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INFLUENCE OF CH₄ AND Ar ON THE MORPHOLOGIES OF Al₂O₃ - CVD COATINGS

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ABSTRACT The influence of CH₄ and Ar addition to the AlCl₃/CO₂/H₂ system on the morphology and grain size of Al₂O₃ CVD deposition was examined. The Al₂O₃ growth rate decreased at a CH₄ concentration of 10 vol%. High concentrations of CH₄ caused fine grained Al₂O₃ crystals but these coatings were porous and consisted of branched crystals. High Ar additions of more than 27 mol% led to the formation of more monolytic Al₂O₃ coatings. The simultaneous addition of CH₄/Ar mixtures during deposition allowed the formation of uniform, compact and extremely fine grained Al₂O₃ coatings. The adhesion of the Al₂O₃ coatings was measured by a simple Rockwell indentation test. The grain refinement is explained by a carbon codeposition resulting from methane pyrolysis.

1 INTRODUCTION

In coating technology the control of the layer structure is of great importance for better performance /1/. The grain size influences the surface roughness of a coating and its mechanical properties. Fine grained coatings can be advantageous for tool life in cutting and milling operations /2/. Dopant compounds can be intentionally added to CVD reaction gases to modify the Al₂O₃ deposition /3,4/. Investigations by H. Altena /14/ indicated a strong reduction in Al₂O₃ grain size resulting from small additions of CS₂ to the reaction gas mixture. In this case carbon was found to be responsible for the observed grain refinement. Organic aluminum compounds have also been used for grain refinement /8-11/. Different metallic (Cr, W) and non-metallic (P, Se, Te) doping compounds exhibited a pronounced grain refining effect on CVD-Al₂O₃. This grain refinement effect was found to be strongly dependent on the doping concentrations /5,6/.

In the present work the influence of different concentrations of methane and argon on the morphology and grain size of CVD-Al₂O₃ was investigated.

2 EXPERIMENTAL METHODS**2.1 Experimental procedure**

The experiments were carried out in a hot-wall CVD reactor, using an AlCl₃/CO₂/H₂ gas mixture. After checking the leakage rate the entire

apparatus was flushed with a H_2/Ar gas mixture for each run. When all parts of the coating apparatus reached the required temperature, $AlCl_3$ and H_2 were introduced into the reactor, followed 2 min later by CO_2 . The deposition parameters are listed in Table 1.

2.2 Characterization of the Al_2O_3 coatings

The Al_2O_3 growth rate was calculated from the weight increase after the deposition.

The structure and morphology of each Al_2O_3 coating was examined by SEM before and after sputtering with a thin gold layer. Differences in the contrast, which are caused by the different electrical conductivities of alpha- and kappa- Al_2O_3 , allow the determination of the Al_2O_3 modifications. For these procedures the Al_2O_3 coatings were investigated by SEM without sputtering a thin gold layer /7,18/.

The Al_2O_3 grain sizes were measured from SEM photos using a digitizer tablet; the grain size distributions were calculated with a computer program.

The adhesion of each Al_2O_3 coating on the TiC underlayers was characterized by the Rockwell indentation test method /20/. This procedure permitted the viewer a judgement of the quality of the adhesion. The load for these tests was 62,5 kg.

Table 1: Constant and varied Al_2O_3 deposition parameters

Constant deposition parameters:

Temperature:	1030 °C
Pressure:	65 mbar
Reaction gas:	4 mol% CO_2 (purity: 99.998%)
	2 mol% $AlCl_3$ (99.99%)
	94 mol% H_2 (99.999%)
Total flow rate:	25.5 l/h
Up stream reactor:	20 mm diameter
Leakage rate:	$< 5 \cdot 10^{-4}$ torr/l.s
Substrate:	76.5% WC, 15% (Ta,Ti,Nb)C, 8.5% Co
	8 μm CVD-TiC (denoted: WC-Co/TiC)
Distance between substrates:	3 mm

Varied deposition parameters:

CH_4 [mol%;l/h]	Ar [mol%;l/h]	gas velocity [m/s]	$CH_4:AlCl_3$	$CH_4:CO_2$
0	0	1.5	--	--
	16.5 ; 5	1.8	--	--
	28.2 ; 10	2.09	--	--
	43.9 ; 20	2.68	--	--
3 ; 0.76	0	1.55	1.5	0.75
	16.0 ; 5	1.84	1.5	0.75
	27.5 ; 10	2.13	1.5	0.75
	43.2 ; 20	2.72	1.5	0.75
4 ; 1.02	27.4 ; 10	2.15	2.0	1.0
5 ; 1.27	27.2 ; 10	2.16	2.5	1.25
6 ; 1.53	0	1.59	3.1	1.5
	15.6 ; 5	1.88	3.1	1.5
	27.0 ; 10	2.18	3.1	1.5
	42.6 ; 20	2.77	3.1	1.5
10 ; 2.55	26.3 ; 10	2.24	5.1	2.5

3 RESULTS

3.1 Al₂O₃ growth rate

- Effect of CH₄ addition: No changes in the growth rates were observed (1.45-1.65 μm/h) up to a doping concentration of 6 vol% CH₄.
- Effect of Ar addition / influence of the flow rate: All Ar additions led to the same growth rate as observed for the undoped AlCl₃/H₂/CO₂-system, in the range of 1.4-1.65 μm/h (Fig.1).
- Effect of different CH₄/Ar gas mixtures: At 10 mol% CH₄ and 26.3 mol% Ar the growth rate decreased slightly to about 1.2 μm/h (Fig.1).

3.2 Al₂O₃ coating morphology and grain size

- The grain sizes and their distribution are shown in Table 2 and Fig.2.
- Effect of CH₄ addition (without Ar): The addition of 3 vol% CH₄ led to a slight increase in the grain size (Fig.2a,b). Concentrations of 6 mol% CH₄ and more led to the formation of ultrafine crystals (0.02 μm). The coatings were uneven, porous and consisted of cauliflower-like crystals (Table 2, Fig.2b,3).
 - Effect of Ar addition (without CH₄) / influence of the flow rate:
 - * Low Ar concentrations showed no influence on the coating morphology; the average grain size was 0.6 μm (Fig.2a,b).
 - * The addition of 28.2 and 43.9 mol % Ar led to the formation of coarser and plate - like Al₂O₃ crystals; the average grain sizes increased to 1.4 and 1.8 μm. (Table 2, Fig.2a,3).
 - Addition of different CH₄/Ar mixtures:
 - * With a gas mixture of 3 mol% CH₄ and 16,5 mol% Ar the grain size increased slightly (Fig.3).
 - * Extremely fine grained Al₂O₃ coatings at 6 mol% CH₄ became denser when Ar was added in the range of 28.2 - 43.9 mol%. The porosity strongly decreased. For these CH₄ additions no changes in the grain sizes due the Ar additions were observed (Fig.2,3).

3.3 Adhesion of the Al₂O₃ coatings

The different CH₄ and Ar additions did not influence the adhesion of the Al₂O₃ coatings. In all experiments the observed crack patterns in the coatings after the indentation procedure and the chipping were the same as those in the coatings deposited with the pure AlCl₃/CO₂/H₂ system (Fig.4).

Table 2: Distribution of the Al₂O₃ grain sizes and the most frequently observed grain sizes

addition of CH ₄ [mol%]; [l/h]	Ar [mol%]; [l/h]	Al ₂ O ₃ grain size		
		range [μm]	most frequent [μm]	[%]
0	0	0.2 - 2.6	0.6	34
	16.2 ; 5	0.2 - 2.4	0.6	27
	28.2 ; 10	0.4 - 3.6	1.4	22
	43.9 ; 20	0.4 - 3.8	1.8	26
3 ; 0.76	0	0.4 - 2.8	0.8	24
	16.0 ; 5	0.2 - 2.4	1.0	26
	27.5 ; 10	0.4 - 3.0	1.2	26
	43.2 ; 20	0.2 - 3.6	1.4	30
4 ; 1.02	27.4 ; 10	0.2 - 2.2	0.6	32
5 ; 1.27	27.2 ; 10	0.1 - 1.0	0.2	26
6 ; 1.53	0	0.02 - 0.1	0.04	30
	15.6 ; 5	0.02 - 0.1	0.04	28
	27.0 ; 10	0.02 - 0.1	0.04	20
	42.6 ; 20	0.02 - 0.1	0.04	24
10 ; 2.55	26.3 ; 10	0.02 - 0.1	0.04	32

Fig.1. Changes in the Al₂O₃ growth rates caused by CH₄ and Ar

Fig.2a: Influence of CH₄ and Ar on the distribution of the Al₂O₃ grain sizes

Fig.2b: Changes of the most frequently Al₂O₃ grain sizes caused by different CH₄ and Ar additions

Fig. 4: Adhesion of the Al₂O₃ layers
Indentations of a Rockwell diamond cone; load: 62,5 kg

Fig.3: Influence of CH₄ and Ar on the Al₂O₃ coating morphology
 CH₄ addition: 0, 3, 5, 6 mol%
 Ar addition: 0 - 43.9 mol%

4 DISCUSSION OF THE RESULTS

4.1 alpha-kappa Al_2O_3

No differences in the contrast of the Al_2O_3 coatings were observed. The flow of the gases in these experiments did not lead to the formation of kappa- Al_2O_3 /7/. The typical differences between the electrical conductivities of alpha- and kappa- Al_2O_3 were not found in any of the specimens produced /18/. Also, X-Ray diffraction showed only pure alpha- Al_2O_3 under all deposition conditions.

4.2 Mechanism of Al_2O_3 deposition

4.2.1 Pure and undoped $\text{AlCl}_3/\text{CO}_2/\text{H}_2$ -system

A. Water formation in the gas phase by a homogeneous reaction mechanism:

The free gas volume around an insert has a strong influence on the growth rate of Al_2O_3 . Observations by J.Lindström /21/ and J.Peng /22/ showed that the Al_2O_3 growth rate increases when the free gas volume around an insert is increased. This behavior can be explained largely by a mechanism involving a homogeneous reaction of water formation which is rate controlling.

B. Water formation on the substrate surface by a heterogeneous reaction mechanism:

This mechanism is characterized by the adsorption of H_2 and CO_2 on the substrate surface where they react to H_2O , forming Al_2O_3 with the adsorbed AlCl_3 . A catalytic influence of Al_2O_3 on the formation of H_2O is reported by Y.Amenomiya /16/, whose results indicated that the rate determining step of the Al_2O_3 deposition is the heterogeneous mechanism /17/.

Which mechanism occurs depends on various deposition parameters and especially on the reactor geometry. In our experiments, where the distance between the substrates was 3 mm, the homogeneously formed water is about 30% of the total water production, with 70% being heterogeneously formed /21/.

4.2.2 Addition of CH_4 to the pure $\text{AlCl}_3/\text{CO}_2/\text{H}_2$ -system

A. Effect of CH_4 addition on the homogeneous water gas reaction:

The water formed during the deposition process in our reactor geometry is totally consumed. Any changes of the Al_2O_3 growth rate would be caused by a shift in the water reaction.

Formation of Al_2O_3 crystals in the gas phase was not observed.

B. Incorporation of solid carbon / formation of carbon films:

The effect of CH_4 on heterogeneously formed H_2O is difficult to determine clearly since CH_4 decomposes at 1030°C into C(s) and H_2 as shown by thermodynamical calculations (Table 3). However, solid carbon, which should form by CH_4 decomposition, should have no influence on the H_2O formation by the CO_2/H_2 reaction /23/.

Earlier investigations using SIMS technique showed that with CS_2 additions carbon was incorporated in the Al_2O_3 coatings /12/. These results indicated that carbon should be deposited at the Al_2O_3 grain boundaries, forming very thin films, so-called "C-networks". The carbon content was found to be between 0.07-0.17at%.

The formation of Al_4C_3 was not detected and should not be formed thermodynamically as shown in Table 3.

C: Explanation of the grain refinement due to CH₄ addition:

Based on the results and the above discussion the grain refining effect of CH₄ can be explained as follows:

A codeposition of carbon with Al₂O₃ apparently stops the regular growth of the Al₂O₃ crystal facets. Small carbon particles or films on the crystal surfaces enhance the branching tendency of the growing Al₂O₃ crystals and lead consequently to an extreme grain refinement /26/. However, high porosity occurs.

4.2.3 Effect of Ar addition to the pure AlCl₃/CO₂/H₂ system

Ar addition led to an increase of the total flow rate. Experiments showed that flow rates higher than 0,8 m/s no longer increased the Al₂O₃ growth rate /25/. In our experiments the flow rates were in the range of 1.5-2.8m/s. No influence on the Al₂O₃ growth was observed within this range, confirming the literature.

The addition of pure Ar (no CH₄) caused coarser, more monolytic Al₂O₃. This can be explained by the lower AlCl₃/CO₂ concentrations in the gas phase and consequently the lower supersaturation of the reactive species at the substrate surface.

4.2.4 Simultaneous addition of CH₄ and Ar

These additions led to dense, non-porous, and extremely fine grained Al₂O₃ coatings. The only indication for this effect of Ar in the case of CH₄/Ar addition is the pronounced decrease in the pore formation. The lower supersaturation leads to the formation of coarser crystals and reduces the porosity between the branched Al₂O₃ crystals. Pore formation is thus prevented. The layer growth rate itself is not influenced by this effect due to the higher flow rates of AlCl₃ and H₂O. Similar effects were found during CVD-diamond deposition where the gas flow rate has no significant influence on diamond growth rate, but on the mass flow of reactive carbon species /24/.

The data listed in Table 3 were calculated with the computer program "Ekvicalc 1.2, Svensk Data".

Table 3: Thermodynamic calculations for C compounds formed from CH₄ during Al₂O₃ deposition
 conditions: T=1030°C; p=50 torr
 2 mol% AlCl₃, 4 mol% CO₂, 94mol% H₂

CH ₄ addition	compounds formed from CH ₄ [mol%]				
	C _{solid}	CH ₄	C ₂ H ₂	C ₂ H ₄	CH ₃
3 mol%	2.93	0.045	7.0·10 ⁻⁵	1.1·10 ⁻⁵	1.3·10 ⁻⁶
4	3.93	0.046	7.1·10 ⁻⁵	1.1·10 ⁻⁵	1.3·10 ⁻⁶
5	4.93	0.047	7.2·10 ⁻⁵	1.1·10 ⁻⁵	1.3·10 ⁻⁶
6	5.93	0.047	7.3·10 ⁻⁵	1.2·10 ⁻⁵	1.3·10 ⁻⁶
10	9.93	0.051	7.8·10 ⁻⁵	1.3·10 ⁻⁵	1.4·10 ⁻⁶

Under these Al₂O₃ deposition conditions neither Al₄C₃ nor AlO_xC_y is formed.

5 CONCLUSION

An extreme grain refinement of CVD-Al₂O₃ at normal growth rates is possible by adding 6 mol% CH₄. Grain sizes were decreased to about 0.02 μm, but the layers were uneven and porous. Ar additions decreased the porosity of these fine grained and non-uniform Al₂O₃ coatings.

Based on these results it is possible to deposit very fine grained Al_2O_3 layers even and compact by the simultaneous addition of CH_4 and Ar at suitable concentrations.

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