INTEGRATED APPROACH FOR HIGH RESOLUTION SURFACE CHARACTERISATION: COUPLING FOCUSED ION BEAM WITH MICRO AND NANO MECHANICAL TESTS

E. Bemporad, M. Sebastiani, V. Palmieri, S. Deambrosis

1 University of Rome “ROMA TRE”, Mechanical and Industrial Engineering Dept
Via della Vasca Navale 79 – 00146 Rome Italy

2 Laboratori Nazionali di Legnaro, ISTITUTO NAZIONALE DI FISICA NUCLEARE, Italy
Viale dell’Università 2 -35020 Legnaro, PADOVA - Italy

3 Science Faculty, University of Padua.
via Jappelli, 1 - 35121 Padova – Italy

At present, mechanical characterisation of engineered surfaces is gaining more and more interest for the growing industrial application of surface modification and coating techniques, which are usually applied to improve either surface mechanical or functional performances (i.e hardness, load bearing capacity, wear resistance, surface free energy and chemical reactivity, electrical resistivity, thermal conductivity,…). Furthermore, it has to be considered that the development of nanostructured materials and the growing use and application of nano-systems and nano-structures make the use of advanced procedures for nano-scale mechanical characterisation strictly necessary; in other cases, mechanical behaviour can be strongly influenced by microstructural and size effects (grain size, defects, interfaces, porosity,…), so multi-scale characterisation procedures are strongly needed for a determination of the correct correlation function among process parameters, surface properties and in-service performances.

It is therefore clear that a comprehensive, statistically reliable, economically sustainable procedure for the characterisation of engineered surfaces has not yet been developed in literature, especially when a strong microstructure and size dependent behaviour is observed.

In the present work, a new developed characterisation procedure for the mechanical characterisation of engineered surfaces is presented, based on the combined use of high resolution microscopy (FIB-SEM, TEM, AFM) and surface mechanical characterisation techniques (nanoindentation, scratch testing).

In particular, two case studies are reported:

- Analysis of residual stresses of engineered surfaces by coupling focused ion beam controlled material removal and nanoindentation testing
- Nano-mechanical characterisation of sputterred niobium thin films for application in accelerating cavities;

All reported results arise from the application of integrated methodologies, which start from indentation or scratch experiments and finally come to the evaluation of mechanical properties of investigated materials, by the support of modelling (both analytical and numerical) and high resolution morphological and microstructural characterisation activities, such as Scanning and transmission electron microscopy (SEM, TEM), Focused Ion Beam microscopy (FIB) and Atomic Force Microscopy (AFM) techniques.

It is shown that only by the combination and synergic use of surface mechanical testing and SEM-TEM-FIB- AFM microscopy a reliable correlation between surface properties and in service performances can be obtained.
INTEGRATED APPROACH FOR HIGH RESOLUTION SURFACE CHARACTERIZATION: COUPLING FOCUSED ION BEAM WITH MICRO AND NANO MECHANICAL TESTS

E. Bemporad¹, M. Sebastiani¹, V. Palmieri²,³, S. Deambrosis²,³

¹ University "Roma Tre", Dep't of Mechanical and Industrial Engineering Via Vasca Navale 79 - 00146 Rome Italy
² Laboratori Nazionali di Legnaro, ISTITUTO NAZIONALE DI FISICA NUCLEARE, Italy Viale dell'Università 2 -35020 Legnaro Italy
³ Science Faculty, University of Padua. via Jappelli, 1 - 35121 Padova Italy

15th International Conference on Condensed Matter Nuclear Science
Roma, Italy
October 5 - 9, 2009
Material Science and Technology Research Group
University “Roma TRE”
Roma, Italy

WEB SITE: www.stm.uniroma3.it and www.lime.uniroma3.it

Address: Via Vasca Navale, 79 00146 – Roma
**Roma Tre, Some Numbers...**

- Founded in 1992
- One of the 4 State University in Rome (9 in total)
- 175,000 m²
- More than 40,000 students (4,100 enrolled in Engineering)
- More than 700 Researchers and Professors

**Faculty of Engineering:**
- Civil
- Computer Science
- Electronic
- **Mechanical**
  - *Materials Science and Technology research group (STM Group)*
EVERGREEN NEEDS

Functional and structural behavior are strongly influenced by micro-structural effects (grain size, defects, precipitates, interfaces, porosity,...)

- Ok, not really a news; however...
- **Engineered surfaces** are spreading quickly also in non high-tech products (also in mass products);
- Industrial application of surface modification and coating techniques requires mechanical and functional characterization of:
  - Nano-structured materials and coatings
  - Nano-systems
  - Nano-structures
- Multi-scale characterization (quick and cheap) procedures are therefore strongly needed for a pletora of needs in:
  - Development
  - Production
  - Maintenance and survey
Conventional characterisation techniques are not completely exhaustive for describing all micro-structural aspects which necessarily determine the actual behaviour of nano-structured materials and coatings.

New developed procedures should also be compatible for in-line quality control processes, or at least cost-saving with respect to traditional high resolution characterisation techniques.

Needs of standards and standardization procedures
Evolution of characterization techniques and new potential of their synergic uses beyond a simple observation
Evolution of characterization techniques and new potential of their synergic uses

“choose, touch, feel and see”
Evolution of two “traditional” techniques

Visualization and machining at the nanoscale
- Resolution
- Other probes than e⁻
- Not only Imaging, but also Milling and Deposition

Mechanical tests (nanoindentation)
- Applied forces and displacement measurement
- CSM method

Examples

I
Nb coatings for superconducting cavities

II
Residual stress measurement at the micro-scale
ROMA TRE DUAL BEAM

FEI
Helios 600
Nanolab

Detectors:
SE, SI, TLD
(SE+BSE), STEM.

TEM lamellae
preparation
system
(Omniprobe)

EDS system
**DUAL BEAM MICROSCOPY (FIB-SEM)**

- **SEM Column**: 0.76 nm @ 15 kV
- **FIB Column**: 5 nm @ 30 kV
  (spatial resolution)

**Integrated approach for high-resolution surface characterization**
HIGH RESOLUTION SEM:
**PRINCIPAL FIB MODES**

**Imaging:**
- Ion beam is scanned over substrate
- Biased MCP

**Milling:**
- Precursor molecules
- Deposited film
- Sputtered material from substrate

**Deposition:**
- Gas nozzle
- Volatile reaction products
- Deposited film

E. Bemporad: Integrated approach for high resolution surface characterisation
**FIB modes: Ion imaging**

- **Voltage contrast**: insulators appear dark while grounded conductors are bright.

- **Materials contrast**: differences in yield of secondary particles due to the way energy is lost in the material.

- **Crystallographic orientation contrast** (channeling contrast): incident ions are channeled down between lattice planes of the specimen.
FIB modes: Ion Milling
FIB modes: Deposition (Pt)

Al Magnifico Rettore
prof. Guido Fabiani
LIME 2008
CROSS SECTIONS
CHARACTERIZATION WITH DUAL BEAM MICROSCOPY
CHARACTERIZATION WITH DUAL BEAM MICROSCOPY

Multiscale and multitechnique approach to mechanical characterization of tribological coatings

Rockwell C adhesion test
CHARACTERIZATION WITH DUAL BEAM MICROSCOPY

Multiscale and multitechnique approach to mechanical characterization of tribological coatings

Scratch test
$L_{c3}$ failure

Image 1: Microscopic view of scratch test area

Image 2: Close-up view of coating edge with $L_{c3}$ failure
TEM SAMPLE PREPARATION WITH FIB

- The sample surface is investigated before cutting to determine the area of interest.
- Then the sample is milled and polished with predefined milling patterns.
- **Time for a lamella preparation: less then 2 hours with expert operator**

![TEM sample preparation with FIB](image-url)
TEM LAMELLAE EXTRACTION

E. Bemporad: Integrated approach for high resolution surface characterisation
SITE SPECIFIC TEM X-VIEW
SITE SPECIFIC TEM X-VIEW
SITE SPECIFIC TEM X-VIEW

STEM image inside the FIB
UNIVERSITY ROMA TRE NANO HARDNESS TESTER

Berkovich tip
## NANO INDENTER

### SYSTEM SPECIFICATIONS

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Indentation Head Assembly</td>
<td></td>
</tr>
<tr>
<td>Displacement resolution</td>
<td>&lt;0.01 nm</td>
</tr>
<tr>
<td>Total indenter travel</td>
<td>1.5 mm</td>
</tr>
<tr>
<td>Maximum indentation depth</td>
<td>&gt;500 µm</td>
</tr>
<tr>
<td>Load application</td>
<td>Coil / magnet assembly</td>
</tr>
<tr>
<td>Displacement measurement</td>
<td>Capacitance gauge</td>
</tr>
<tr>
<td>Loading capability</td>
<td></td>
</tr>
<tr>
<td>Maximum load (standard)</td>
<td>500 mN</td>
</tr>
<tr>
<td>Maximum load with DCM option</td>
<td>10 mN</td>
</tr>
<tr>
<td>Maximum load with high-load option</td>
<td>10 N</td>
</tr>
<tr>
<td>Load resolution</td>
<td>50 nN</td>
</tr>
<tr>
<td>Contact force</td>
<td>&lt;1.0 µN</td>
</tr>
<tr>
<td>Load frame stiffness</td>
<td>5 x 10^6 N/m</td>
</tr>
<tr>
<td>Indentation placement</td>
<td></td>
</tr>
<tr>
<td>Useable sample area</td>
<td>100 x 100 mm</td>
</tr>
<tr>
<td>Position control</td>
<td>Automated remote with mouse</td>
</tr>
<tr>
<td>Positional accuracy</td>
<td>1 µm</td>
</tr>
</tbody>
</table>

---

### CSM Method

![Load-P Displacement Chart](chart.png)
INTEGRATED CHARACTERIZATION APPROACH

Models

Indentation Size Effect (ISE) curves: analysis of hardening behaviour
Fracture toughness of bulk ceramics
Elastic modulus and mechanical anisotropy
Intrinsic hardness of thin films
Adhesion of thick coatings

Correlation to microstructure
Correlation to in-service behavior and/or functional properties

Advanced Microscopy Techniques
HR-SEM
FIB
AFM
TEM
**NANOINDENTATION ON NB THIN FILMS**

- Pt deposition and FIB sectioning

500 nm

Partial recrystallization during plastic deformation; Relative sliding of columnar grain

Direct measurement of piling-up
Evaluation of the effects of roughness on contact area
Analysis of deformation mechanisms
CASE STUDY I

- Characterization of Nb superconductive coating through nano-mechanical testing and AFM-FIB / SEM-TEM analyses
Resonant Cavities for Particle Accelerators

**Niobium Coated (PVD) Copper cavity**

**Bulk Niobium**

Very low surface electrical resistance (\(\sim n\Omega\) a 1.8 K)

Lower costs
Higher thermal stability
But...
**Significantly lower superconducting properties; WHY?**
MATERIALS: COMPARISON OF TWO DEPOSITION PROCEDURES

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>765</td>
<td><strong>CERN</strong> type sputtering</td>
</tr>
<tr>
<td>12</td>
<td>766</td>
<td><strong>CERN</strong> type sputtering</td>
</tr>
<tr>
<td>YY</td>
<td>767</td>
<td><strong>BIAS</strong> type sputtering (100V)</td>
</tr>
<tr>
<td>R</td>
<td>768</td>
<td><strong>BIAS</strong> type sputtering (100V)</td>
</tr>
</tbody>
</table>

- Same coatings both on Copper and Quartz substrate.
Resonant CAVITIES FOR PARTICLE ACCELERATORS

- Quality control measurement (RRR and $T_c$) are usually performed on Nb film deposited on Quartz substrate
  - Even if useful as threshold parameters, RRR and $T_c$ measured on Quartz, can lead to erroneous extrapolation for coatings deposited on copper substrate
A critical temperature of 9.5 K is very unusual.

- This suggests that strong microstructural differences do exist for BIASED coatings (density, grain size, lattice distortion, residual stress, resputtering).
Coatings on different substrate

- Nb on **COPPER** substrate
  - BIASED (a-b)
  - UNBIASED (c-d)

- Nb on **QUARTZ** substrate
  - BIASED (e-f)
  - UNBIASED (g-h)

A different behaviour is expected for the BIASED Nb coating deposited on **Quartz** substrate.
CORRELATION OF MECHANICAL WITH FUNCTIONAL PROPERTIES

- Superconducting properties of MS-PVD Nb films are significantly affected by
  - Grain size
  - surface roughness
  - coating density
  - interfaces integrity

- So are Mechanical properties:
Can hardness testing (coupled with FIB-SEM validation) be useful for the prediction of functional performances of Nb thin films?
NANOINDENTATION ON Nb THIN FILMS

1000 nm

500 nm

200 nm

100 nm

Bempora

Resolution surface characterisation
# Hardness Measurements on Functional Coatings

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Description</th>
<th>Nanoindentation</th>
<th>Standard micro-indentation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H (GPa)</td>
<td>E (GPa)</td>
</tr>
<tr>
<td>796</td>
<td>Nb on Cu BIAS type</td>
<td>3,10 ± 0,58</td>
<td>101,5 ± 23,61</td>
</tr>
<tr>
<td>797</td>
<td>Nb on Quartz BIAS type</td>
<td>1,63 ± 0,30</td>
<td>76,22 ± 48,99</td>
</tr>
<tr>
<td>803</td>
<td>Nb on Cu CERN type</td>
<td>2,59 ± 0,35</td>
<td>108,68 ± 11,65</td>
</tr>
<tr>
<td>804</td>
<td>Nb on Quartz CERN type</td>
<td>2,19 ± 0,31</td>
<td>95,95 ± 26,31</td>
</tr>
</tbody>
</table>

FIG. 1. Schematic cross section of Nb/substrate composite. (a) Nb film oxidized along column/grain boundaries. (b) Thick Nb film with compressed Nb layer by oxidation along the columns up to a depth of about \( d = 0.01-3 \) \( \mu \)m removing \( H_2 \) out of the interface layers. Below the surface layer column/grains are under tensile stress depending on sputter condition and on implanted sputter gas.
**Elastic modulus at 25 nm:**
94.1 ± 22.27 GPa

**Elastic modulus at 100 nm:**
112.9 ± 12.22 GPa
OXIDE LAYER CHECK VIA NANOINDENTATION

Niobium film load-depth curve

Niobium film: Detail of a load-depth curve

Indenter pop-in systematically at ~ 10 nm depth
TEM ANALYSIS OF THE OXIDE LAYER

TEM sample preparation by FIB lamella thinning
CASE STUDY I: CONCLUSIONS

- In case of a soft-on-hard system, substrate can significantly affect the mechanical behavior of the coating;

- Different micro-structural effects and deformation mechanisms were observed at different applied loads

- Surface micro-roughness, coating density, and thickness of the surface oxide layers are strictly related to superconducting properties;

- The coupled use of microscopy techniques and hardness testing has been the key point of all research activities
Residual Stress Evaluation at the Micrometre Scale: FIB Ring Drilling, Digital Image Correlation and Nanoindentation
INTRODUCTION

- **Residual stresses** (RS) play a crucial role in determining the deformation behaviour and performance of engineered components and materials at any scale;
- They come from unreleased (inelastic) deformation that remain after external forces has been removed.
FIRST METHOD, USING IMAGING CORRELATION:

1. Deposition of a Pt slice and milling of a reference dot pattern.
FIRST METHOD, USING IMAGING CORRELATION:

2. Measuring the holes displacement (in X, Y and 45°) used to calibrate the FEM model.

**IN THIS WAY IS POSSIBLE TO MEASURE ALL IN-PLANE RELAXATION STRAIN COMPONENTS.**
## RESULTS – ONE STEP MILLING

<table>
<thead>
<tr>
<th></th>
<th>Strain at maximum depth [um]</th>
<th>Calculated stress (FEM) [Pa]</th>
<th>Corrected with slope [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test-1</td>
<td>0.009</td>
<td>-6.00E+09</td>
<td>-5.96E+09</td>
</tr>
<tr>
<td>Test-2</td>
<td>0.0082</td>
<td>-5.47E+09</td>
<td>-5.35E+09</td>
</tr>
<tr>
<td>Test-3</td>
<td>0.009</td>
<td>-6.00E+09</td>
<td>-5.87E+09</td>
</tr>
<tr>
<td>Test-4</td>
<td>0.0097</td>
<td>-6.47E+09</td>
<td>-6.33E+09</td>
</tr>
<tr>
<td>Test-5</td>
<td>0.0103</td>
<td>-6.87E+09</td>
<td>-6.72E+09</td>
</tr>
</tbody>
</table>

- Analysis of the actual geometry of the pillar;
- The actual slope of the pillar is reproduced in the FEM model for **stress-strain** calibration

Calculated average stress: **-6.04 ± 0.51 GPa**
METHOD VALIDATION VS XRD-SIN²ψ

- Data from XrD measurement not easily readable due to a strong texturing of the TiN coating;
- Nevertheless, obtained values are comparable with FIB obtained values

\[ \varepsilon_{\psi} = \left(\frac{1+\nu}{E}\sigma_\phi\sin^2\psi - \frac{\nu}{E}(\sigma_{11} + \sigma_{22})\right) \]

\[ \sigma_\phi = -5.840 \text{ GPa} \]
PROCEDURE DETAILS

- Incremental Milling;
- Steps of 200 nm
- The pillar size \( d \) is equal to the coating thickness
- The maximum milling depth is equal to the coating thickness (3.8 µm)
EXPERIMENTAL DATA

![Graph showing relaxation strain vs. relative milling depth](image)

- **Modelled**
- **0°**
- **45°**
- **90°**

**Axes:**
- Y-axis: Relaxation strain
- X-axis: Relative milling depth (h/d)
SECOND METHOD, USING NANOINDENTATION:

- A difference in the shape of the load-depth curve is therefore directly correlated to the presence of a biaxial residual stress state, due to changes in the actual contact area during indentation.
SECOND METHOD, USING NANOINDENTATION:

Load On Sample vs Displacement Into Surface

- Stressed "halfspace" coating
- Relieved pillar

Displacement Into Surface (nm)

Load On Sample (mN)
RESULTS – STRESS CALCULATIONS

a) Pillar – stress free – as measured

b) Halfspace stressed coating – as measured

- Evaluation the contact stress field in the moment of unloading for both stressed surface and stress relieved pillar.

- In this way, a residual stress stat of – 5,653 Gpa was evaluated by comparison of the two set of load-depth data.

c) Modelled: Halfspace coating + RS
CONCLUSIONS

- Research activities at LIME are focused on the development and application of high resolution, multi-technique, multi-scale procedures for the mechanical/micro-structural characterisation of surfaces.

- In case of non homogeneous materials and coatings, the use of nano-indentation techniques, even at very low indentation depths, can be useful for a quick detection of important micro-structural aspects.

- By the combination of micro- and nano-hardness testing and SEM-TEM-FIB-AFM microscopy techniques, a comprehensive characterisation of nanostructured coatings and complex structures can be achieved.
Possible contribution to Condensed Matter Nuclear Science, some ideas:

- Residual stress Measurements on Pd foils or tubes:
  - Young’s Modulus (E): 118-124 Gpa
  - Poisson ratio (nu): 0.385-0.395
  - Yield Stress (YS): 50-200 MPa (Pd bulk)

100 MPa residual stresses (0.5 YS), would led to 0.05% relative relaxation
\( \varepsilon = \frac{\sigma}{E}(1-\nu) \)
Possible contribution to Condensed Matter Nuclear Science, some ideas:

- Surface and local mechanical properties (even inter-grain):
  - density gradients
  - real and apparent elastic modulus
  - Embrittlement phenomena
Possible contribution to Condensed Matter Nuclear Science, some ideas:

- Site specific investigation on surface and subsurface:
  - micro/nano-structural changes (micro-cavities formation concerns)
  - Elemental analyses via FIB TEM of the very surface and interfaces at grain boundaries (gradients)
  - Electrodes decoration or patterning for a systematic study of roughness influence to micro-structural changes during the experiment
  - High aspect ratio patterning (i.e. pillar forest) to investigate surface vs. volume and fluido-dynamic effects during the experiment
  - More to your imagination...!
THANK YOU FOR YOUR KIND ATTENTION

e.bemporad@stm.uniroma3.it