a specific interval after the AlCl_3/H_2 gas mixture is added in order to allow full coverage of the virgin TiC surface with adsorbed AlCl_3 . This prevents the TiC underlayers from being oxidized by CO_2 and H_2O .

6 ACKNOWLEDGEMENT

The authors wish to thank SANDVIK AB, Stockholm, for supplying free-of-charge specimens and for financial support. Helpful discussions with Dr. Mats Sjöstrand and particularly Dr. Jan Lindström are gratefully acknowledged.

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