Integrated approach for high resolution surface characterization: coupling focused ion beam with micro and nano mechanical tests.

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Abstract. In the present paper, we will give a brief overview about the synergic use of two high resolution techniques with focus on applications on thin coatings: Focused Ion Beam (coupled with electron beam) imaging, milling and deposition technique (briefly called FIB) and Nanoindentation. After a basic description of both techniques (architecture, probe-sample interaction basics and operation modes), we will demonstrate effectiveness of this approach for microstructural investigation on very small samples without any sample preparation or pre-processing by presenting two case studies:
(i) Analysis of residual stresses of engineered surfaces by coupling focused ion beam controlled material removal and nanoindentation testing, and
(ii) Nano-mechanical characterization of sputtered niobium thin films for application in accelerating cavities.

1. Introduction

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) [1].

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 [2]; in other cases, mechanical behaviour can be strongly influenced by microstructural and size effects (grain size, defects, interfaces, porosity,…), so multi-scale characterisation procedures [3] 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).

Mechanical characterization activities are essentially based on nanoindentation testing, which at present is the prime technique used in nanomechanics to investigate the mechanical properties of the materials on the sub-microscale. It has long been used to study the elastic, plastic and fracture properties on the surfaces of bulk samples, as well as for thin-films [4-6]. More recently, it became possible to perform controlled compression, shear, and bending tests on nanostructures smaller than a micron, such as nanospheres , nanowires and nanopillars [7-8].

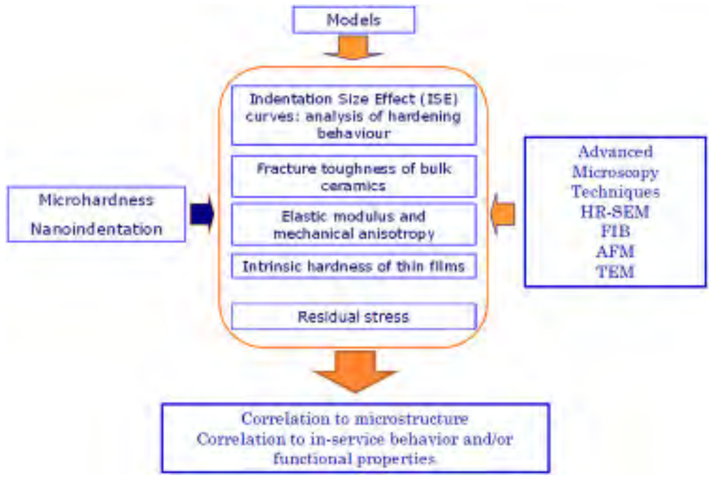


Fig. 1 – Concept scheme representing how the proposed integrated approach can be applied for improving the understanding of mechanical behavior of nano-structured systems and then give the correlation to microstructure and functional properties.

On the other hand, focused ion beam techniques are used for advanced sample preparation and microstructural characterization. FIB systems [9] utilize a finely focused beam of gallium ions (Ga+) operating at low beam currents for imaging and at high beam currents for site-specific milling. By controlling the location, beam size and current density of the ion beam, material can be selectively removed from sub-micron areas. Most apparatus nowadays available in the market also contains in situ scanning electron microscopy (SEM) capabilities for real time imaging of the ion milling site and even 3D tomography. The capability of high-resolution imaging using both secondary electron and secondary ion signals has made the FIB microscope a unique imaging tool. Stress-free cross sectioning using the primary gallium ion beam provides valuable microstructure information beneath the specimen surface. FIB techniques can be also used for TEM specimen preparation: a finished electron transparent portion of the sample (usually 5 µm x 20 µm) is obtained by FIB micro-milling and then placed by a micromanipulator on a sample holder to be inserted into the TEM microscope: this procedure at present represents the one site-specific and artefact-less outstanding TEM sample preparation techniques.

One of the present challenges in the field of material science and surface engineering is represented by the development of new integrate methodologies which are based on the combined use of nanoindentation techniques and high resolution microscopy, with the main aim of investigating the structural and microstructural evolution during nano-mechanical testing of nano-scale systems [7-8].

Following this approach (see figure 1), results arise from the application of integrated methodologies (see figure 1), which start from indentation 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.

In this paper, two case studies are reported, explaining how the combined use of FIB and nano-mechanical testing can be crucial for the correct evaluation of mechanical and functional performances of nano-structured systems:

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

2. Case study 1: Analysis of residual stresses of engineered surfaces by coupling focused ion beam controlled material removal and nanoindentation testing

Residual stresses play a crucial role in determining the deformation behaviour and performance of engineering components and materials, from bulk alloys and composites used in construction and manufacturing industries down to micro-mechanical studies of stresses in individual grains within polycrystalline aggregates, thin films and coatings, and MEMS/NEMS systems [10].

At present, one of the main challenges in the field of residual stress measurement in nanostructured systems is represented by the development of site-specific micro-scale evaluation techniques, which should be also semi-destructive method that allow routine determination of residual stress in engineered components.

In a previous work some of the authors [10], a new optimised method for the determination of residual stress at the microscopic scale was presented, based on focused ion beam (FIB) controlled material removal and relaxation strain mapping by Digital Image Correlation (DIC) techniques [11].

The newly proposed approach (figure 1) involves incremental focused ion beam (FIB) milling of annular trenches (ring-drill) at material surface, combined with high resolution SEM imaging of the pattern of markers previously deposited at the sample surface.

An optimised procedure for FIB milling is presented, allowing a complete automation of the procedure, also reducing the artefacts due to the ion milling of the stubs. Digital image correlation (DIC) analysis of the relative displacements between markers with respect to the undisturbed state provides a measure of strain relaxation.

The comparison of these strain relief measurements with finite element modelling (FEM) allows the evaluation of the residual stress state, in a manner similar to that used in macroscopic incremental hole drilling. Furthermore, the assessment of complete biaxial residual stress state is possible in this configuration, by measuring the relaxation strains along three different directions, in contrast with earlier studies that involve the machining of linear slots.

Results were presented [10] for residual stress evaluation of a 3.8 μm TiN coating on WC-Co substrate obtained by cathodic arc evaporation physical vapour deposition (CAE-PVD) techniques, showing an average compressive stress state of -5.63 GPa. This result was in good agreement with the estimate obtained by XRD (sin2ψ method) analysis of -5,84 GPa on the same sample, adopting the same elastic constants [10].

Nevertheless, further studies are still needed in the sense of exploring potentialities of the new proposed technique in terms of strain resolution and sensitivity, by testing soft metallic coatings, which are also expected to be in a low tensile residual filed.

Here we present some original results on a 1,5 μm Au coating on silicon substrate deposited by DC sputtering PVD techniques (voltage 410 V, current 0.2 A). This coated system is particularly relevant for the fabrication of MEMS structure, where residual stress plays a significant role in determining the final shape of the structure. In this case, residual stress was measured both by the new FIB-DIC technique [10] and by curvature measurement and application of the Stoney equation [12].

On the basis of several repeated tests carried out in this study the value of residual stress in the coating was then found to be equal to +270.64±88.62 MPa for the DC sputtered Au coating. These results are in good agreement with the estimate obtained by curvature measurement +280 MPa for the Au coating.

These results also confirm that even low tensile residual stress states can be evaluated by the ring-drill technique, with a spatial resolution of the order of 1 μm, which is comparable with the resolution obtained by the use of synchrotron sources.

In addition, the combination of FIB milling and SEM imaging within a single experiment ensures the ease and efficiency of use of the present method, since it does not require the laborious and time-consuming transfer of samples between instruments. In fact, the current procedure can be successfully automated for systematic automatic residual stress mapping across significant areas.

This technique seems therefore to be absolutely relevant also in the case of stress analysis on MEMS structures, where an in-situ evaluation of residual stress should be strongly needed, and was not possible to be performed by the conventional XRD or curvature-based methods.

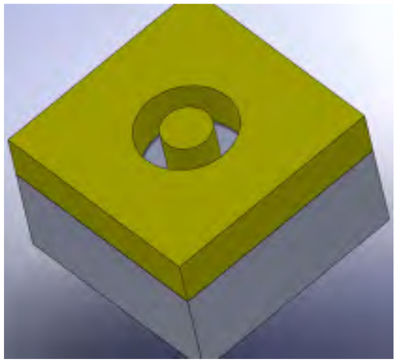


Fig. 2 – Illustration showing principle of ring-core milling, and the idealized geometry of the remaining "stub"

Fig. 3 – Example of one of the realized pillars on a PVD Au coating on Silicon substrate.

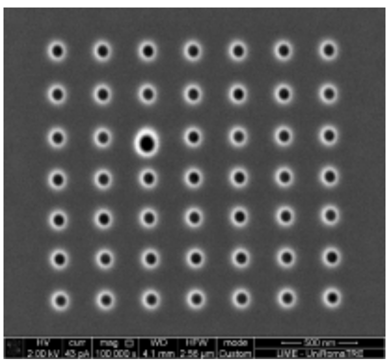


Fig. 4 – Example of the patterning realized over the surface before ring-drilling

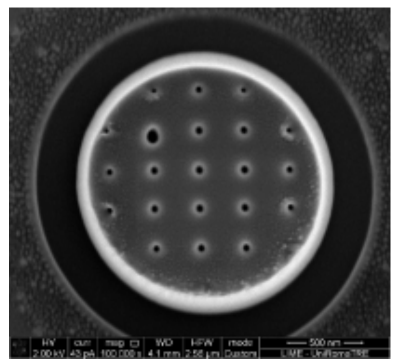


Fig. 5 –.Micrograph of the patterning after ring drilling. The measured displacements of the milled dots gives the relaxation strain related to the stress relief process.

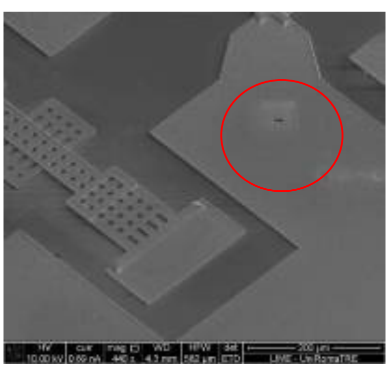


Fig. 6 – In-situ residual stress measurement in proximity of a MEMS structure (red circle) by the ring-drill method

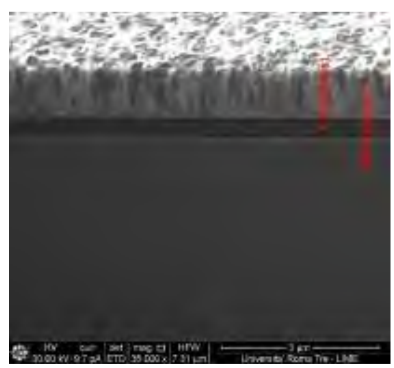


Fig. 7 – FIB cross section (imaging by using the ion probe) of the PVD Au coating under investigation

5. Case study 2: Nano-mechanical characterization of sputtered niobium thin films for application in accelerating cavities

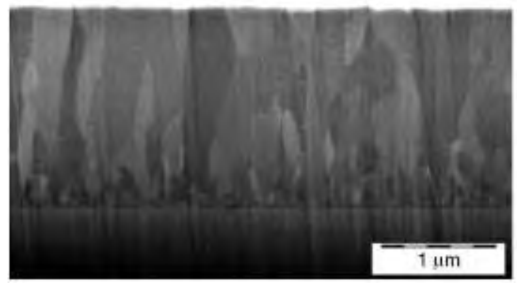
Niobium films obtained by Magnetron Sputtering PVD have been used for many years in superconducting and RF cavity applications [13-14].
Several experimental studies have underlined the strong influence of coating thickness, microstructure and density, coating/substrate interface and surface oxide layer on its Residual Resistance and superconducting properties [13-14].
For these reason, a comprehensive surface chemical, morphological and mechanical surface characterisation is required, in order to find out the appropriate correlation functions among process parameters\microstructure\surface properties\RF performances, and an exhaustive and statistically well-founded procedure has not yet been developed.
The objective of this work [15] was to determine the influence of applied bias Voltage on morphological and Mechanical surface properties of MS-PVD Nb thin films on OFHC Cu substrate, and its correlation with their superconducting properties.
The idea at the basis is that the use of the developed advanced methodologies for surface mechanical characterisation could be successfully used also for acquiring information on microstructural and even functional behaviour of coatings
Experimental activities were focused on the analysis of the influence of the applied BIAS voltage during PVD deposition on mechanical and microstructural properties and functional performances of coatings, with the main aim of proposing indentation techniques as a complementary quality control tool for the indirect evaluation of coating performances.
Two sets of coatings were then realized, characterised by different values of applied bias voltage (100 V and 0 V, respectively) ; process parameters are reported in [15].
Cross-section coating investigations were performed by using Focused Ion Beam (FIB) techniques: SEM microstructural investigations have been performed after FIB sectioning, while interfaces structure and microstructure and thickness of the surface oxide layer have been investigated by TEM after FIB sample preparation. Surface mechanical properties (intrinsic hardness, elastic modulus, surface oxide layer properties) were analysed by means of nano-indentation testing: 25 tests (Agilent G200 Nanoindenter equipped with Continuous Stiffness Measurement). Test parameters and calculation procedures are reported in [15].
All microstructural and surface mechanical obtained information were then correlated to superconducting properties, evaluated by Critical Temperature T_C and Residual Resistance (***RRR***) measurements of coatings on Quartz substrate.
In fact, results of nano-mechanical testing on the BIASED and UNBIASED PVD Nb coatings showed significant and often unexpected differences, between coating on different substrate and obtained with or without an applied Bias voltage during deposition.
As shown in table 1, which summarises results of mechanical characterisation activities, significant differences in hardness and modulus were measured for the same **Biased** coating on Copper or Quartz substrate.
In particular, a much lower hardness and higher scatter of experimental data were observed in case of Biased coating on Quartz, compared to the same on Copper substrate.
As a confirmation of this, contrasting microstructural characteristics were observed on biased and unbiased coatings on different substrates: biased Nb films on copper showed higher roughness and finer

Table 1. Summary of mechanical characterization activities and comparison with T_C measurements

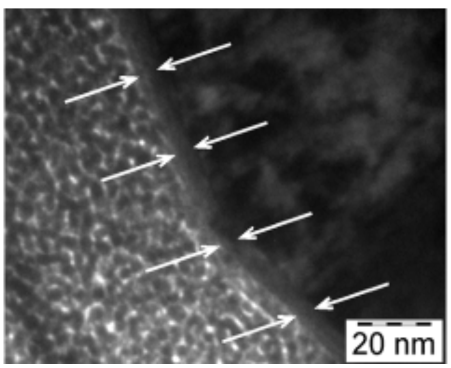
Sample code #	Description	Nanoindentation		Critical temperature measurement
		H (GPa)	**E (GPa)**	T_C (K)
796	**Nb on Cu BIAS type**	3,10 ± 0,58	101,5 ± 23,61	Not measured
797	**Nb on Quartz BIAS type**	1,63 ± 0,30	76,22 ± 48,99	9.45 ± 0.025
803	**Nb on Cu CERN type (NO BIAS)**	2,59 ± 0,35	108,68 ± 11,65	Not measured
804	**Nb on Quartz CERN type (NO BIAS)**	2,19 ± 0,31	95,95 ± 26,31	9.38 ± 0.05

grain size, compared to the unbiased samples on the same substrate, while opposite results were obtained for coatings on quartz substrate. Such results suggest that attention should be paid to the use of ***RRR*** and $\boldsymbol{T_C}$ results (obtained for coatings on quartz substrate) for making conclusions on cavity performances. Focused ion beam (FIB) analysis confirms that biased films on copper have finer grain size than unbiased films, while the use of FIB techniques in sample preparation, coupled with TEM observation, gave a much deeper understanding of the coating microstructures at the nanoscale: in particular, the presence of the surface oxide layer was observed, and an estimation of its thickness was performed. It has to be

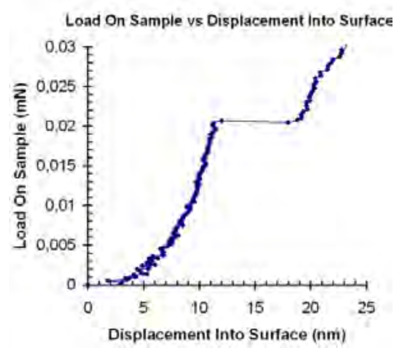
TEM lamella obtained by FIB milling and thinning. In-situ SEM-FEG observation (SE, 5 KV), 12000x



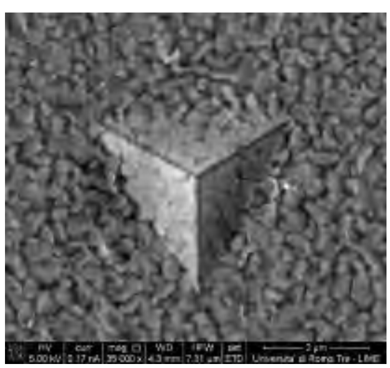
Microstructure of a Nb coating on Copper substrate. SEM-FEG (SE, 5 kV, 60000x) observation after FIB cross-section.



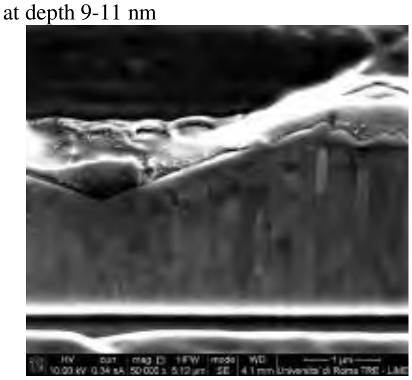
Detail of the surface oxide layer, Nb on Cu BIAS type (TEM BF 660000X after FIB lamella thinning)



Nanoindentation testing on Nb thin films: Detail of the L-d curve highlighting brittle failure of the surface oxide layer at depth 9-11 nm



SEM-FEG imaging of a Berkovich nanoindentation mark



FIB/SEM cross-section analysis of a Berkovich nanoindentation mark. Analysis of piling-up and deformation mechanisms of columnar grains during indentation

Fig. 8.

underlined that at present no other technique can give equivalent morphological and microstructural thin film characterization, including speed of analysis, site-specific morphology, and composition and crystal orientation.
In addition, nanoindentation testing also allowed an indirect (and cheaper compared to high resolution microscopy techniques) evaluation of the presence and thickness of this surface oxide layer (Figure 8), which has been already correlated to coating's superconducting performances.
All these considerations confirm how important and effective can be a comprehensive multiscale-multitechnique mechanical and microstructural characterisation procedure, also in case of functional coatings.

5. Conclusions

In this paper, the application of high resolution - multitechnique – multiscale procedures to the nano-mechanical characterisation of engineered surfaces is presented.
It is observed that only by the combination and synergic use 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.
Two case studies are presented, both showing how nano-mechanical testing in combination with high resolution microscopy can be usefully applied to the characterization of coatings and nano-structured systems for functional (or non-mechanical) application.
In particular, (i) the use of FIB-DIC techniques for high resolution residual stress measurement on coatings for MEMS structures and (ii) the use of nano-mechanical testing for the investigation of microstructural effects of the functional performance MS-PVD Nb thin coatings are described and discussed.
These two applications gives an idea of how relevant can be the proposed procedure in many field of scientific and industrial interest, coming from coatings for applications in particle accelerators to thin films for wear resistant applications, up to in-situ microstructural and nano-mechanical characterization in MEMS structures.

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7. References

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