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Extended summary

Nanoindentazione: dalla calibrazione all'applicazione ai materiali metallici massivi e ai rivestimenti

Curriculum: Ingegneria Meccanica e Gestionale

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Abstract. Evaluation of mechanical properties is of great importance for design and development of engineering components with enhanced structural and wear performance. As mechanical systems in today's technology tend to decrease in size down to nanometers, characterization technique for mechanical properties of materials shifted its range from mN to μN.

Nanoindentation is a recent technique developed to measure mechanical properties on nano scale based on the continuous recording of applied force and depth. Initially used for the evaluation of hardness and elastic modulus of small material volumes and thin films, emerging uses are for the evaluation of a broad range of mechanical behavior, such as fracture, time dependent behavior, and residual stress. Although largely used to characterize nanostructured materials, this technique can be successfully applied also in bulk alloys. The method stands out by the high inherent measurement accuracy and easy of automation compared to most of the mechanical test methods. Nevertheless, many phenomena play an important role in the accurate determination of the materials properties.

The first goal of this study is to analyze the influence of these sources of data distortion. The second part of the study, aims to give a solid starting point for developing some measurement standards in new fields of application and for defining and preparing new standards to support measurement technology in nanomaterials characterization. Finally, different applications of nanoindentation technique are presented and discussed both on coating and bulk materials.

Keywords. Calibration, hardness, nanoindentation, round-robin, thin films.

1 Problem statement and objectives

Nanoindentation is a relatively new technique for the measurement of hardness, reduced Young modulus, and strain rate sensitivity of typically coatings and thin films [1-6].
Continuously recording indentation techniques have become rapidly established as a means of determining nano-scale mechanical properties of materials because of their high resolutions in load, position, and displacement [4,7]. One of the key advantages of this technique is that many mechanical properties, namely nano-hardness and reduced Young modulus, can be directly determined by the analyses of the indentation load-displacement data, and thus avoiding the need to image the hardness impression. This facilitates the mechanical properties measurement on sub-micron scale.
Nowadays, different nanoindenter instruments are commercialized and used for this purpose. Every instrument is equipped with his own analysis software for the measurements of the hardness and the reduced Young modulus out of the obtained raw data. These data are mostly acquired through the Oliver and Pharr method. In all cases, the calibration of compliance and area function are mandatory.
The first part of this study illustrates and describes a calibration procedure and an analysis approach of the raw data carried out for different nanoindentation instruments through several round robin experiments. The second part aims to show how this technique, although largely used in nano-science to characterize nanostructured materials, can be successfully applied also in bulk materials.

2 Research planning and activities

2.1 Calibration

The goal of the round robin international calibration experiments were to calibrate the machine compliance and the area function, and therefore calibrate the measurements of hardness (H) and reduced Young modulus (E_r) among the different used instruments, using different indenters. The major steps of these experiments were:

- definition and distribution of same reference samples;
- definition of a common measurement protocol;
- definition of a common analysis protocol;
- data analysis using the common protocol.

The consistency and goodness of the protocol was tested by comparing data spread yield using it with the data spread obtained through the instrument default procedure. The raw data were obtained using common reference samples for all the different nanoindentation instruments. The data-point spread evaluation also served as mean for the identification of sources of misalignment, yielding possible further improvements hints to the used protocol.
The commercially available reference samples were Fused quartz (*Fq*: E_r=72 GPa, ν=0.17) as hard material, Sapphire (*Sa*: E_r=410 GPa, ν=0.234) for its high Young modulus, Polycarbonate (*Pc*: E_r=3.3 GPa, ν=0.37) as soft material. The Table 2.1 includes the partners and their nanoindentation instruments. Three different indenters were used: Berkovich (*B*), cube corner (α), and spherical (*Sp*).

Instrument	***Institute***	***Acronyms***
Hysitron UBI	Polytechnic University of Marche (UNIVPM)	Hys-U
Hysitron Triboscope	Politechnika Warszawska (WUT)	Hys-T
Micro Materials	Aston University (AU)	MM
Agilent Nanoindenter G200	V. Bakul Institute for Superhard Materials of the National Academy of Sciences of Ukraine (ISM)	Agil
UNAT	ASMEC GmbH (ASMEC)	UNAT
MTS Nanoindenter XP	Weizmann Institute of Science (WIS)	MTS

Table 2.1 Nanoindentation instruments used by different partners.

The measurement protocol consists of two parts: *process 1* devoted to the calibration of the stiffness (inverse of machine compliance) and the area functions for each available instrument and indenter; *process 2* devoted to the measurements of H and E_r on the reference samples and using the calibration results of *process 1*.
For the *process 1*, measurements were carried out on *Fq* and *Sa* for all the three indenters with a trapezoid-shaped function having t_{load}= 20 s, t_{hold}= 10 s, t_{unload}= 20 s (Fig. 2.1a). The maximum load was in the range 100 to 10000 μN, for the low range, and between 10 and 100 mN, for the high range. The *process 2* consisted in the H and E_r measurements on *Fq* and *Pc*, with function loads as described in Fig. (2.1b) and (2.1c), respectively.

(a) (b) (c)

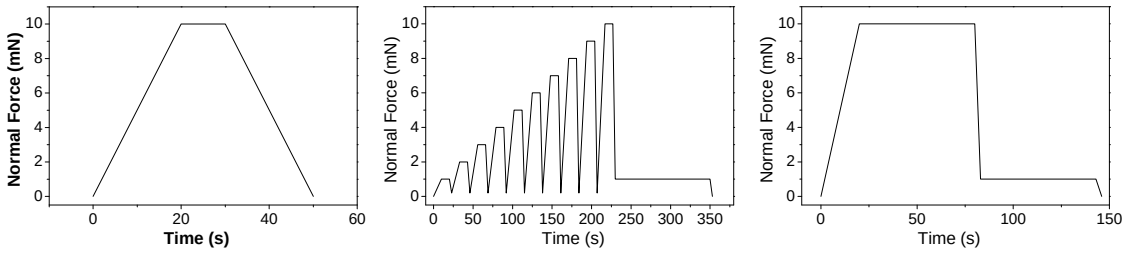

Figure 2.1 Load functions of process 1 (a), process 2 on fused quartz (Fq) (b), and process 2 on polycarbonate (Pc) (c).

The H and E_r on *Fq* were measured using a cycle load function with t_{load}= 10 s, t_{hold}= 10 s, t_{unload}= 3 s, 10 steps with 10% load increment to the final holding time of 120 s at the 10% of the maximum load. Maximum load was 2 mN and 10 mN, for instruments using low loads, and 20 mN and 100 mN for the instruments using higher loads. The H and E_r on *Pc* were measured using a single cycle load function with t_{load}= 20 s, t_{hold}= 60 s, t_{unload}= 3 s to 10% of the maximum load followed by a final holding time of 60 s. Maximum load was 0.1, 1 and 10 mN for instruments using low loads, and 1, 10, 100 mN, for the instruments using higher loads. All measurements of *process 2* were repeated 10 times per each maximum load. Fig. 2.1 reports the load function of the three above described calibration procedures. All data were collected and analyzed using a dedicated software (*ASMEC Indent Analyser*).

2.2 Applications

New applications of nanoindentation technique are presented:

- study of mechanical properties of the different constituents in a Duplex stainless steel in as received and hot-deformed conditions;
- nano-hardness characterization of an optimized FSW AZ31 alloy butt joint;
- analysis of the dependence of the hardness on the indentation depth in bulk materials;
- thermal stability of nanostructured Ti-B-N based coatings on aluminium alloy.

However, this part of the work is not discussed in this section.

3 Analysis and discussion of main results

The first step consisted in the *ab initio* calibration of the different available instruments among the partners, according to the instrument's user manual, to ensure the highest accuracy of the measurements eventually performed using the here described protocol.
After having determined the instrument/indenter stiffness function, the area function was calculated using the data recorded using *process 1*, for each indenter, on *Fq* and *Sa* samples. For the same instrument, stiffness function of different indenters are remarkably different, which indicates the need of performing separate stiffness measurements for each instrument and each indenter. The range of load (and therefore depths) over which the calibration was performed depended on the maximum load force available to the different instruments. These data also confirm the importance and utility for using both *Sa* and *Fq* in the stiffness calibration process. A key aspect of the common analysis software is that it uses a stiffness function, rather than a single stiffness value for the area function analysis (as suggested in many instrument manuals). This allows variations of the stiffness value for different loads.
The calibration processes were used by all partners to evaluate the hardness (H) and reduced Young modulus (E_r) of hard (*Fq*) and soft (*Sa*) reference samples. Measurements on these samples were first performed following the common protocol, and then using the instrument data analysis tool available for each instrument. To compare the data and then evaluate the goodness and reproducibility of the different instruments data, a set of 10 measurements was averaged for each partner and each available indenter and specific instrument maximum load.
These values were compared to evaluate the goodness of the alignment of the different used instruments after having followed the common calibration procedures. Figs. 3.1 and 3.2 report the results of such a comparison. The goodness of the calibration procedure was evaluated in terms of the spread of H and E_r obtained among partners using different instruments and indenters.

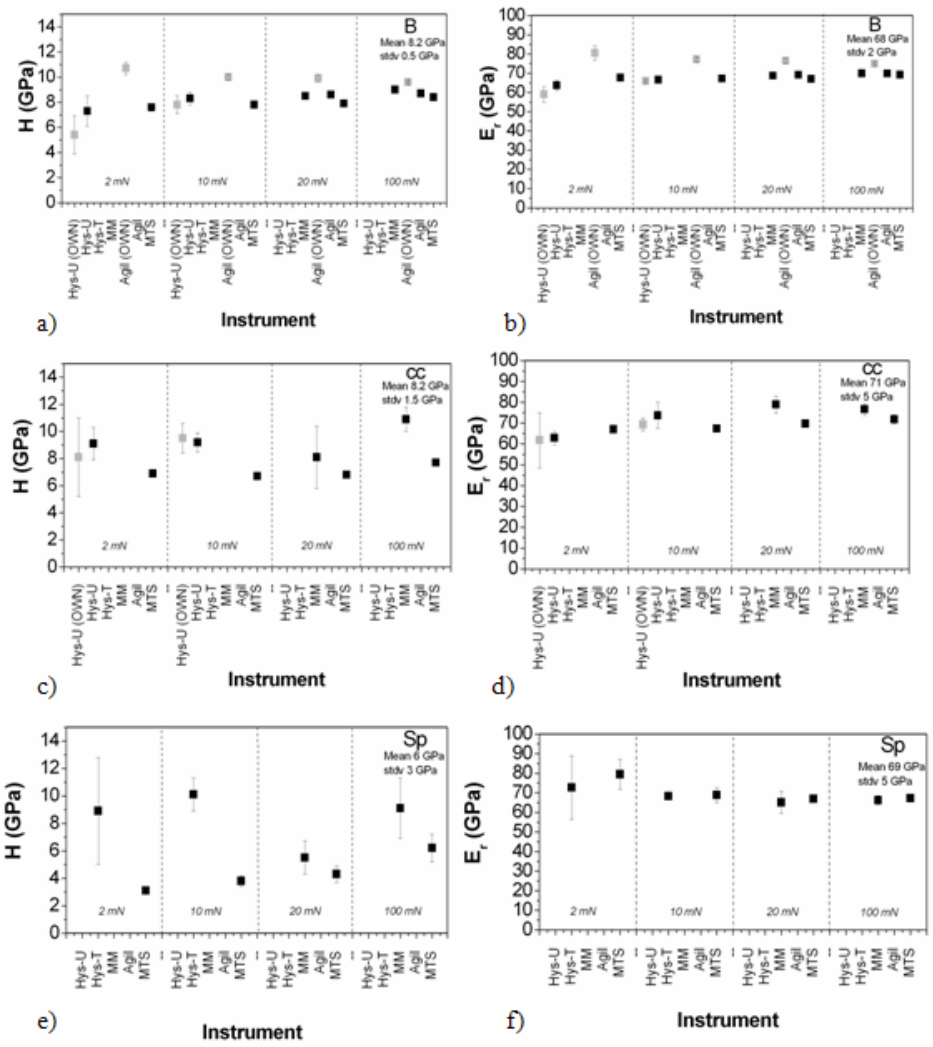

Figure 3.1. Results of process 2 of the calibration protocol on fused quartz (Fq). H as a function of maximum load for the different used instruments with Berkovich (a), cube-corner (c), spherical (e) indenters; E_r as a function of maximum load for the different used instruments with Berkovich (b), cube-corner (d), spherical (f) indenters. Data obtained using the procedures and instrument software of Hysitron (Hys-U) and Agilent (Agil) are also reported as bright solid square data points. Mean values and related standard deviation are also reported.

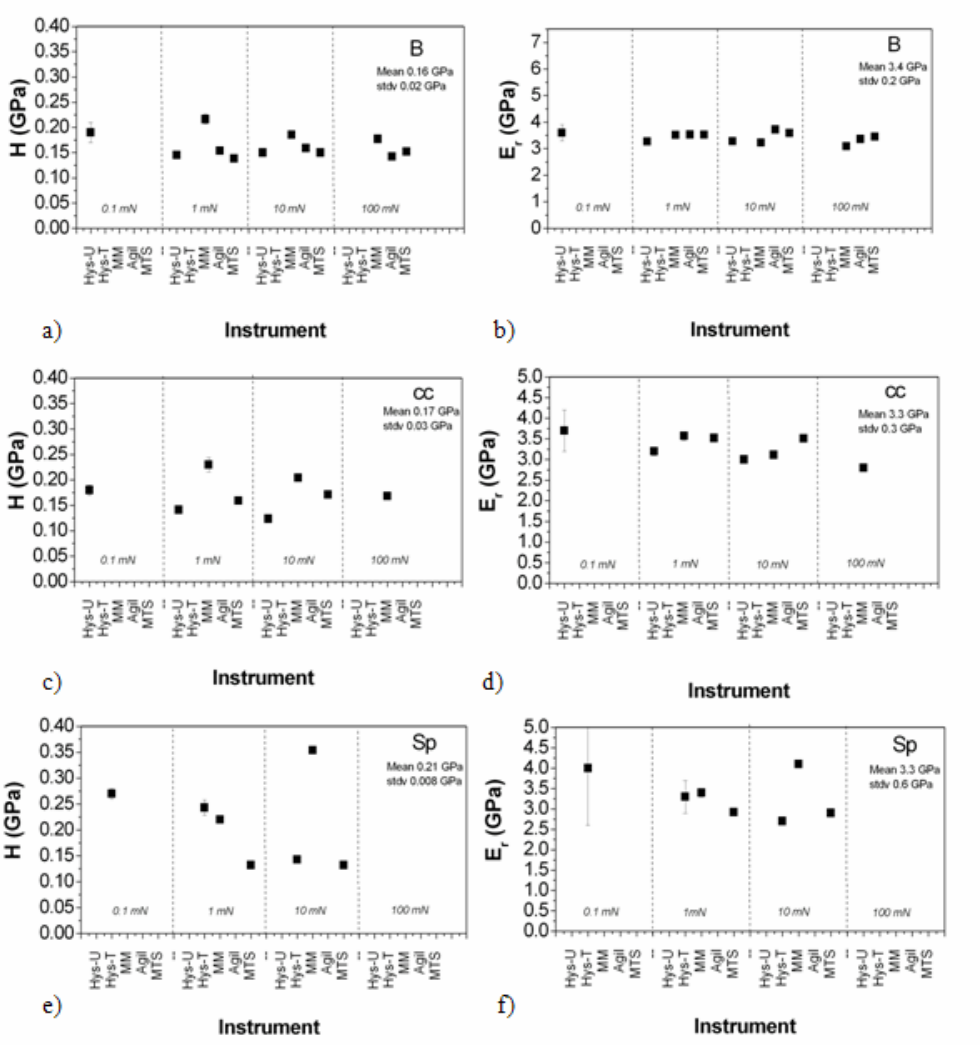

Figure 3.2. Results of process 2 of the calibration protocol on polycarbonate (Pc). H as a function of maximum load for the different used instruments with Berkovich (a), cube-corner (c), spherical (e) indenters; E_r as a function of maximum load for the different used instruments with Berkovich (b), cube-corner (d), spherical (f) indenters. Mean values and related standard deviation are also reported.

In the case of the Berkovich indenter, data converged to a common value of H = 8.2, 0.16 GPa, and E_r = 68, 3.4 GPa, for the hard *Fq* and soft *Pc* samples, respectively. In the case of the cube corner indenter, data converged to a common value of H = 8.2, 0.17 GPa, and E_r = 71, 3.3 GPa, for the hard *Fq* and soft *Sa* samples, respectively. These values were quite close, even if affected by a slight underestimation, to the expected values of H = 9.25, 0.16 GPa, and E_r = 69.6, 3.3 GPa, respectively for *Fq* and *Pc*. As for the spherical indenter the hardness values were slightly different compared to the results obtained with the former two indenters. Hardness was 6.0, 0.21 GPa, and E_r = 69, 3.3 GPa, for the hard *Fq* and soft *Sa* samples, respectively. The reason why these data showed a better estimation and lower standard deviation of the Young modulus lies in the calibration procedure of the *ASMEC Indent Analyser* which is based on the E_r calibration.

Fig. 3.1 gives an example of two sets of data obtained either using the common protocol and using the instrument existing standards. In particular, ISM performed measurements and analyses using the instrument software Agilent and a Berkovich indenter; UNIVPM used the instrument software Hysitron with Berkovich and cube-corner indenters. Fig. 3.1 shows how lower is the scatter of data when using the common protocol respect to the case of evaluation the raw data with the instrument available analysis procedure.
The main differences between the common analysis protocol (*ASMEC Indent Analyser*) and instrument software/protocol are the use of only *Fq* for the calibration of stiffness and area function rather than *Fq* and *Sa*, and the use of a single value for the stiffness, rather than a stiffness function, as in the case of the *ASMEC Indent Analyser* protocol.
It is also important to note that the dispersion of results obtained without using the common protocol (either for measurements or analysis) was larger than when the protocol was used.
The importance and utility of the results obtained using this protocol is twofold. On one side, they can be used to interpret the spread in the results in nano-mechanical testing (namely for H and E_r measurement) which is not due to a different way of performing the calibration of the area function or stiffness, to the type of reference samples used, to the way of performing the measurements of H and E_r to the tested sample, to the way of analysing the results, as all this parameters were fixed among all partners. The spread obtained can then be attributed, in the first approximation, to intrinsic instrument differences (e.g. as the level of drift, instrument noise, geometrical defects of a given nanoindenter), superimposed to statistical spread due to random variations (e.g. accurateness of operator). On the other side, it can be used as a starting point to compare this calibration procedure to other existing calibrations, suggested by the different nano-mechanics companies. With this respect, the present protocol need some improvement concerning its application to the spherical indenter, as shown in the Figs. 3.1 and 3.2, where hardness data averaged to a lower value, on *Fq*, and a slightly higher value, on *Pc*, compared to the results obtained using the sharper tips. Moreover, the data acquired using the spherical indenter suffer form a considerably coarser standard deviation. Some possible improvements is likely to concern the type of load curves used for H and E_r measurements. It was in fact noticed that the drift rate of some instruments was large in comparison to the duration of the measurement, which is likely to cause the risk of a change of drift during the measurement and hence of applying a wrong correction. One solution would be the use of separated load-unload curves rather than one load curve with multiple load-unload cycles.

4 Conclusions

The collection and direct comparison of data from different types of nanoindentation instruments using a common procedure of analysis on same materials, is quite unique, as, to the authors knowledge, it has been done in very few cases before [8,9].
A new protocol for calibration and data analyses of hardness and reduced Young modulus of hard and soft samples was created and successfully tested among different partners and different nanoindentation instruments. This protocol is designed to be used by users of different nanoindentation instruments.

Comparison of the results obtained by different instruments was used to estimate the spread of results obtained in common nano-mechanical testing. Such results were used to identify the major sources of spread strictly related to the different instruments. It was shown that the use of a function, rather than a simple value, for the stiffness improve the calibration accurateness. The hardness and reduced Young modulus data spread was considerably lowered on using this calibration protocol, respect of the instrument calibration procedure available in the tested instruments.
This protocol can be considered a starting point for the formulation of a new standard in nano-mechanical testing of hardness and reduced Young modulus.
The present work showed the usefulness and advantages potentially resulting from the introduction of common standards and protocols.

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