Measuring Hardness and More through Nanoindentation

Author- Rahul Nair, Fischer Technology, Inc.

Co-authors- Matt Taylor, Fischer Technology, Inc., Bernd Binder, Helmut Fischer, GmbH.

Introduction

Indentation Testing is the technique of using a harder material commonly referred to as an indenter to deform a softer material. The calculated hardness (H) is the applied force (F) divided by the corresponding area of contact (A); $H = F/A$. One of the first modern forms of this technique was implemented by Johan August Brinell in 1900 [1]. A very heavy load, up to 30,000 N, is applied through a 10mm diameter hard ball onto the test material. The hardness of the material is calculated by measuring the diameter of the residual imprint.

As materials increased in hardness over the years new techniques had to be developed to measure this property. Patented in 1914 the Rockwell Test employs smaller indenters; a diamond cone or a 1/16 inch diameter steel ball [1]. A lower fixed load in the range of 600 N to 1,500 N is applied, the penetration depth measured and the corresponding area of contact calculated.

While the aforementioned techniques are used to measure hardness of metals and ceramics, Durometers were developed to measure the hardness of soft polymeric materials. Developed in the 1920s, 'Shore' hardness of material is characterized through this technique using Durometers with different spring constants and a conical or spherical shaped indenter per ASTM D 2240 and ISO 868.

Surface treatments of soft steels like case hardening, carburizing and carbonitriding require the surface mechanical properties to be measured, not the bulk. In order to limit the stress field from an indent to the treated surface, lower loads have to be applied through smaller indenters. The Vickers and Knoop hardness were developed in 1921 and 1939 respectively to meet this need. Indenters used in these techniques are diamond pyramids where the four sides meet at a point. Low loads of up to 5N are applied through these indenters and the area of the residual imprint is optically measured per ISO 6507-1, 2, ISO 4545-1, 2 or ASTM E384.

Developments in deposition technology have resulted in an increase in the use of thin films and coatings for aesthetic, tribological as well as functional purposes. These materials are used for a wide range of applications like automotive clear coatings, protective metallic coatings, cutting tools, integrated circuits and biomaterials. While traditional indentation testing can be used to characterize bulk steel, micro/nano scale layers and components have brought more challenges.

Until recently, measuring the Pencil hardness of thin films according to ISO 15184 has been commonplace especially in the automotive paint industry. With this method, pencils of different hardness are moved at a certain angle and with a certain force across the paint surface to be tested. The 'pencil hardness' of the coating is defined by two consecutive levels of pencil hardness, where

the softer pencil leaves only a writing track, while the harder pencil causes a tangible deformation of the paint coating.

While Pencil, Vickers and Knoop hardness are still in use, the reliability and reproducibility of these methods are contentious for reasons mentioned later in this article. Due to stringent quality standards in the coating industry, it is necessary to be able to test the hardness of coatings with accuracy and repeatability. The hardness of thin coatings on tool bits, the viscoelasticity of protective coatings on optical lenses, the low friction coatings in consumer products all require precision application of millinewtons of force and corresponding measurements of depth in nanometers. This has led to the development of nanoindentation.

Nanoindentation

Instrumented indentation testing more commonly referred to as nanoindentation or in simpler terms depth-sensing indentation employs high-resolution instrumentation to continuously control and monitor the loads and displacements of an indenter as it is driven into and withdrawn from a material. The analysis of the measured force-displacement curves described in ISO 14577 is based on work by Doerner and Nix and Oliver and Pharr [2, 3].

Developed in the mid-1970s, nanoindentation is used to characterize a variety of mechanical properties of any material that can be measured in a uniaxial tension or compression test. While nanoindenation is most often used to measure hardness, it is also possible to calculate the modulus and creep using the data collected in this test. Methods using nanoindentation testers have also been devised for evaluating the yield stress and strain-hardening characteristic of metals, the storage and loss modulus in polymers, the activation energy and stress exponent for creep. The fracture toughness of brittle materials can be estimated as well using optical measurement of the lengths of cracks that have formed at the corners of hardness impressions made with sharp indenters.

Construction of Testing Equipment

Equipment used to perform nanoindentation consists of three basic components as shown in Figure 1.

(a) An indenter mounted onto a rigid column

(b) An actuator for applying the force

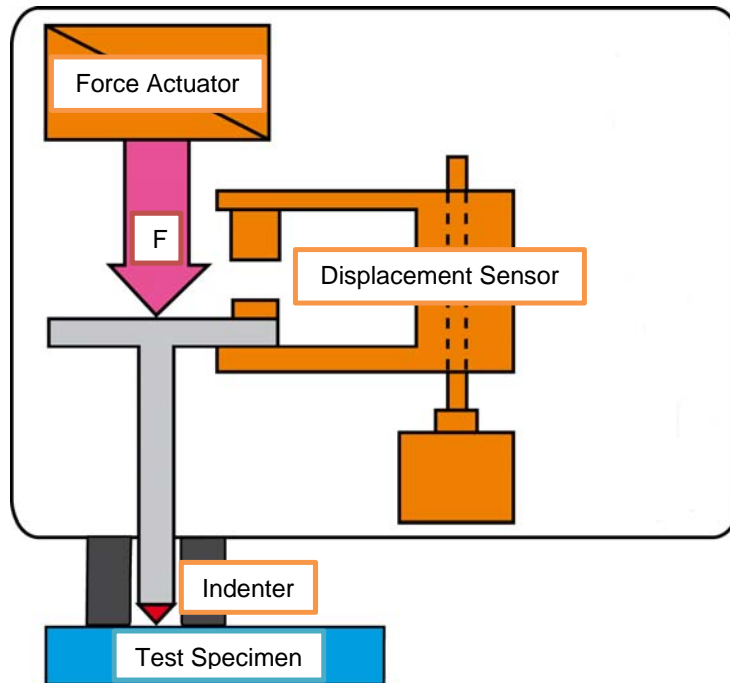(c) And a sensor for measuring the indenter displacements

Figure 1: Schematic of typical nanoindentation tester with a force actuator and displacement sensor

Small forces are generated either electromagnetically with a coil and magnet assembly or electrostatically using a capacitor with fixed and moving plates or with piezoelectric actuators. Displacements may be measured by eddy current sensors, capacitive sensors, linear variable differential transducers or laser interferometers.

A diamond is typically used to make indenters because it has high hardness and elastic modulus. This minimizes the contribution to the measured displacement as compared to those that are made of other less-stiff materials like sapphire or tungsten carbide in which case the elastic displacements of the indenter must be accounted for. Vickers geometry indenter, a four-sided pyramid, is most commonly used in higher load nanoindentation tests for its durability. The Berkovich geometry indenter is used for measurements of a few nanometers for two reasons; they are very sharp thus they cause plastic deformation even at very small loads and they are easier to manufacture precisely as they have only three sides. Cube corner indenters are even sharper than the Berkovich causing higher stresses and strains. They can be used to estimate fracture toughness at relatively small scales. While using spherical indenters as the contact stresses small and produce only elastic deformation at low loads, they could be used to examine yielding and work hardening, and to generate the entire uniaxial stress-strain curve [4].

Hardness, Modulus and Creep

During a nanoindentation measurement the indenter is driven into the material as shown in Figure 2, both elastic and plastic deformation processes occur. This produces an impression with a projected area A_p and surface area A_s of contact that depends on the shape of the indenter to a contact depth, h_c.
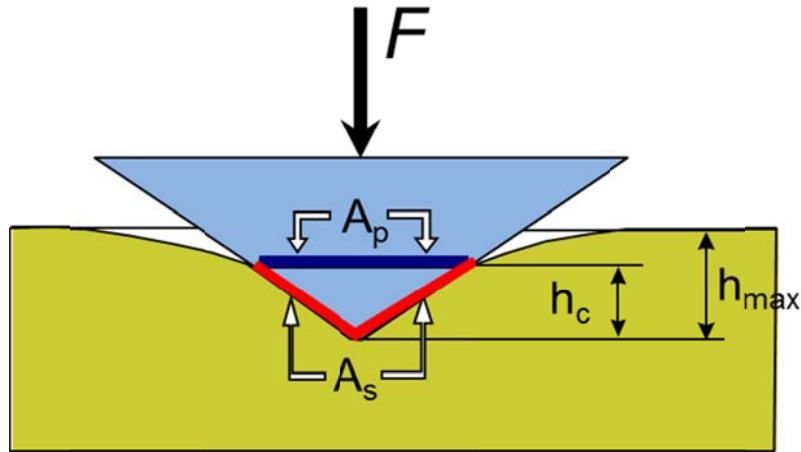
Figure 2: Schematic of indenter (blue) deforming test material (green)

The nanoindentation measurement includes a loading and unloading cycle. Figure 3 shows indentation load (F) plotted against the displacement (h) relative to the surface before deformation, where the data was obtained for one complete indentation cycle. The important quantities are the maximum depth (h_{max}) of penetration, the peak load (F_{max}), and the final depth after unloading (h_r). The slope of the upper portion of the unloading curve, S is known as the contact stiffness. The contact depth and stiffness are determined using the Oliver-Pharr method as described in ISO 14577 and ASTM E2546. The hardness and elastic modulus are derived from these quantities.
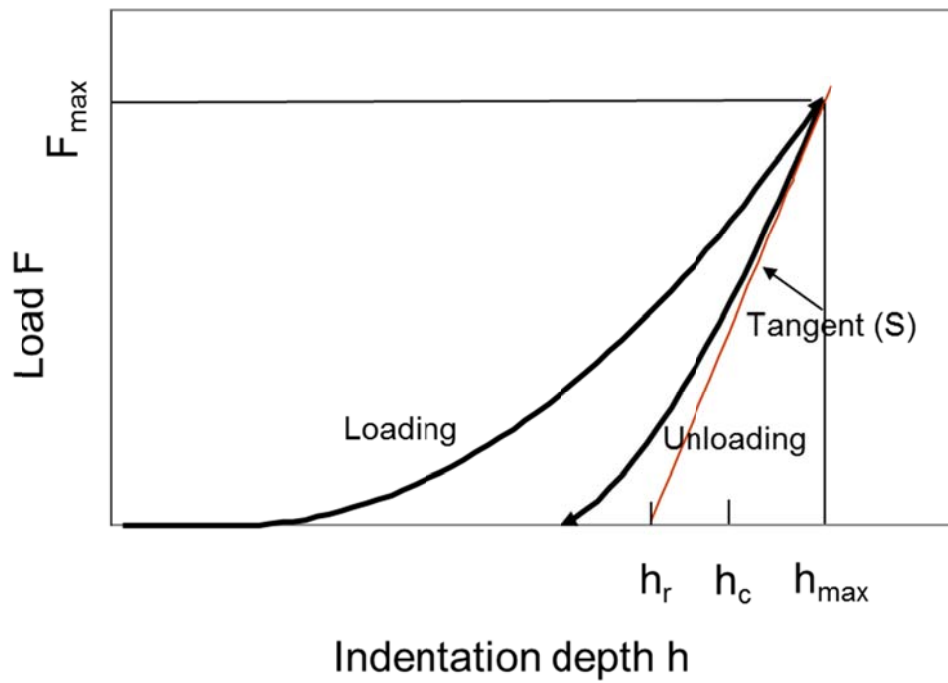

Figure 3: Load-displacement curve measured on a nanoindentation tester

In nanoindentation the Martens Hardness is determined from the loading portion of the load-displacement curve and includes the materials resistance to both plastic and elastic deformation. The Martens Hardness can be plotted as a function the indentation depth. Martens Hardness is given by,

$$HM = \frac{F}{A_s(h)}$$

Instrumented Indentation Hardness correlates to traditional forms of hardness as it is a measure of the resistance to plastic deformation. Instrumented Indentation Hardness is given by

$$H_{IT} = \frac{F_{max}}{A_p}$$

Reduced elastic modulus, E_r that is indicative of the stiffness of the sample is given by

$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A_p}}$$

β is a constant that depends on the geometry of the indenter.

The reduced elastic modulus accounts for the elastic displacement that occurs in both the indenter and the sample. For a test material with elastic modulus E_{IT} it can be calculated by

$$\frac{1}{E_r} = \frac{1 - v^2}{E_{IT}} + \frac{1 - v_i^2}{E_i}$$

Here v is the Poisson's ratio for the test material, and E_i and v_i are the elastic modulus and Poisson's ratio of the indenter, respectively.

Creep can be used to characterize material behavior at a constant load. Indentation Creep is defined as an increase in penetration depth under constant load. As shown in Figure 4 the selected final load is kept constant for defined time duration and the indentation depth is measured.

Indentation Creep, C_{IT} is calculated as

$$C_{IT} = \left(\frac{h_2 - h_1}{h_1} \right) . 100 \%$$

h_1: indentation depth at the start of the creep test

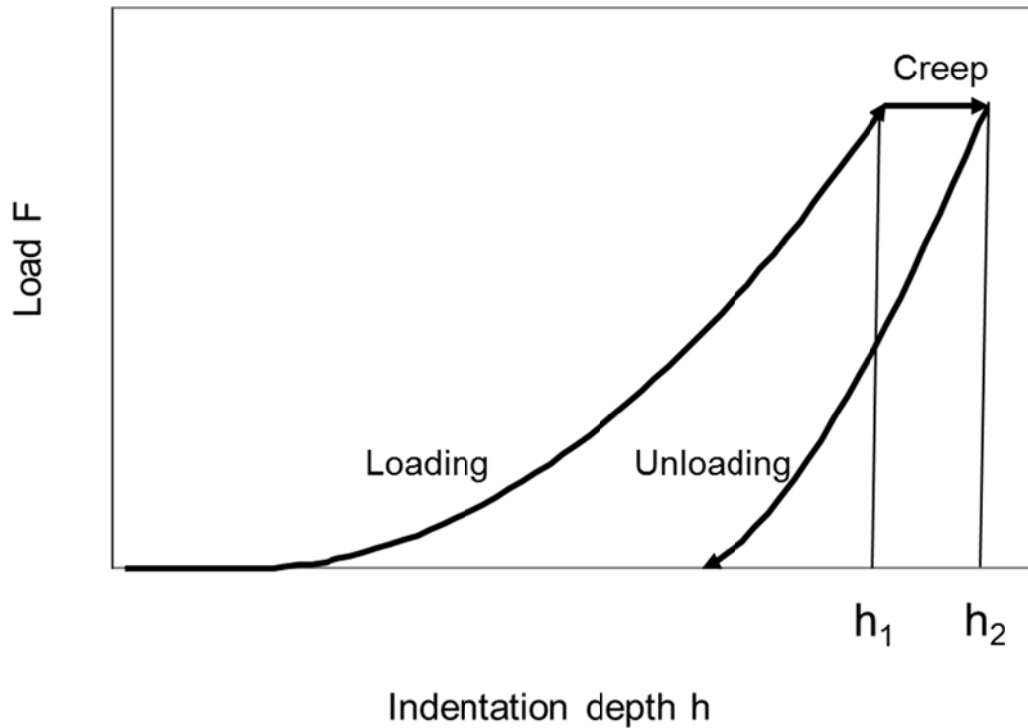h_2: indentation depth at the end of the creep test

Figure 4: Load-displacement curve with defined creep period at maximum load measured on a nanoindentation tester

Comparing Traditional Hardness Testing to Nanoindentation Hardness

As hardness is already being measured for most applications it is important to understand the correlation between these traditional forms of hardness and Instrumented Indentation Hardness.

Vickers Hardness vs. Nanoindentation Hardness

Surface hardness of hard materials is commonly measured with Vickers or Knoop indenters with traditional microhardness testers. While these tests are still reliable to characterize the hardness of most bulk materials they are not as effective for coatings and thin films. The loads used in traditional microhardness testers are usually too high and results are affected by the properties of the underlying layer. And because the indentation is measured optically, reproducibility and accuracy of the data collected are affected by the quality of optics and user's definition of the diagonals of the residual indent. In nanoindentation the measured depth is used to calculate the area of contact. But there is still a relationship between Instrumented Indentation Hardness and Vickers Hardness as a Vickers geometry indenter is used in both tests. Even the Berkovich geometry indenters that are also used in nanoindentation simulate the same strain rates as a Vickers geometry indenter. Thus the relationship between Instrumented Indentation Hardness and Vickers Hardness is defined as

$$H_V = 0.0945\ H_{IT} \quad [5]$$

Shore Hardness vs. Nanoindentation Hardness

A study measuring Martens hardness of Shore A standards with the FISCHERSCOPE® HM2000 S, a nanoindentation tester shown in Figure 5, shows a very linear correlation at relatively low loads. The data in graph in Figure 6 are from indents with 50mN maximum load with loading and unloading time of 60 seconds and a creep time of 10 seconds. These testing parameters are similar to those used for soft coatings and thin films when shallow indentation depths are required to prevent substrate effects.

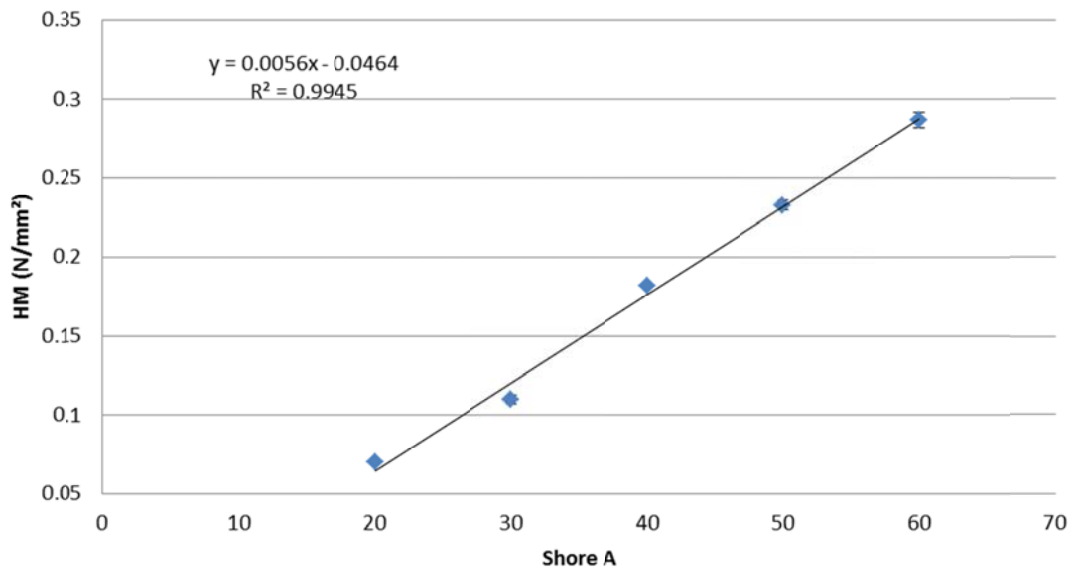**Figure 5:** FISCHERSCOPE® HM2000 S for the determination of the Martens Hardness

Figure 6: Martens Hardness (HM) of Shore A standards performed with a FISCHERSCOPE® HM2000 S

Pencil Hardness vs. Nanoindentation Hardness

In the following study the Martens hardness was measured for a set of graded pencils used in Pencil hardness testing. The tests were carried out with the FISCHERSCOPE® HM2000 S. Figure 7 shows the results of multiple measurements on pencils of various hardness levels. The large standard

deviations of the individual test series show the limitations of the pencil hardness method. Especially in the higher range, the nominal hardness (B, HB, F, H, etc.) of pencils are not a dependable indicator of their actual hardness.

With a nanoindentation tester the hardness of paint coatings can be measured directly and accurately. In addition, other characteristics can be determined, such as creep and relaxation behavior, as well as the modulus of elasticity. All of these parameters provide a true indication of the paint quality.
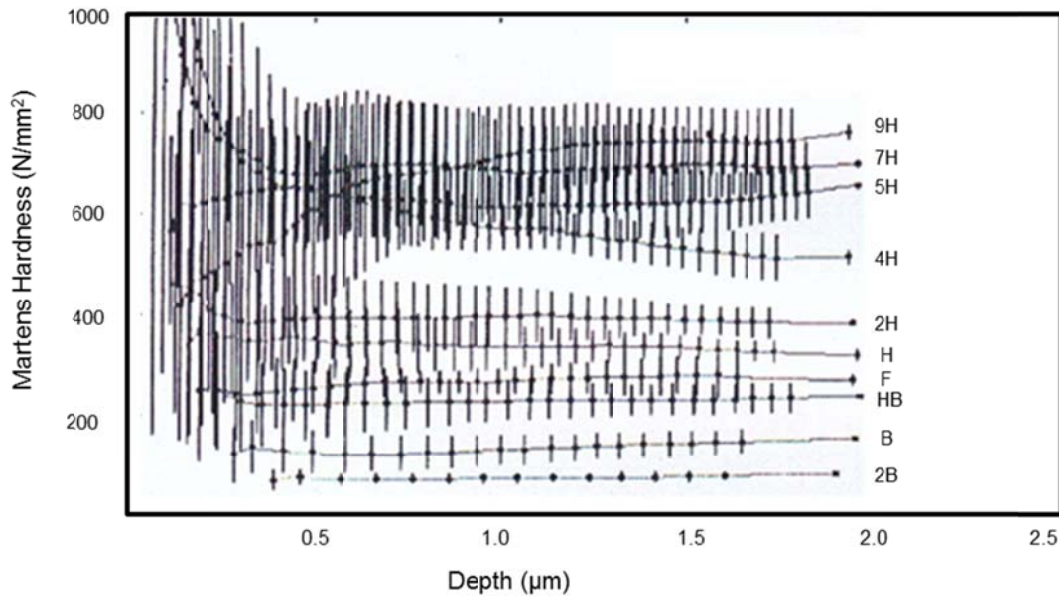

Figure 7: Comparison of the Martens Hardness of pencils of different hardness, shown with the standard deviation of the measurements

Example of Applications

Nanoindentation testers available in the market have a variety of features, load and displacement ranges and resolutions. The following examples discuss two very different coatings that are commonly characterized with the FISCHERSCOPE® HM2000 S nanoindentation tester. Key features and capabilities that are essential for the nanoindentation tester in each application are described below.

Mechanical characterization of lacquer coatings in automotive applications

In the automotive industry clear coatings for paint are used as protection from corrosion and external damage. These lacquers are exposed to environmental influences such as extreme temperature fluctuations or moisture and salt. In addition, automotive coatings must exhibit a certain toughness to make them resistant to mars and scratches. This requires the right balances between hardness and

elasticity. A quick differentiation and determination of these coating properties is possible with the nanoindentation test.

Influence from underlying layers or the substrate can be avoided by selecting a sufficiently low maximum load that keeps the penetration depth of the indent below 10% of the coating thickness. At the beginning of the curing process the clear coats are relatively soft. One of the key features of a nanoindentation tester is a sensitive automated surface detection. As the measured mechanical properties polymers are influenced by rate of loading and unloading a thermally stable nanoindentation system is also essential. Drift in the depth measurements caused by changes in environmental temperature must be avoided or accounted for.

The Martens hardness (HM) and the Martens hardness after creeping (HM_{CR}) are values which specify plastic and elastic properties of the paint coating. The indentation hardness (H_{IT}) considers only the plastic portion of the material deformation. The hardness parameters allow for better understanding of aging, curing, cross-linking, embrittlement through UV radiation, hardness change through temperature influences and the degree of polymerization of the lacquer.

Figure 8: Weathering rack at Atlas' facility in Florida with various car body parts

One of the most important advantages of the instrumented indentation test is the determination of elastic properties. The indentation modulus (E_{IT}), creep at maximum load (C_{IT}) can be determined using this method and provides information regarding the visco-elastic properties of lacquer coatings. These properties show the ability of the lacquer to resist weather degradation and heal in case of scratches.

Nanoindentation on wear-resistant DLC coatings applied to engine components

In order to reduce emissions in combustion engines without sacrificing performance, manufacturers are continually working to improve the ability of the moving components (e.g. camshafts, valve lifters, piston rings and gears) to resist abrasion and reduce friction. Protective coatings such as diamond-like carbon (DLC) are increasingly used in such applications. As DLC coatings can have a wide range of hardness depending on the deposition process it is important to measure the fundamental mechanical properties of this hard, low friction coating.

Traditional hardness measurements would involve applying a load though a sharp indenter and measuring the residual imprint under a microscope. However this is almost impossible due to the elastic nature and dark color of the DLC coating.

As these coatings are only a few microns in thickness the nanoindentation tester should have high depth resolution to allow for shallow indents to be performed thus preventing the substrate material from influencing the measurements. And because ceramics have higher stiffness the instrument must have a rigid frame to eliminate instrument compliance and only deform the material being tested.

Figure 9: DLC-coated engine components

In this example, the measurement results of a 3 μm thick DLC layer are shown. The values for indentation hardness (H_{IT}), Martens Hardness (HM) and indentation modulus (E_{IT}) for the coating is listed in Table 1. The converted Vickers hardness (HV) helps correlate these measurements with traditional microhardness testers. The graph in Figure 10 maps the measured Martens Hardness as a function of indentation depth. Minimal change in this measurement with increasing depth indicates that even at maximum load there is no influence from the under lying substrate.

Table 1: Hardness and elastic modulus measured by nanoindentation. The table shows mean value, standard deviation and coefficient of variation of five measurements.

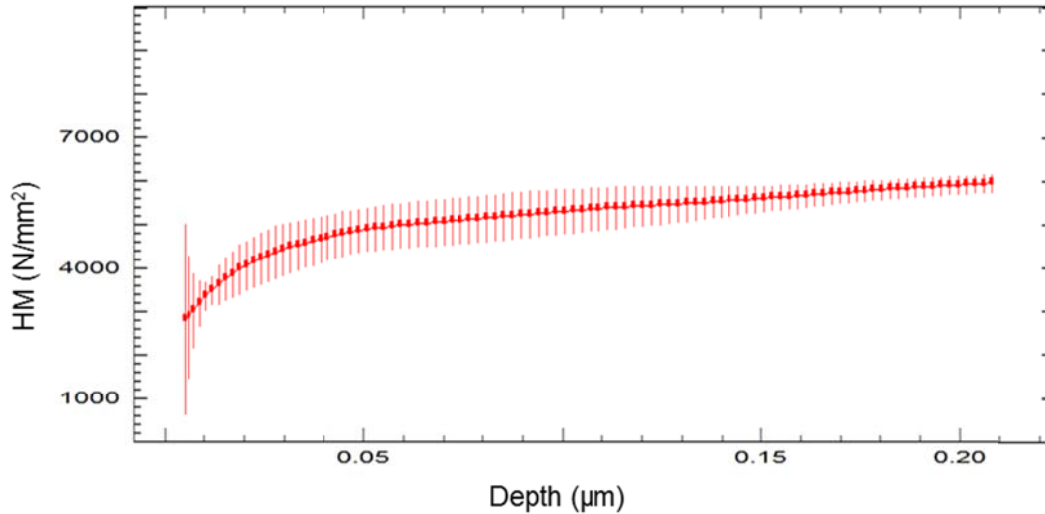| DLC coating	HM	HIT	HV	EIT/(1-v_s^2)
	N/mm²	N/mm²		GPa
Mean	5903.9	12038.64	1137.65	123.4
Standard deviation	224.45	644.67	60.92	5.41
Variation %	3.8	5.36	5.36	4.38
Minimum	5671.9	11454.8	1082.5	118.6
Maximum	6198.1	12836.5	1213	130.3

Figure 10: The graph shows the depth-dependent profile of the Martens Hardness of the DLC coating

Conclusion

Improving the surface mechanical properties of materials boosts performance and increases life cycle of products. New developments in coating and surface treatment technology has seen nanoindentation gain wider acceptance. Combination of ISO and ASTM standards for nanoindentation and availability of off-the-shelf options from different vendors has also contributed to adoption of this technique in many industries.

Given the limitations of traditional hardness testing techniques, nanoindentation testers are viewed as tools that can give a better understanding of the interactions between surfaces or against abrasive elements. The wealth of information about the mechanical properties derived from a nanoindentation test defines the true strength of a material. Additionally, a single tool can be used to characterize a wide variety of materials ranging from soft polymers to hard ceramics. Most importantly, this technique removes the majority of the user-influence and subjectivity from the test and allows one to quantitatively analyze a surface or coating.

References

1. The Hardness of Metals, D. Tabor, Oxford University Press, Aug 3, 2000, ISBN 0198507763, 9780198507765

2. A method for interpreting the data from depth-sensing indentation instruments, M.F. Doerner, and W. D. Nix, Journal of Materials Research, Vol. 1, No. 4, Jul/Aug 1986

3. Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology, W.C. Oliver and G.M. Pharr, Journal of Materials Research, Vol. 19, No. 1, Jan 2004

4. A simple predictive model for spherical indentation, J.S. Field and M.V. Swain, Journal of Materials Research, Vol. 8, No. 2, 1993

5. The IBIS Handbook of Nanoindentation, Anthony C. Fischer-Cripps, ISBN 0 9585525 4 1