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IAM

Constitution, Microstructure and Mechanical Properties of Magnetron-sputtered TiC/a-C Nanocomposite Coatings

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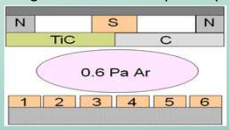
Motivation

Carbon-based nanostructured composite coatings are attracting steadily increasing attention due to their promising properties. These materials often consist of nanocrystalline phases, clusters or particles homogeneously dispersed in an amorphous carbon matrix or covered by an amorphous carbon grain boundary phase. Advanced nanocomposite films providing simultaneously wear protection and low friction are required in engineering applications. We report on the synthesis and correlation between constitution, microstructure and properties of non-reactively magnetronsputtered TiC/a-C nanocomposite coatings.

Deposition

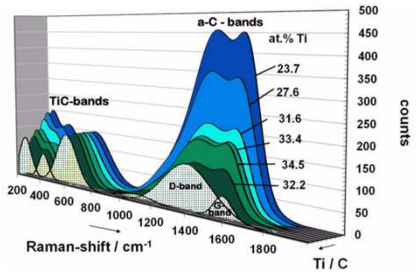
rf magnetron sputtering from a segmented TiC / Graphite target in an Ar atmosphere (0.6 Pa)
1 power supply, Power density 11.3 W/cm^2
target-substrate distance 60 mm
Substrates: cemented carbide (Pos.1 - Pos. 6).
rf substrate bias voltage: 0, -150 V or -300 V
substrate temperature < 250°C



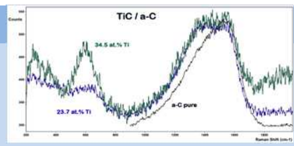
Analyses of mechanical properties, microstructure and constitution

EPMA: Cameca Camebax microbeam system
XRD: Seiffert PAD II using Cu K_a radiation (λ = 0.15418 nm)
Micro Raman: Renishaw Raman System 1000 spectrometer, Ar ion laser, 514.5 nm, ≤ 1 mW
AFM: Digital Instruments, Dimension 3100, Si tip (Nanosensors LFM-20; tip radius < 10 nm) in contact mode
Nanoindentation: CSIRO Umis 2000, load 20 mN, 50 steps.

Raman spectroscopy of TiC/a-C coatings



0 V substrate bias	Pos. 1	Pos. 2	Pos. 3	Pos. 4	Pos. 5	Pos. 6	a-C
Position G-Peak / cm^{-1}	1569	1565	1565	1568	1565	1567	1567
I_D/I_G	2,16	2,22	2,00	2,09	2,12	1,99	1,31
FWHM G-Peak / cm^{-1}	115	116	132	122	129	126	172
area ratio (TiC-bands / a-C -bands)	0,99	0,73	0,78	0,76	0,53	0,44	



- 150 V substrate bias	Pos. 1	Pos. 2	Pos. 3	Pos. 4	Pos. 5	Pos. 6
Position G-Peak / cm^{-1}	1580	1574	1570	1571	1572	568
I_D/I_G	1,66	1,71	1,88	1,80	1,94	2,05
FWHM G-Peak / cm^{-1}	110	118	117	121	121	125
area ratio (TiC-bands / a-C -bands)	0,47	0,48	0,47	0,44	0,35	0,28

changes with with increasing carbon content of the TiC/a-C-coatings

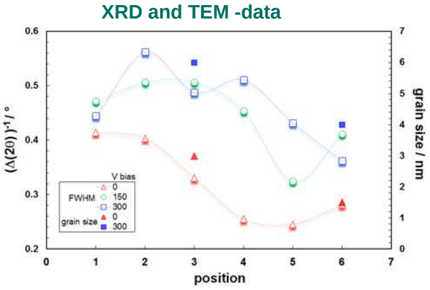
G-peak position unchanged → vibration frequency is related to the average C-C bond length → no change in a-C structure
G-FWHM increases → FWHM is uniquely related to the sp^2 clustering→ decrease in crystallinity
I_D/I_G ratio → decreasing with progressive disordering of the sp^2-bonded rings and increase of sp^3 sites → bias influence
area ratio (TiC-bands / a-C -bands) → directly related to Ti/C ratio
→ linear decrease with rising C content → dereasing TiC grain size

- 300 V substrate bias	Pos. 1	Pos. 2	Pos. 3	Pos. 4	Pos. 5	Pos. 6
Position G-Peak / cm^{-1}	1578	1575	1566	1566	1573	1569
I_D/I_G	1,69	2,25	2,22	1,76	2,19	2,02
FWHM G-Peak / cm^{-1}	125	128	143	147	141	145
area ratio (TiC-bands / a-C -bands)	0,80	0,54	0,68	0,57	0,43	0,43

bias influence

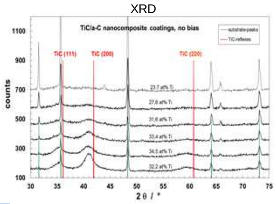
G-peak position: rising for -150 V, greater variance for -300 V
→ higher vibration frequency → shortening of the average bondlenght
G-FWHM: comparable for no bias or -150 V, rising for -300 V → broader spectra → less sp^2-clustering
I_D/I_G ratio: no change for 0 V, greater variance for -300 V, for -150 V increase with rising C content → more sp^2 clustering, ring structures
area ratio: for comparable Ti/C: lower for -150 V, max. for 0 V
→ TiC-crystallite size increasing with bias, grain size from TEM: Pos 3: 2-4 nm for 0 V, 5-7 nm for -300 V, Pos 6: 1-2 nm for 0 V, 3-5 nm for -300 V

XRD and TEM -data

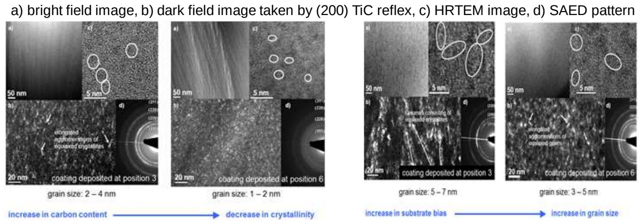


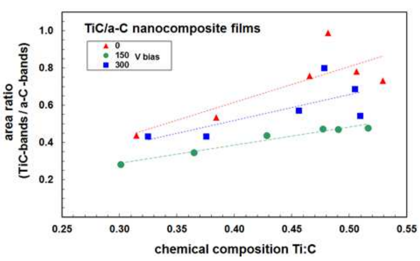
Microstructure of TiC/a-C coatings deposited without bias / at -300 V bias

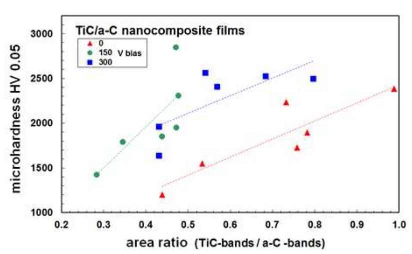
XRD



a) bright field image, b) dark field image taken by (200) TiC reflex, c) HRTEM image, d) SAED pattern







Composition and properties of TiC/a-C coatings

deposited at 0 V substrate bias	Pos. 1	Pos. 2	Pos. 3	Pos. 4	Pos. 5	Pos. 6
Ti content / at.-%	32.2	34.5	33.4	31.6	27.6	23.7
C content / at.-%	66.9	65.1	65.9	68.0	71.9	75.4
Ti:C ratio	0.48	0.53	0.51	0.47	0.38	0.31
microhardness HV0.05	2384	2235	1899	1730	1548	1204
nanohardness / GPa	26.1	24.6	22.0	20.3	19.0	16.2
red. Young`s modulus / GPa	380	266	221	230	232	200
friction coefficient vs. 100Cr6	0.25	0.21	0.20	0.17	0.13	0.11
Roughness R_t / nm	174,5	170,2	99,6	87,5	80,6	114,0
deposited at - 150 V substrate bias	**Pos. 1**	**Pos. 2**	**Pos. 3**	**Pos. 4**	**Pos. 5**	**Pos. 6**
Ti content / at.-%	32,4	33,3	31,4	29,2	25,9	22,4
C content / at.-%	66,2	64,5	65,9	68,1	71,1	74,3
Ti:C ratio	0,49	0,52	0,48	0,43	0,36	0,30
microhardness HV0.05	2844	2307	1950	1852	1791	1421
nanohardness / GPa	28,4	24,9	23,4	22,4	21,8	21,3
red. Young`s modulus / GPa	385,9	360,6	295,6	234,4	252,3	246,6
friction coefficient vs. 100Cr6	0,22	0,22	1,23	0,18	0,16	0,13
Roughness R_t / nm	281,2	221,5	295,3	261,4	488,6	197,1
deposited at - 300 V substrate bias	**Pos. 1**	**Pos. 2**	**Pos. 3**	**Pos. 4**	**Pos. 5**	**Pos. 6**
Ti content / at.-%	31.5	32.8	32.7	30.5	26.5	23.8
C content / at.-%	65.8	64.3	64.7	66.8	70.5	73.2
Ti:C ratio	0.48	0.51	0.51	0.46	0.38	0.32
microhardness HV0.05	2494	2560	2521	2402	1958	1634
nanohardness / GPa	32.5	27.4	28.6	26.8	24.1	23.9
red. Young`s modulus / GPa	405	344	348	329	282	270
friction coefficient vs. 100Cr6	0.22	0.21	0.23	0.23	0.17	0.16
Roughness R_t / nm	456,2	341,9	308,9	330,1	385,0	216,5

Summary

From the results of the combination of Raman spectroscopy, XRD, TEM, AFM and nano-indentation it is concluded that at least 3 effects play together in the formation of nanocomposite TiC/a-C films:

- formation of both the crystalline TiC and amorphous carbon phase
- densification of the amorphous carbon network by the ion bombardment
- preferential resputtering of the C atoms.

The most interesting growth effects are observed at -150 V bias voltage at the center positions 3 and 4. In this case the structure-property correlation is influenced by the interplay off all three effects, whereas in the outer sample positions and for the other bias voltages, always one of the three effects is dominating the formation of the TiC/a-C nanocomposite structure.