NUCLEATION AND GROWTH IN TiN CVD ON GRAPHITE SUBSTRATES

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ABSTRACT

Morphology and preferential crystallographic orientation were studied in TiN CVD on graphite substrates. Three types of isostatically pressed graphite were used, both in as delivered and in purified condition. Using X-ray diffractometry and optical as well as scanning electron microscopy, the results were analyzed after various deposition times. Three deposition temperatures: 850, 900 and 950°C were used. Except for the deposition temperature, the process conditions were not varied. In an experiment where instead of TiCl_4 , H_2 and N_2 only TiCl_4 and H_2 were used as reactants, it was demonstrated that the deposition of TiN on graphite substrates is probably preceded by the formation of a monolayer of TiC.

1. INTRODUCTION

TiN is widely used as a coating in applications requiring wear resistance e.g. cutting tools. TiN may be deposited either by PVD processes^{1,2} or by CVD processes. PVD processes have the advantage that the substrate does not need to be heated to high temperatures like in CVD processes. On the other hand CVD processes often provide better adherence of the coating to the substrate.

Some studies have been performed in order to determine the relation between CVD process conditions, growth rate and microstructure^{3,4,5}. We were interested in the influence of the substrate on nucleation behaviour, microstructure and preferential texture. Various grades of graphite were used as substrate material, whereas in previous studies substrates mostly consisted of steel^{6,7,8} or hardmetal^{9,10,11,12,13}.

We expected that nucleation, in thin (1 - 4 μm) TiN coatings, would be affected by impurities and that this might have an effect on the preferential texture and microstructure of the coatings. Preferential texture and microstructure are known to have a strong effect on the mechanical properties of the coatings.

In this study TiCl_4 , N_2 and H_2 were used as reactants. The overall deposition reaction at temperatures over 800°C is:

The process conditions have been studied by Kim and Chun⁴. Kim and Chun found that the deposition process is dominated by a surface reaction when the deposition temperature is kept below 1000°C (We varied the deposition temperature from 850°C to 950°C). Nucleation and kinetics of TiN CVD were studied before by Roman et al.¹⁴.

2. EXPERIMENTAL PROCEDURE

TiN was deposited in an industrial vertical hot wall reactor. The gas feed to the reactor was obtained by mixing 70 vol. % H_2 gas, 29 vol. % N_2 gas and 1 vol. % $TiCl_4$ vapour. The gaseous mixture entered the reactor at the bottom. The total reactor pressure was 760 Torr.

Three types of graphite were selected as substrate materials (UT91, UT145 and UT218). The samples were small platelets (length and width 40 mm, thickness 5 mm), which were all ground and polished. In our experiments we used purified and unpurified samples. The overall concentration of contaminating elements was smaller than 10 ppm.

The deposition experiments were carried out at three different reactor temperatures: 850 °C, 900 °C and 950 °C. Four different deposition times were used: 10, 20, 30 and 360 minutes.

In order to verify the hypothesis that a monolayer of TiC would be formed prior to any TiN deposition, a CVD experiment was carried out at 850°C for one hour with a mixture of 99 vol. % H_2 gas and 1 vol. % $TiCl_4$ vapour.

All substrates were analyzed prior to, as well as after coating, by Scanning Electron Microscopy (JEOL JSM 840A), Energy Dispersive X-ray analysis (Tracor Northern 5500) and X-ray Diffraction (Rigaku Geigerflex D-max II).

3. RESULTS

The morphology of the TiN layers was characterized by analyzing the coated substrates by SEM. Differences in coating morphology were observed in coatings deposited with short deposition times (deposition time < 30 minutes). The following results were obtained:

- No strong variations in coating morphology were observed in TiN layers which were deposited at a temperature of 850°C.
- At a deposition temperature of 900°C (see fig. 1,2 and 3) an increase in coating roughness was observed when UT91, UT218 and UT145 is used as substrate material respectively.
- TiN layers deposited at a 950°C, showed nearly the same differences in coating morphology as the TiN layers deposited at 900°C. TiN layers deposited at 950°C were less rough than TiN layers deposited at 900°C.
- The coatings deposited on unpurified substrates were smoother than coatings deposited on purified substrates.
- These variations in coating morphology were not found after longer deposition times.

XRD measurements were carried out in order to find an explanation for the observed variations in coating morphology. The aim of these measurements was to try to find a possible preferential texture in the (un)coated substrates or a possible variation in crystallinity. Differences in preferential texture might explain the observed variations in coating morphology.

The purity of the substrates was checked by EDX. The surfaces and cross-sections of the substrates were analyzed. No impurities were found in any of the samples.

From the data obtained by XRD measurements we could conclude that, compared with the other substrates, the UT145 substrates are more crystalline. The X-ray data (see appendix 1) were used to calculate texture coefficients using a method by Barret and Massalski¹⁵. They define the texture coefficient as:

$$TC(hkl) = I(hkl)/I_0(hkl) \{ (1/n) \sum (I(hkl)/I_0(hkl)) \}^{-1} \dots 2$$

In which:

TC	=	texture coefficient
$I(hkl)$	=	a measured intensity of the (hkl) plane
$I_0(hkl)$	=	the standard intensity listed in the JCPDS powder diffraction file
n	=	the number of reflections

The formation of TiC was demonstrated in an experiment (see appendix 2) in which $TiCl_4$ and H_2 were used as reactants, UT91p was chosen as substrate material. The deposition was carried out for one hour at a temperature of 850°C.

Table 1: Preferential texture in the graphite substrates and in the TiN CVD-layers deposited, at a temperature of 850°C, on them, as a function of the deposition time.

Sample ¹⁾	Deposition time [min.]				
	0	10	20	30 ²⁾	360
UT 91 u	(002)	(200)	(200)	(111)	(311)/(220)
UT 91 p	(002)	(200)	(200)	(111)	(311)/(220)
UT145 u	(002)	(200)	(200)	(200)	(311)
UT145 p	(002)	(200)	(200)	(200)	(220)
UT218 u	(002)	(200)	(200)	(111)	-
UT218 p	(002)	(200)	(200)	(200)	(220)

¹⁾ u = unpurified

p = purified

²⁾ The 30 min. TiN deposition was interrupted after 10 min. After cooling down to room temp., some of the specimen were taken out of the reactor. Then the reactor was heated up again and TiN deposition was resumed for another 20 min.

Table 2: Texture of TiN coatings deposited on various graphite substrates during 6 hours at 850°C, 900°C and 950°C.

Sample ¹⁾	Deposition temperature [°C]		
	850	900	950
UT 91 u	(311)/(220)	(311)/(220)	(220)
UT 91 p	(311)/(220)	(311)/(220)	(220)
UT145 u	(220)	(220)	(220)
UT145 p	(220)	(220)	(220)
UT218 p	(220)	(220)	(220)

¹⁾ u = unpurified

p = purified

In the figures 1,2 and 3 the differences in coating morphology for TiN coatings, deposited for 20 minutes at a deposition temperature of 900°C, is shown.

Fig. 1: Morphology of a 3.5 µm thick Tin coating grown on substrate UT91p at 900°C. Magnification 3,000X (SEM).

Fig. 2: Morphology of a 3.5 μm thick TiN coating grown on substrate UT145p at a deposition temperature of 900°C. Magnification 3,000X (SEM).

Fig. 3: Morphology of a 3.5 μm thick TiN coating grown on substrate UT218p at a deposition temperature of 900°C. Magnification 3,000X (SEM).

At a deposition temperature of 950°C the deposition rate was 4 $\mu\text{m}/\text{h}$. The morphology of the TiN coatings produced at that temperature all showed a surface dendritic structure from which the initial nucleation proceeds in five directions (see fig. 4).

Fig. 4: Morphology of a 26 mm thick TiN coating grown on substrate UT218p. Magnification 4,000X (SEI).

4. DISCUSSION

In the case of high vacuum thin film deposition, in particular for physical deposition processes, the theory has been well developed and verified by in situ electron microscopic observations^{16,17}. In the case of atmospheric CVD processes, this tends to be rather more complicated because so many factors may influence nucleation and growth processes.

In the experiments described here, the texture of the thin TiN layer may be caused by the formation of $\text{TiC}/\text{TiC}_x\text{N}_y$ nuclei. We assume that a reaction occurs between carbon atoms of the substrate and the chemisorbed Ti and N atoms. The thickness of this initial TiC_xN_y layer is probably not more than one monolayer because of the slow diffusion rate of carbon through stoichiometric TiC ¹⁸. TiN will grow epitaxially on this TiC_xN_y monolayer. Gass, Mantle and Hintermann studied the influence of various substrate materials among which carbon-coated alumina on TiC-CVD¹⁹. They found that nucleation and growth of TiC on cobalt covered carbon was much faster than on carbon directly. This confirms that the growth of TiC on graphite is rather slow, due to the low carbon activity in graphite.

TiC growing on graphite does not show a nucleation induced texture. The carbon is the diffusing element. So the texture that we found must be a growth induced texture. In the case of TiN CVD one would expect to find a (220) growth texture, because of the FCC crystal lattice of TiN. In fact in the TiN, deposited at 850°C, after 6 hours deposition, we find a mixed (311) and (220) growth texture for some of the samples (Table 1/2). In the TiN deposited at 900°C we also see a mixed (311) and (220) growth texture after 6 hours deposition time (Table 2). It is only at 950°C, that we see a simple (220) growth texture in all of the for 6 hours deposited samples (Table 2). This texture is similar to that which Yoon c.s. found when growing TiC on plain carbon steels. At a deposition temperature of 1050°C, after 90 minutes deposition time, they found a (220) texture in the TiC ²⁰.

The texture we find in the very thin layers is rather weak and may be partly attributed to the fact that the TiN layer is so thin that the first reflections of the diffractogram are relatively stronger due to the low incidence angle of the X-ray beam.

The observed difference in coating morphology may be a result of a difference in crystallinity of the substrate material. The purification process of the graphite results in a coarsening of the microcrystalline material. This results in a roughening of the graphite surface that is replicated by the TiC_xN_y mono-layer.

5. CONCLUSIONS

The morphology and preferent texture of a thin TiN coating on a graphite substrate can be influenced by the choice of the graphite substrate. The following points have to be considered in making an appropriate choice:

- The morphology of the graphite substrates has an influence on the morphology of the deposited TiN layers. The deposition starts with the formation of $\text{TiC}/\text{TiC}_x\text{N}_y$ nuclei.
- At deposition temperatures of 850 and 900°C, growth induced textures, (311) and (220), are found in the TiN layers after prolonged deposition times. At 950°C only the (220) growth texture prevails.
- Purification of the graphite substrates will, in the case of the deposition of thin TiN coatings, lead to rougher coatings.
- In TiN coatings (deposited at 950°C, for 6 hours) the TiN crystals at the surface show a surface dendritic structure, from which the initial nucleation proceeds in five directions.

6. REFERENCES

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Appendix 1: X-ray diffraction intensities and texture coefficients of (un/TiN) coated graphite substrates
Table 3: X-ray diffraction intensities and texture coefficients of carbon crystals in the substrates at a deposition temperature of 850°C

(hkl)	I_0	UT91p		UT91u		UT145p		UT145u		UT218p		UT218u	
		I	TC	I	TC	I	TC	I	TC	I	TC	I	TC
(002)	100	100	3.31	100	3.55	100	3.38	100	3.63	100	3.55	100	3.55
(100)	10	3	0.99	3	1.06	4	1.35	3	1.09	3	1.06	3	1.06
(101)	50	3	0.20	3	0.21	2	0.14	2	0.15	3	0.21	3	0.21
(004)	80	4	0.17	4	0.18	3	0.13	3	0.14	4	0.18	4	0.18
(103)	10	1	0.33	0	0	0	0	0	0	0	0	0	0

Table 4: X-ray diffraction intensities and texture coefficients of TiN crystals deposited on graphite substrates at a deposition time of 10 minutes and at a deposition temperature of 850°C

(hkl)	I_0	UT91p		UT91u		UT145p		UT145u		UT218p		UT218u	
		I	TC	I	TC	I	TC	I	TC	I	TC	I	TC
(111)	75	5	1.11	8	1.26	27	1.14	18	0.99	4	1.07	5	1.11
(200)	100	8	1.33	12	1.41	41	1.30	29	1.20	7	1.40	8	1.33
(220)	55	3	0.90	4	0.86	16	0.92	13	0.98	2	0.73	3	0.90
(311)	25	1	0.66	1	0.47	5	0.63	5	0.83	1	0.80	1	0.66

Table 5: X-ray diffraction intensities and texture coefficients of TiN crystals deposited on graphite substrates at a deposition time of 20 minutes and at a deposition temperature of 850°C

(hkl)	I_0	UT91p		UT91u		UT145p		UT145u		UT218p		UT218u	
		I	TC	I	TC	I	TC	I	TC	I	TC	I	TC
(111)	75	17	1.16	9	1.11	50	1.05	36	1.14	17	1.08	14	1.15
(200)	100	23	1.18	14	1.30	76	1.19	50	1.19	27	1.29	8	1.33
(220)	55	9	0.84	5	0.84	31	0.88	23	1.00	10	0.87	8	0.89
(311)	25	4	0.82	2	0.74	14	0.88	7	0.67	4	0.76	3	0.74

Table 6: X-ray diffraction intensities and texture coefficients of TiN crystals deposited on graphite substrates at a deposition time of 10 minutes (at a redeposition time of 20 minutes) and at a deposition temperature of 850°C

(hkl)	I_0	UT91p		UT91u		UT145p		UT145u		UT218p		UT218u	
		I	TC	I	TC	I	TC	I	TC	I	TC	I	TC
(111)	75	25	1.18	39	1.21	28	1.02	41	1.02	12	1.13	29	1.19
(200)	100	32	1.14	21	0.89	48	1.31	64	1.19	20	1.41	36	1.11
(220)	55	15	0.97	21	0.89	18	0.90	29	0.98	7	0.90	17	0.95
(311)	25	5	0.71	9	0.84	7	0.77	11	0.82	2	0.56	6	0.74

Table 7: X-ray diffraction intensities and texture coefficients of TiN crystals deposited on graphite substrates at a deposition time of 6 hours and at a deposition temperature of 850°C

(hkl)	I ₀	UT91p		UT91u		UT145p		UT145u		UT218p	
		I	TC	I	TC	I	TC	I	TC	I	TC
(111)	75	77	0.81	100	0.98	100	1.07	22	0.37	34	0.49
(200)	100	41	0.32	47	0.35	58	0.47	13	0.16	24	0.26
(220)	55	100	1.44	83	1.11	79	1.15	100	2.30	100	1.96
(311)	25	45	1.42	53	1.56	41	1.31	23	1.16	30	1.29

Table 8: X-ray diffraction intensities and texture coefficients of TiN crystals deposited on graphite substrates at a deposition time of 6 hours and at a deposition temperature of 900°C

(hkl)	I ₀	UT91p		UT91u		UT145p		UT145u		UT218p	
		I	TC	I	TC	I	TC	I	TC	I	TC
(111)	75	71	0.65	52	0.62	34	0.57	21	0.35	30	0.49
(200)	100	22	0.15	18	0.16	7	0.09	5	0.06	7	0.09
(220)	55	100	1.25	100	1.62	100	2.29	100	2.28	100	2.21
(311)	25	71	1.95	45	1.60	21	1.06	26	1.30	25	1.22

Table 9: X-ray diffraction intensities and texture coefficients of TiN crystals deposited on graphite substrates at a deposition time of 6 hours and at a deposition temperature of 950°C

(hkl)	I ₀	UT91p		UT91u		UT145p		UT145u		UT218p	
		I	TC	I	TC	I	TC	I	TC	I	TC
(111)	75	298	0.33	223	0.25	371	0.43	167	0.19	124	0.14
(200)	100	229	0.19	225	0.19	103	0.09	146	0.12	73	0.06
(220)	55	2244	3.37	2389	3.59	2036	3.22	2444	3.75	2876	4.31
(311)	25	198	0.65	176	0.58	208	0.72	191	0.65	99	0.33

Appendix 2:X-ray diffractogram of a deposition experiment on UT91p starting from TiCl₄ and H₂

Fig. 5:X-ray diffractogram of a deposition experiment on UT91p starting from TiCl₄ and H₂
Deposition time: 1 hour, deposition temperature: 850°C.