

F7360 Characterization of thin films and surfaces

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Outline

- Paper introduction
- Experimental details and coatings
- Characterization methods
- Appropriateness of the methods
- Achieved results

Introduction

- Tribological behaviour of titanium carbide/amorphous carbon nanocomposite coatings: From macro to the micro-scale
- J.C. Sánchez-López , D. Martínez-Martínez ¹, C. López-Cartes, A. Fernández [1]
- Motivation of the study – quality nanocomposite coatings (low friction and wear resistance, good toughness)

Experimental details and coatings

- DC (graphite target) and RF (Ti target) magnetron sputtering
- SPR (Sputtering power ratio) $\sim P(\text{C})/P(\text{Ti})$
- Argon gas, total pressure = 0.75 Pa
- TiC/a-C nanocomposite coatings

Characterization methods

1. X-ray diffraction

- Atomic and molecular structure of crystal
- Diffraction of X-ray beam on crystal lattice
- Bragg's law:

$$2d \sin \theta = n\lambda$$

- Structure factor [2]

$$F(h, k, l) = \sum_n f_n e^{-2\pi i (hu_n + kv_n + lw_n)}$$

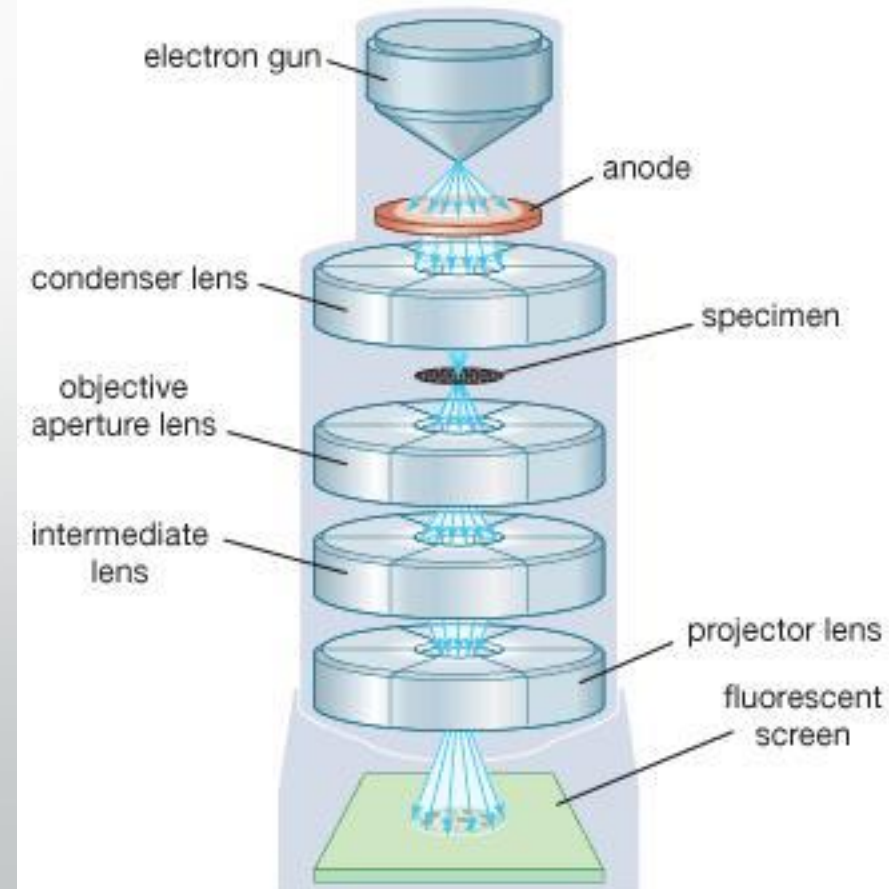
d – spacing between diffracting planes
 Θ – the incident angle (X-ray and planes)
 n – integer
 λ – wavelength of the beam (0,01-10keV)

f_n - an atom's structure factor
 h, k, l - Millers index
 u, v, w – coordinates of an atom

Characterization methods

2. Transmission electron microscopy (TEM)

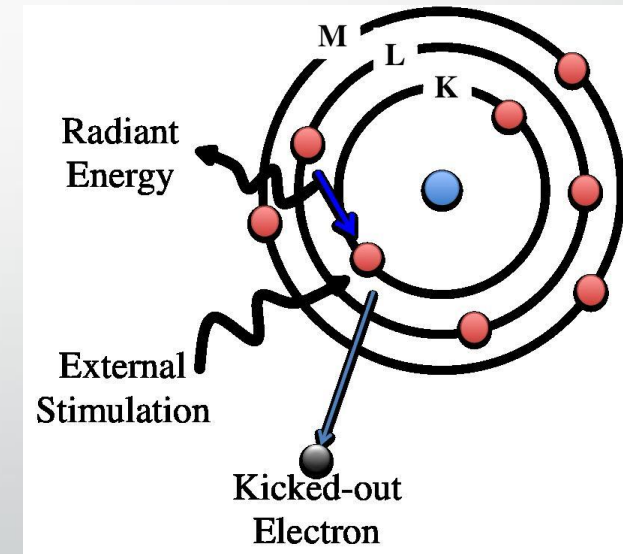
- Crystal structure, dislocations and grain boundaries in structure
- High energy beam of electrons (keV)
- Thin sample (nm)
- Absorption of el. in material [3]



Characterization methods

3. Electron energy-loss spectroscopy (EELS)

- Elemental compositions, chemical bonds
- The study of the vibrational motion of atoms and molecules
- On or near the surface
- Interaction between the electron beam (0.1-10keV) and the specimen [4]



Characterization methods

4. Micro-Raman spectroscopy

- The study of the interaction between light (inelastic scattered) and matter
- Photons of a single wavelength
- Stokes Raman scattering

- Functional group, the structure of the molecules

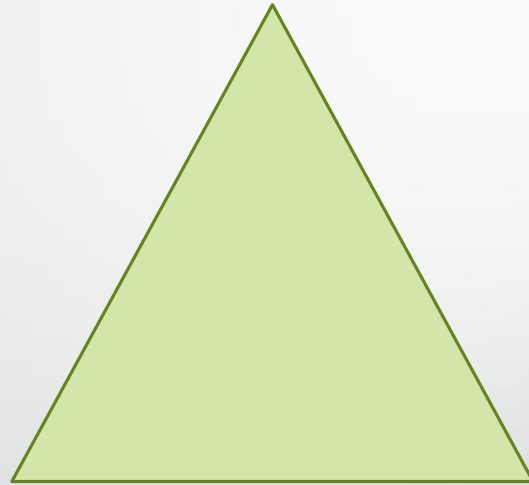
- Micro-Raman spectroscopy – microscopic samples [5]

Appropriateness of the methods

- XRD – crystal structure of the films
- EELS, Raman, XRD – a-C/TiC rates, chemical composition, phases proportion inside the film
- Combination of TEM with EELS spectrometer
- Pin-on-disk tribometer – tribological tests for friction coefficients, wear rates

Achieved results

Tribological properties



Film microstructure

Phase composition

Achieved results

1) TEM

- Fig.1: a) SPR = 1, TiC crystal (5-10nm) with random orientation
- Fig.1: b) SPR = 4, 1 nm sparticles, amorphous matrix

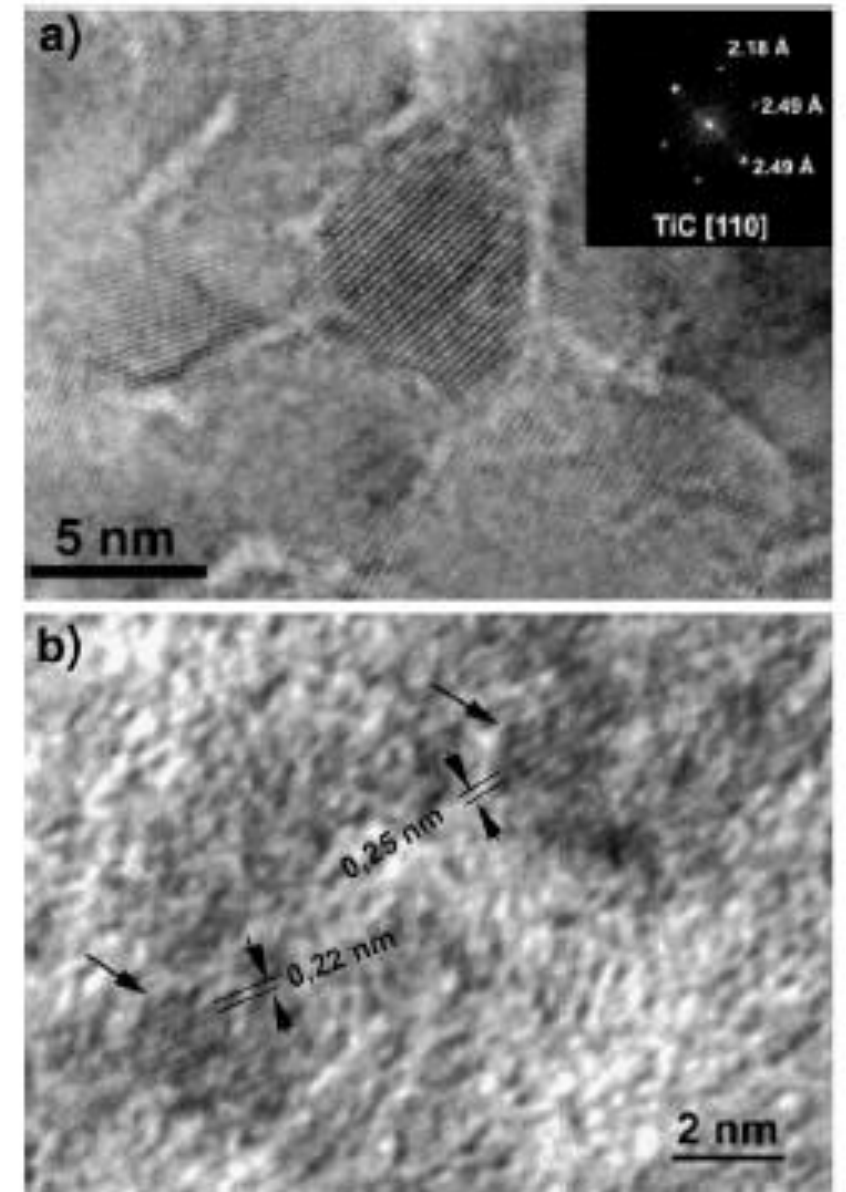


Fig. 1. HRTEM micrographs and corresponding electron diffraction patterns for nc-TiC/a-C nanocomposite coatings prepared at sputtering power ratios of 1 (a) and 4 (b) respectively.

Achieved results

2) EELS

- EELS spectra on the C K-edge core loss
- Shape and position of the spectra changed gradually (from TiC to a-C phases)
- The best tribological performance (low friction, low instabilities) – for the highest a-C contents

Film	% TiC	% a-C	<i>H</i> (GPa)	<i>f</i>
A	15	85	8	<u>0.13</u>
B	21	79	7	0.12
C	23	77	7	0.10
D	25	75	7	0.09
E	30	70	16	0.10
F	45	55	18	0.26
G	47	53	27	0.25
H	90	10	16	0.25
I	95	5	22	0.31
J	>100*	0	11	0.6

Table 1: Summary of samples, phase contents and tribomechanical properties

Achieved results

3) XRD

- TiC phase – crystal size is strongly reduced as the carbon content increases (5% to 85%)
- Sample J – non-stoichiometric Ti-enriched TiC phases

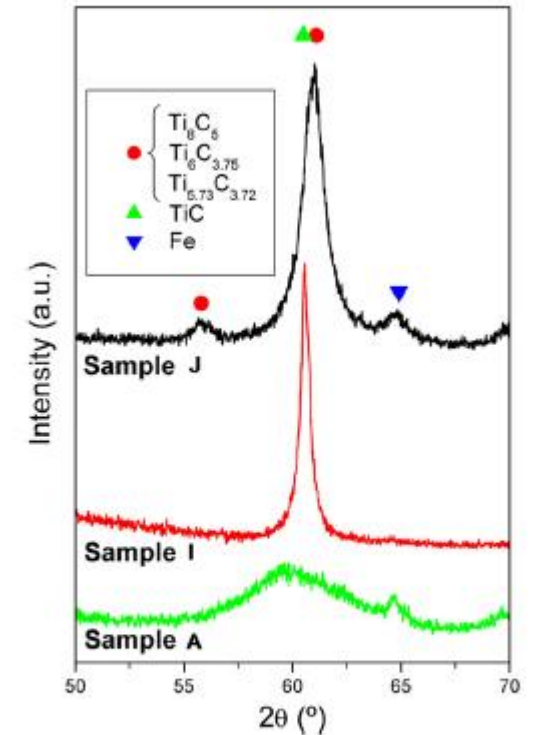


Fig. 3. XRD diffractograms for films A, I and J as representative examples of different type of friction behaviour (zoom 2θ 50–70°). The database numbers for the identified crystalline phases are the following: TiC phase (database no. 32-1383), Ti_6C_5 (database no. 72-2496), $\text{Ti}_6\text{C}_{3.65}$ (database no. 79-0971) and $\text{Ti}_{5.73}\text{C}_{3.72}$ (database no. 77-1089).

Achieved results

4) Raman spectroscopy

- a) sample A: a-C content 85%
 - two bands: 1370 cm^{-1} and 1565 cm^{-1} (sp² content)
- b) sample I: a-C content 5%
 - understoichiometric TiC (active due to carbon vacancies)
- c) sample J: a-C content 0%
 - Iron oxides formation by tribochemical reaction of the steel ball with the atmosphere

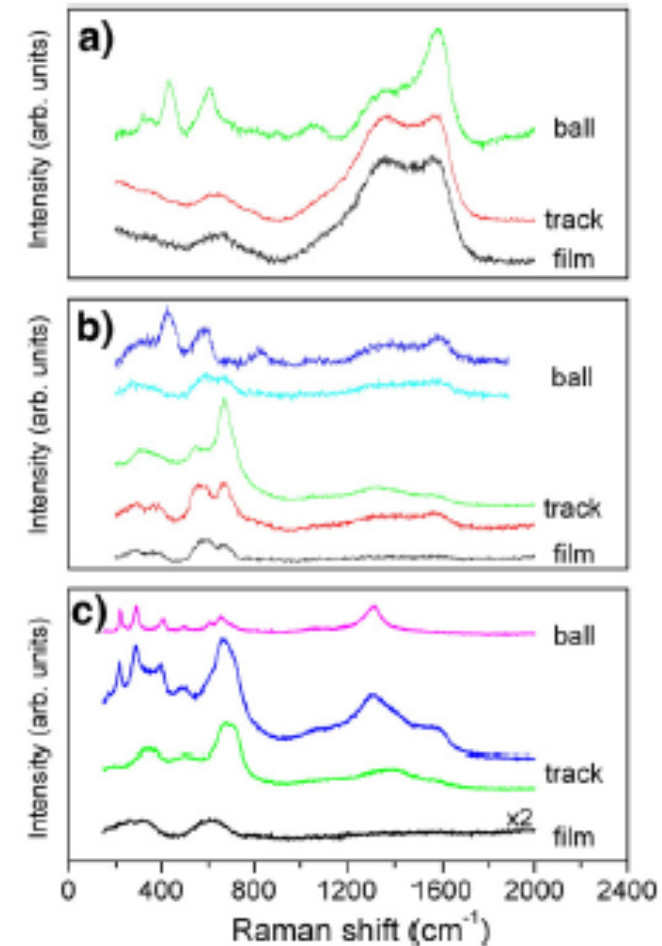


Table 2

Summary of main phases detected on the counterfaces after friction testing of samples A, I and J

	Raman analysis		
	Film	Track	Ball
Sample A	a-C	a-C	a-C, no-graphite+FeTiO ₃ /TiO _x
Sample I	TiC _x	TiC _x +Fe ₃ O ₄ +a-C (small)	TiC _x +TiO _x +a-C (small)
Sample J	TiC _x	α-Fe ₂ O ₃ +Fe ₃ O ₄ +γ-Fe ₂ O ₃	α-Fe ₂ O ₃

Conclusion


a-C content

> 60-65%

Surface prevention from
Mechanical wear and oxidation

References

- [1] J.C. Sánchez-López □, D. Martínez-Martínez 1, C. López-Cartes, A. Fernández, *Surface & Coatings Technology* 202 (2008) 4011–4018
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