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) ~ P(C)/P(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]

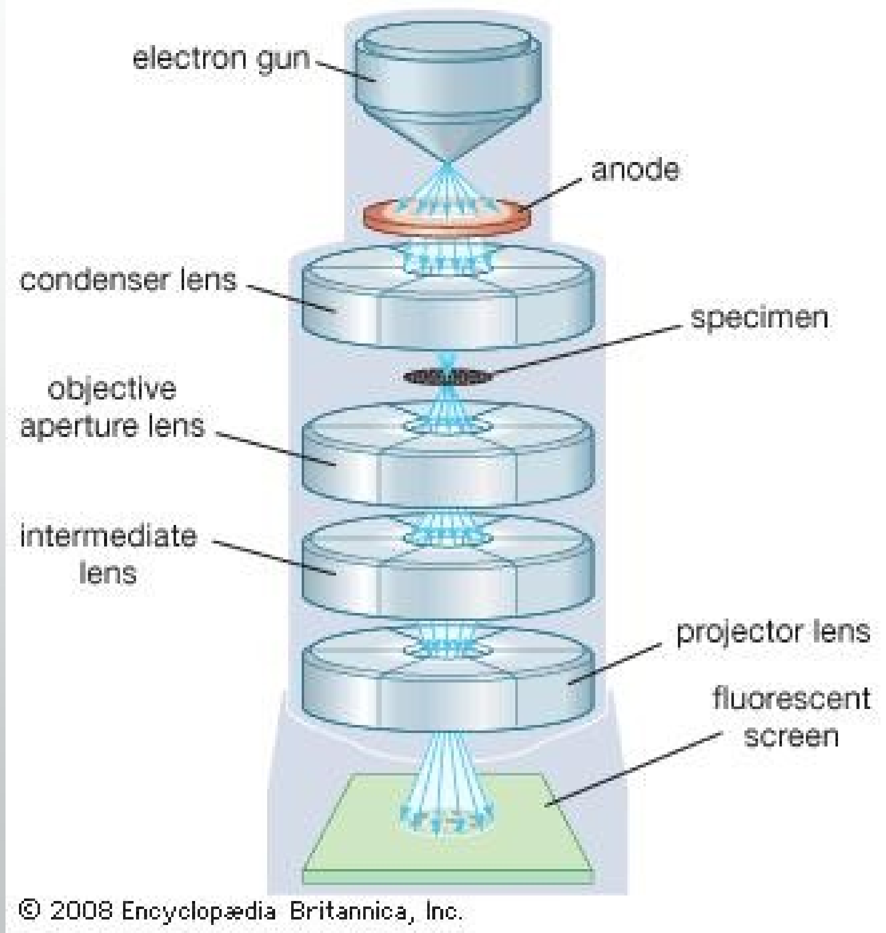
$$F(h,k,l) = \sum_{n} f_n e^{-2\pi i (hu_n + kv_n + lw_n)}$$

d – spacing between diffracting planes
Θ – the incident angle (X-ray and planes)
n – integer
λ – wavelenght 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]



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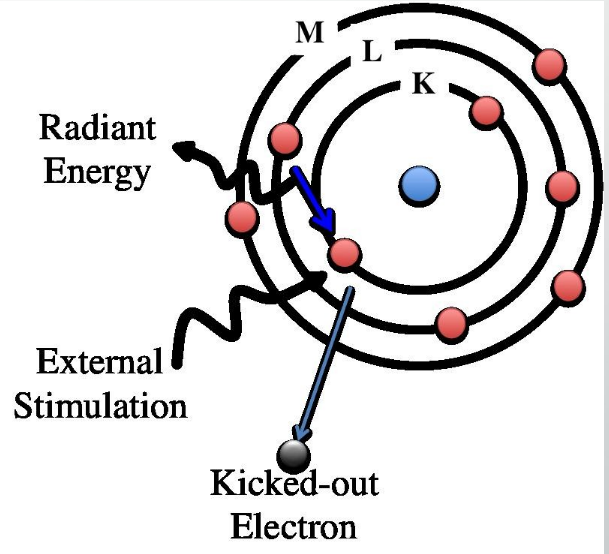
Characterization methods
3. Electron energy-loss spectroscopy (EELS)

- 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

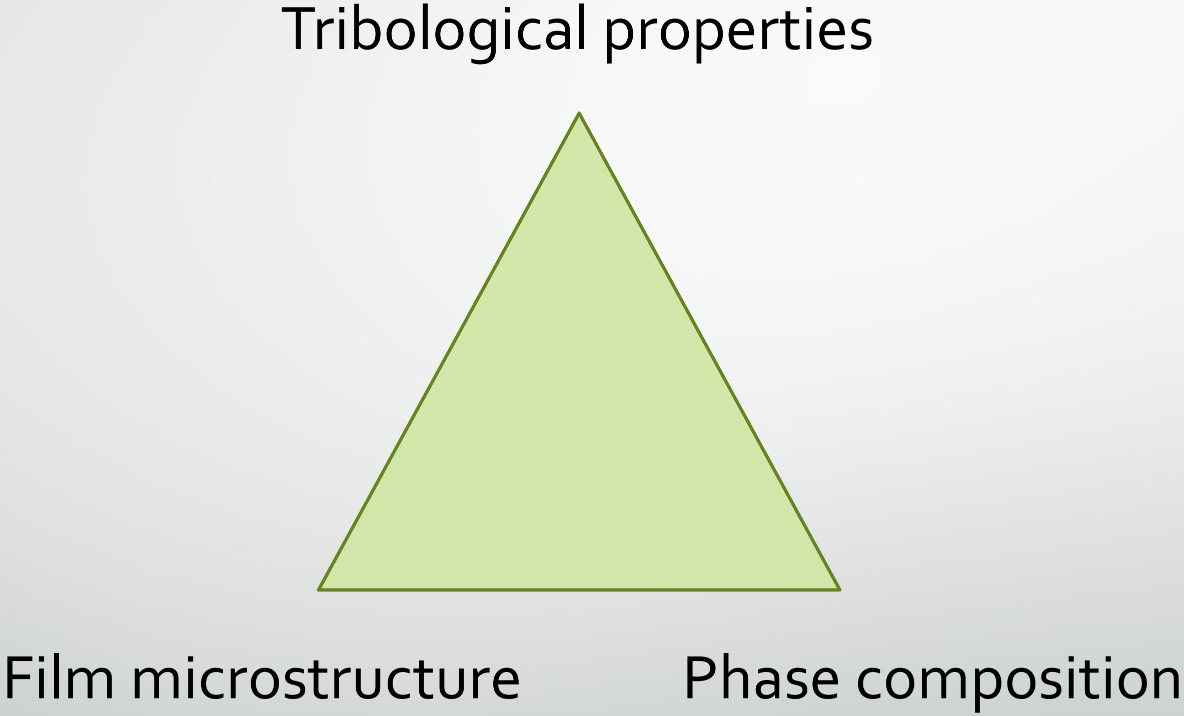
- Functional group, the structure of the molecules

- 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

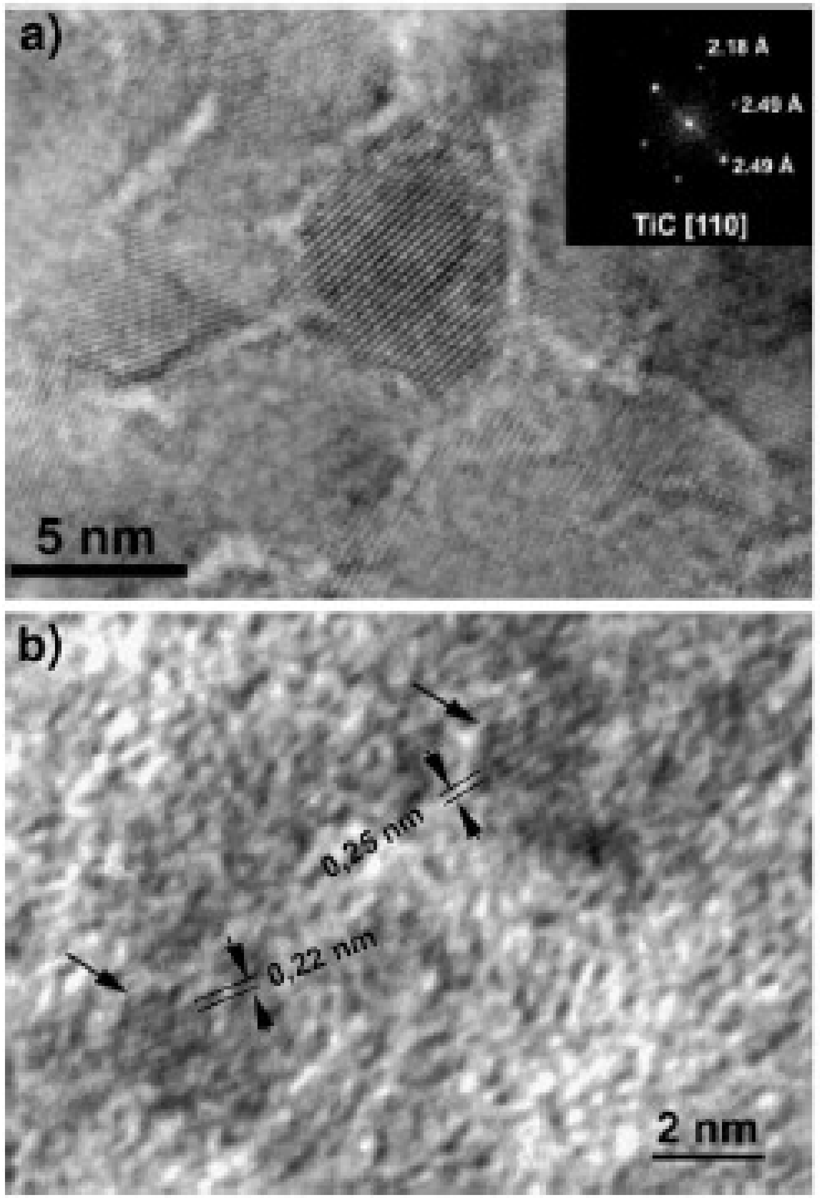
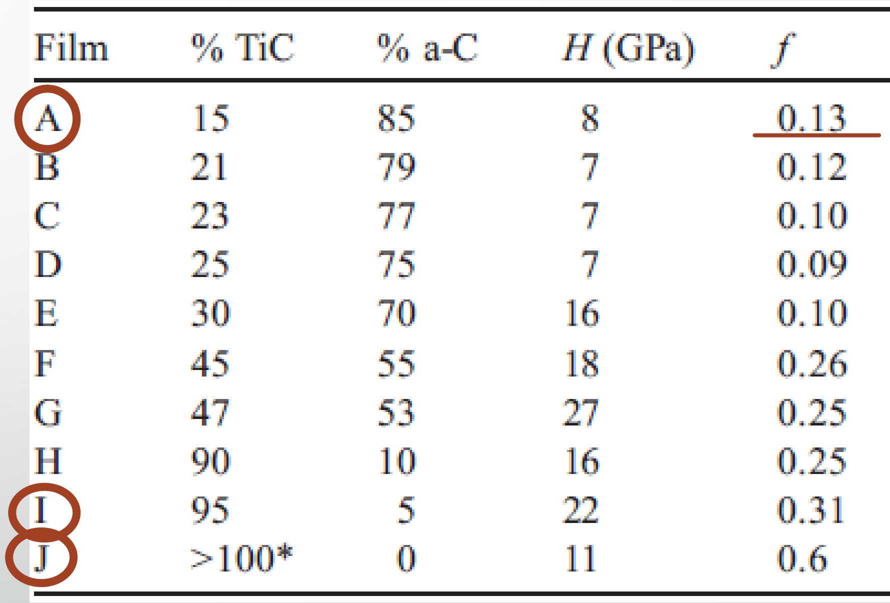


Fig. 1. HRTEM micrographs and corresponding electron diffraction patterns for nc-TiC/a-C nanocomposite coatings prepared at sputtering power ratios of 1 (a) and 4 (b) respectively.

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	*H* (GPa)	*f*
A	15	85	8	0.13
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-stochiometric Ti-enriched TiC phases

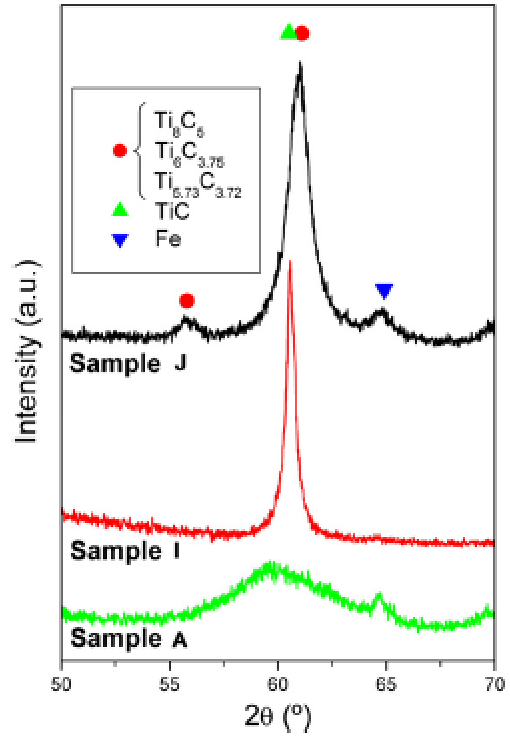


Fig. 3. XRD diffractograms for films A, I and J as representative examples of different type of friction behaviour (zoom 2Θ 50–70°). The database numbers for the identified crystalline phases are the following: TiC phase (database no. 32-1383), Ti_8C_5 (database no. 72-2496), $Ti_6C_{3.65}$ (database no. 79-0971) and $Ti_{5.73}C_{3.72}$ (database no. 77-1089).

Achieved results

4) Raman spectroscopy

- a) sample A: a-C content 85%

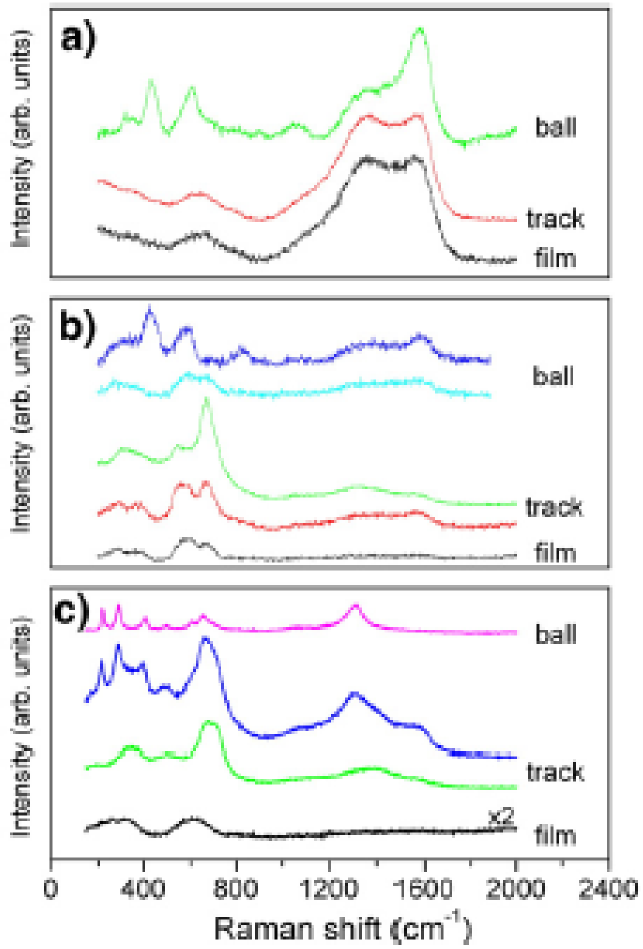
  - two bands: 1370 cm^{-1} and 1565 cm^{-1} (sp2 content)

- b) sample I: a-C content 5%

  - understochiometric 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



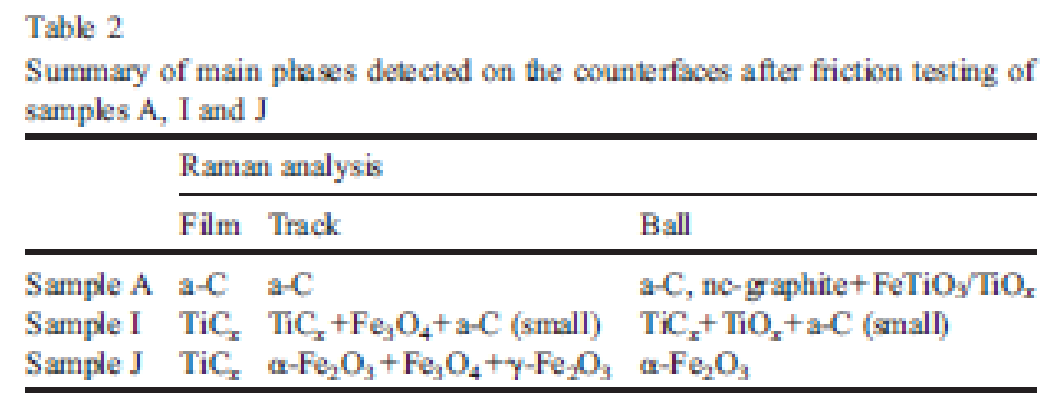


Table 2

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, nc-graphite + $FeTiO_3/TiO_x$
Sample I	TiC_x	$TiC_x + Fe_3O_4$ + a-C (small)	$TiC_x + TiO_x$ + a-C (small)
Sample J	TiC_x	$\alpha\text{-}Fe_2O_3 + Fe_3O_4 + \gamma\text{-}Fe_2O_3$	$\alpha\text{-}Fe_2O_3$

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

[2] *Rentgenová spektroskopie a difrakce* [online]. Univerzita Karlova v Praze, [cit. 2012-5-5]. Dostupné na <http://physics.mff.cuni.cz/vyuka/zfp/>.

[3] http://www.britannica.com/technology/transmission-electron-microscope
https://www2.warwick.ac.uk/fac/sci/physics/current/postgraduate/regs/mpags/ex5/techniques/structural/tem/

[4] **http://iopscience.iop.org/article/10.1088/0034-4885/72/1/016502/pdf**

http://tpm.amc.anl.gov/Lectures/EELSAEMShortCourse.pdf

[5] **http://www.microspectra.com/support/technical-support/raman-science/35-technical-support/126-science-of-micro-raman-spectroscopy**

Thank you for your attention!