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GRAIN REFINEMENT OF CVD TiC LAYERS BY AlCl_3 , ZrCl_4 AND BCl_3 IMPURITIES

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Abstract - The influence of small amounts of AlCl_3 , ZrCl_4 and BCl_3 on CVD of TiC with a $\text{TiCl}_4/\text{H}_2/\text{CH}_4$ gas mixture under reduced pressure was investigated. Grain refinement of TiC coatings could be obtained by adding dopant compounds at suitable concentrations. Their interactions are explained by the formation of co-deposited phases which interfere with the growth of TiC crystals and promote surface nucleation. The effectiveness of dopants to decrease the grain size is explained by the formation of thin films on the growing TiC crystals having a different chemical bonding than TiC.

1. INTRODUCTION

Cutting tools coated with TiC by chemical vapor deposition (CVD) are widely used today because of their high wear resistance and toughness. Many investigations have been carried out to further enhance the cutting performance of coated tools. One approach is to develop new coating materials such as mixed layers (e.g. Ti-Zr-C [1], Al-O-N [2]) or mixed crystals (e.g. Ti-Al-N [3], Ti-B-C [4]). Another approach is to improve the properties of the coating materials by forming a finer grained structure or a more uniform layer thickness, which can be achieved by the improvement of the technological process, for example by controlling impurities [5-6].

The ternary systems of Ti-Al-C, Ti-Zr-C and Ti-B-C have already been investigated using the CVD method [1,7] and the PVD method [3,8-9]. It was also reported [7,10] that Al or Mg as dopants in the deposition process of TiC had a positive catalytic influence on the deposition rate and the grain refinement. However, there is still no theoretical explanation for the mechanism of this influence. In the work reported here the influence of small amounts of AlCl_3 , ZrCl_4 and BCl_3 additions on the deposition process and on the morphologies of TiC coatings was investigated.

2. EXPERIMENTAL PROCEDURE

The experimental setup for TiC deposition is described in Fig.1. The TiC CVD process was carried out with the system $\text{TiCl}_4/\text{H}_2/\text{CH}_4$ under the conditions indicated in Table 1. ISO K20 cemented carbide (commonly called WC-Co) was used for the substrates. Before deposition all substrates were cleaned with methanol. The solid impurities AlCl_3 and

ZrCl_4 were sublimated. The doping concentration was controlled by the temperature in a sublimator and the flow rate of the H_2 carrier gas. A known quantity of BCl_3 was feed into an Ar-filled bottle with constant volume. During the BCl_3 addition to the CVD reactor the amount of B added was controlled by the pressure drop occurring in the bottle.

1. Flow meter
2. Pressure gauge
3. TiCl_4 evaporator
4. Saturator
5. Isothermal water-circulating unit
6. Regulating valve
7. Sublimator for impurities
8. Thermocouple
9. Reaction chamber
10. Liquid N_2 cold trap
11. Mercury pressure gauge

Fig.1: Schematic diagram of CVD equipment

Table 1: Experimental conditions

Constants	Temperature	: 1050°C
	Pressure	: 50 torr
	Total flow rate	: 20 l/h
	TiCl_4 flow rate	: 1 l/h
	CH_4 flow rate	: 2 l/h
	Deposition time	: 1 h
Variables	Doping concentrations	
	AlCl_3	: 0, 10, 1.000, 100.000 (mol-ppm*)
	BCl_3	: 0, 1.000, 100.000, 1.000.000 (mol-ppm*) (carried by 5 l/h Ar)
	ZrCl_4	: 0, 10, 1.000, 10.000 (mol-ppm*) (carried by 5 l/h H_2)

*: The unit "mol-ppm" refers to the concentration per mole TiCl_4 and not to the total gas volume.

3. RESULTS

3.1. Growth rate

The TiC growth rate did not change when $ZrCl_4$ was added as a dopant, but increased with the addition of $AlCl_3$ and of BCl_3 . With $AlCl_3$ the growth rate increased at low and decreased at high doping concentrations. However, for BCl_3 , it increased with doping concentration higher than 100,000 ppm (Fig.2).

Fig.2: Influence of impurities on the deposition rate of the TiC coating

3.2. X-ray diffraction analysis

Table 2 lists the solid phases deposited after the CVD reaction with different impurities and concentrations. For $AlCl_3$ and $ZrCl_4$ no phases other than TiC and eta-phase (W_6Co_6C) could be detected, while for BCl_3 the TiB_2 and CoWB peaks were observed at dopant amounts of 100,000 ppm and higher.

Table 2: Influence of impurities on deposited phases and relative X-ray intensities

concentrations	relative X-ray intensities of deposited phases $AlCl_3$	$ZrCl_4$	BCl_3
0 ppm	TiC (100%) eta (< 5%)	TiC (100%) eta (< 5%)	TiC (100%) eta (10%)
10 ppm	TiC (100%) eta (< 5%)	TiC (100%) eta (< 5%)	—
1,000 ppm	TiC (100%) eta (< 5%)	TiC (100%) eta (< 5%)	TiC (100%) eta (12%)
10,000 ppm	—	TiC (100%) eta (< 5%)	—
100,000 ppm	TiC (100%) eta (< 5%)	—	TiC (100%), CoWB (5%) eta (10%), TiB_2 (3%)
1,000,000 ppm	—	—	TiC (50%) TiB_2 (100%)

3.3. Grain size

The changes of the TiC crystal habit at different doping concentrations and impurities are shown in Fig.3. Grain refinement of the TiC coating could be obtained by doping with AlCl_3 or BCl_3 . For both impurities there were so-called "critical concentrations" at which the grain refinement effect showed a maximum [11]. Below the critical concentrations the grain size decreased with increasing dopant concentration and above it increased with increasing dopant concentration. The critical concentrations were different for each impurity. The TiC crystal morphology changed remarkably when BCl_3 exceeded the critical concentration. This change could be due to the increasing amounts of TiB_2 deposition.

Fig.3: Grain size of TiC coatings deposited at different impurity concentrations

4. DISCUSSION

The grain refinement of the TiC coating by AlCl_3 or BCl_3 can be explained by the formation of new phases which were co-deposited simultaneously with the TiC by the reaction between the doped impurity and the reaction gas. Similar to an intermediate layer in a multilayer coating, a co-deposited phase inhibits the continued growth of the crystals and forces a new nucleation step on the surface, which basically promotes the grain refinement of the main constituent.

In the case of BCl_3 doping, X-ray diffraction and electron probe micro analysis showed TiB_2 formation and co-deposition when high BCl_3 amounts (above 100,000 ppm) were added. The co-deposition of the two phases leads in this case to the grain refinement. However with AlCl_3 and ZrCl_4 no co-deposited phases could be detected, either by X-ray diffraction or by electron probe micro analysis, at any of the

concentrations. This might be due to the very small amounts of the co-deposited phase, i.e. amounts below the limit of detection (0.1 at%) for electron probe micro analysis. The reason that such small amounts of the co-deposited phase influence the grain size could be a difference in chemical bonding. These films are very thin and could even be monomolecular. For AlCl_3 addition the carbide Al_3C_4 , which has an ionic bonding, might be the co-deposited phase. Such a mechanism could be explained as follows:

Stage 1: TiC crystals grow on the substrate surface.

Stage 2: A very small amount of Al_3C_4 (e.g. an extremely thin film) might deposit on the TiC crystal facets. Such a simultaneous deposition of a phase with ionic bonding should stop the further growth of TiC crystals.

Stage 3: New heterogeneous nucleation of TiC must occur on this extremely thin film.

The consequence is a reduction of the grain size. This mechanism is shown schematically in Fig.4. Just a small amount of Al_xC_y on the crystal surface should restrain the TiC crystal growth more effectively than ZrC or TiB_2 because of the greater difference in chemical bonding as well as the structural difference between the TiC (metallic bonding, cubic structure) and Al_xC_y (ionic bonding) than between the TiC and ZrC or TiB_2 (metallic bonding). Table 3 shows the chemical bonding and structures of selected hard materials.

For the ZrCl_4 additions, no effect on the grain refinement was observed. It can be assumed that a new nucleation of TiC is not necessary during the co-deposition of the two phases because their chemical bondings and structures are similar to those of TiC.

Stage 1: TiC crystal growth

Stage 2: Formation of an extremely thin film of Al_xC_y and stopping of the TiC crystal growth.

Stage 3: Nucleation of TiC on the extremely thin film

Fig.4: Mechanism of the grain refinement of the TiC coating by the co-deposition of Al_xC_y

Table 3: Chemical bonding and structures of hard materials

Phase	Bonding	Structure
TiC	metallic	cubic
TiN	metallic	cubic
ZrC	metallic	cubic
ZrN	metallic	cubic
TiB ₂	metallic	hexagonal
Al ₄ C ₃	ionic	hexagonal
AlN	ionic	hexagonal

Similar results were reported by P.Wilhartitz et al.[12]. They analyzed Al₂O₃-CVD with CS₂ additions using SIMS and reported that carbon incorporated in the Al₂O₃ coating appeared to be responsible for the grain refinement of this coating [13]. These results can be explained by the same mechanism: The epitaxial growth of the crystal facets is stopped because of the co-deposition of carbon which has a different chemical bonding (covalent) than Al₂O₃(ionic); new nucleations have to occur to continue the deposition, which leads to the grain refinement.

5. CONCLUSION

Small amounts of AlCl₃ and BCl₃ added to the commonly used TiCl₄/H₂/CH₄ CVD gas mixture can strongly influence the layer growth and the grain size, while ZrCl₄ doping showed no influence. The differences in the influence on the grain size due to the various impurities can be explained by the differences in chemical bonding between the deposited impurity compounds and the TiC.

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