Nanohardness and nanoindentation

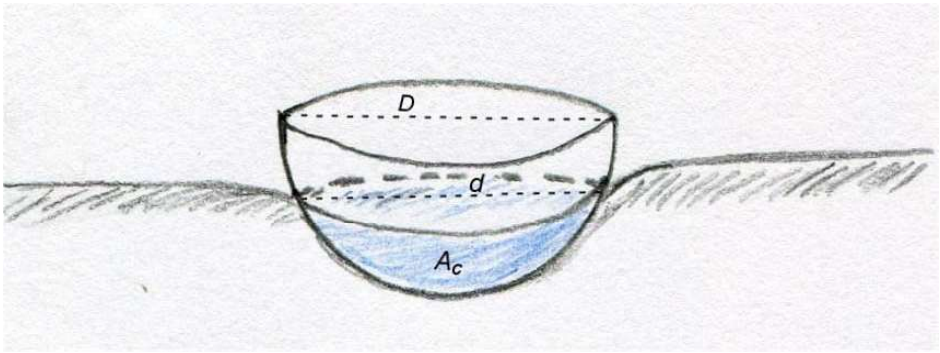
As the Materials Science is progressing, nowadays several types of nanocrystal materials, nanoobjects, or thin films are developed and studied; nanoindentation becomes more and more important investigation method. However, when we say that we need the nanoindentation, we have to know about both micro- and nanoindentation, which are complementing each other so that both the bulk – global – and local behaviors of the materials can be studied. The principles of these methods are the same.

The hardness test is almost the first material-testing method in Materials Science, by which we can estimate the mechanical properties qualitatively and quantitatively in relatively simple way, relatively quickly. The method is almost the destructive-free one, because the measurements do not make damage on the samples. The hardness method is very useful, because the issues of many processes can be followed in only one sample by using microhardness test.

Part I:

The general characterizations of the hardness tests: macro- and microhardness

I.1) The first hardness tests (1990): Brinell (spherical) indenter



The first hardness tests were made by Brinell, using hard steel ball (spherical indenter), later tungsten carbide or diamond indenter was used. During the hardness test, the ball, the indenteris pressed by a given F load into the polished surface of the investigated sample, leaving an A_c contact area. The hardness (***H***) is defined as:

$$HB = \frac{F}{A_c}, \qquad \text{where} \qquad A_c = \frac{\pi D}{2}\left[D - \sqrt{D^2 - d^2}\right]$$

That is

$$HB = \frac{2F}{\pi D\left[D - \sqrt{D^2 - d^2}\right]}$$

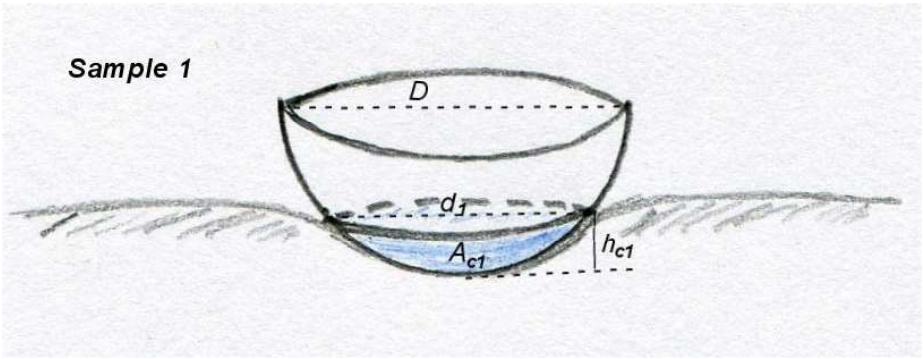
D is the diameter of the indenter ball $D \approx 1-3\ mm$

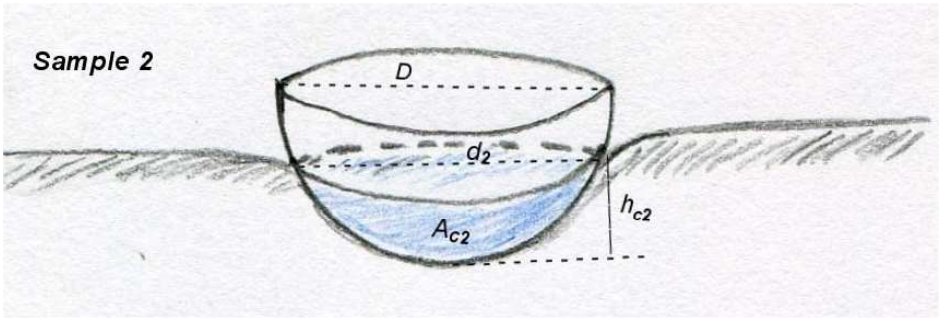
and d is diameter of the projected circle: $d \approx 100-300\ \mu m$, ***reading by using light microscopy***

At every conventional hardness test, or microhardness tests, light microscope is needed to read the size of the contact impression to determine the contact area.

By this way, the hardness of two different subjects can be compared. On the harder subject, the ball can indent with lower depth, the size of the projected circle is smaller and the higher hardness value will be obtained.

F = const





Sample 1: h_1, A_{c1}

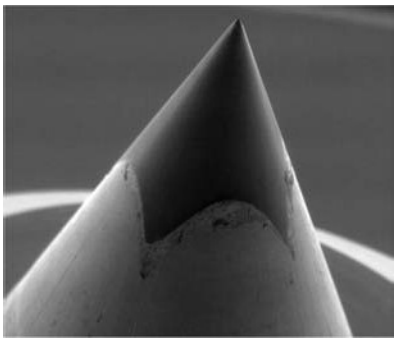
Sample 2: h_2, A_{c2}

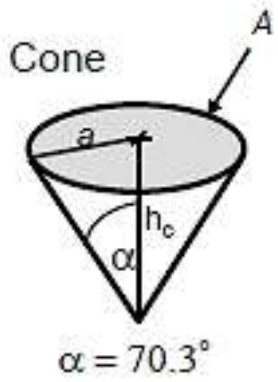
$$h_1 < h_2 \quad \Rightarrow \quad A_{c1} < A_{c2} \quad \Rightarrow \quad HB_1 > HB_2$$

The sample 1 is harder than sample 2.

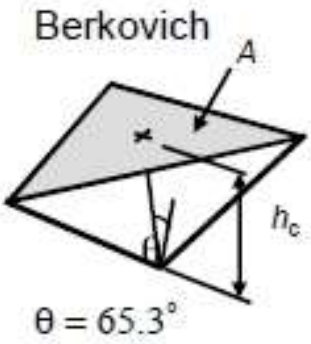
I.3.2. Characterization of the different shape indenters

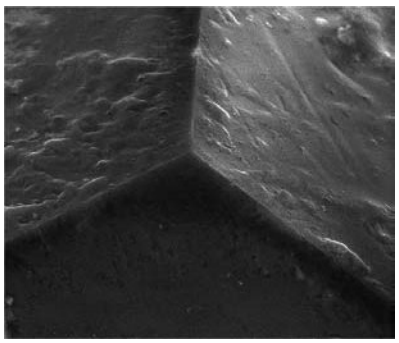
In order to correct the limitations of the Brinell method, different shapes of the indenters were late considered to be used. First, the conical indenter was developed to keep somehow the spherical tip, but the conical indenter is charaterized by the constant *d/h* ratio, the so-called "indentation strain". This is the ratio of the diameter of the projected circle and the indentation depth. The values of this ratio can be changed by changing the value of the semi-angle, α. Normally, $\alpha = 70.3^{o}$

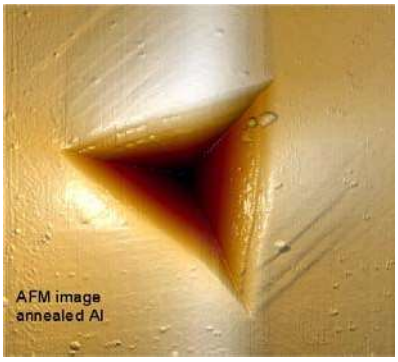




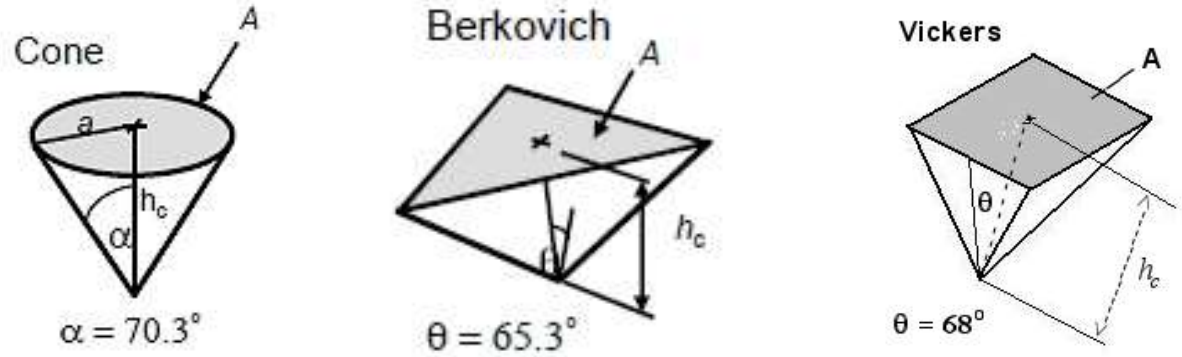
The most recently developed indenter one is the Berkovich, which was in fact born (1992) with the real nanoindentation, and a real tip was needed. In this case, theoretically we can have an absolute point-tip at the intersection of 3 planes.







These indenters were prepared to have the same *d/h* ratio. The important parameters of these indenters are given in the table.



Indenter type	**Impression shape**	**Semi-angle**	**Projected area at h_c**
Sphere		-	$A \approx 2\pi R h_c$
Cone		$\alpha = 70.3^{\circ}$	$A \approx \pi h_c^2 \tan^2 \alpha$
Berkovich		$\theta = 65.3^{\circ}$	$A \approx 3\sqrt{3} h_c^2 \tan^2 \theta$
Vickers		$\theta = 68^{\circ}$	$A \approx 4 h_c^2 \tan^2 \theta$

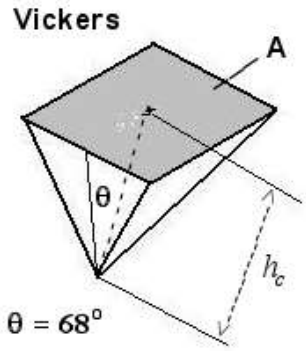
I.3.3 Micro-hardness measurements with Vickers pyramidal indenter

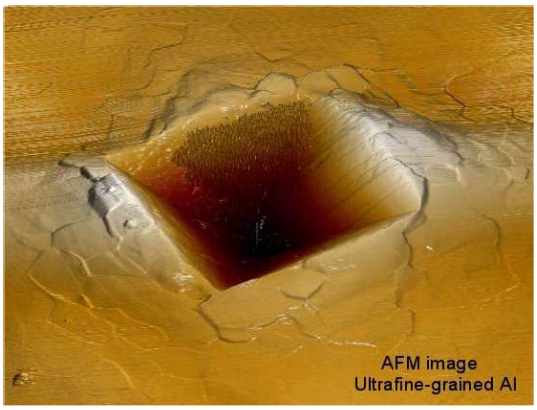
The Vickers indenter has been used for more than 80 years, in most of micro-hardness machines. Let see shortly some characteristics of the microharness tests with Vickers indenter. The formulas discussed here are valid also for the conical and Berkovich indenters.

a) Geometrical parameters:

The Vickers indenter is a tetragonal pyramidal, which has a square shape impression on the surface of the measured sample.

The angle between the opposite faces is 136^{o}, and that between the opposite edges is 148^{o}. In contrast to the Brinell indenter, where relatively high load should be applied to reach the fully plastic zone under the indenter, in the case of Vickers and other sharp tips, the fully plastic zone can be reached at relatively low load.





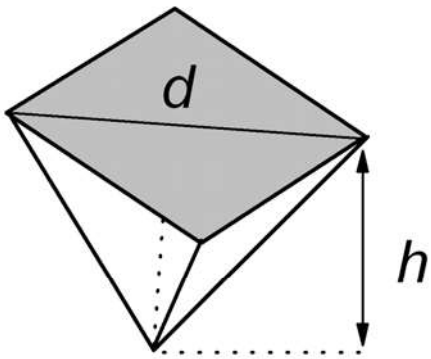
b) Vickers hardness:

Similarly to the Brinell hardness, the Vickers hardness (HV) is also defined as the ratio of the applied load and the contact area:

$$HV = \frac{F}{A_c}$$

where the value of the contact area can be determined by measuring the diagonal of the square shape impression by using light microscope.

$$A_c = \frac{d^2}{2} \cdot \frac{1}{\cos 22^o} = \frac{d^2}{2 \cdot \cos 22^o} = \frac{d^2}{1.8544}$$



$$HV = \frac{F}{A_c} = 1.8544 \cdot \frac{F}{d^2}$$

According to the geometry of the Vickers indenter, the projected area A_p is about 0.927-time of the contact area A_c:

$$A_p = A_c \cdot \cos 22^o = 0.927\, A_c$$

using the mean contact pressure :

, $$p_m = \frac{F}{A_p} = \frac{F}{0.927\, A_c},$$

from which $$0.927\, p_m = \frac{F}{A_c} = HV$$

that is $$HV \cong 0.927\, p_m$$

Part II:
Indentation tests, nanoindentation

II.1) Nanohardness, why nanoindentation?

(Not only for the hardness, but also for the elastic behaviors)

We have seen that the conventional (static) hardness measurement is relatively simple, useful and material-saving method. However, we can see that there are also some trivial limitations with this method. First of all, in this method, we have to use light microscopy to measure the size of the pattern, and the measurement will become difficult when the size of the pattern is very small, the error of the measurement will become relatively high.

For example, with a good microscope we can read the size of 10-20 micron with the error of about 1 micron, having the relative error of about only 5-10%. But in the case of small size of about 1 micron, the error may become about 100%.

In general, with the conventional microscope we cannot measure the size smaller than 1 micron. We can say that the conventional static hardness measurement is typical micro- or macro-hardness method.

Nowadays, as the materials science is progressing, several types of nanocrystal materials, nanoobjects, or thin films are developed and studied. In several cases, the conventional hardness measurement is not suitable for the investigation of the mechanical properties of these materials. For example, if we want to determine the mechanical properties of the thin films, or thin coating layers having the thickness lower than 200-300 nm, or if we want to study the local mechanical properties of nanocrystalline materials, the conventional microhardness measurement is not suitable for this kind studies, only nanohardness could be used to characterizing the mechanical properties of these materials. Nanohardness can be obtained by applying nanoindentation.

According to the theoretical calculations, the size of the pattern or the contact area can be calculated by using the indentation depth, by which the punch indented into the sample. When using the indenter having known geometry, by measuring the indentation depth, the contact area can be given so that the hardness can be estimated without the use of a light microscope.

When the size of the pattern is dropping into the rang of submicro-or nano-scale, we will have submicro- or nanohardness, which can be determined only by micro or nanoindentations, During the indentation process the load and depth data are recorded as function of time.

It should also be noted that when we determine the hardness of a given material, not only the applied load, F is affecting the magnitude of the contact area, A_c, but the effect of elastic deformation should also be taken into account. This means that whenever both the loading and unloading process are recorded, it is possible to study also the elastic behavior of the material by determining its elastic modulus. This is a significant advantage of the indentation method against the conventional one.

Finally, the development of the electronic industry is a most important factor for introducing nanoindentation method. From the 1990-ies the computer, PC-controlling is fine enough for doing precise nanoindentation measurements.

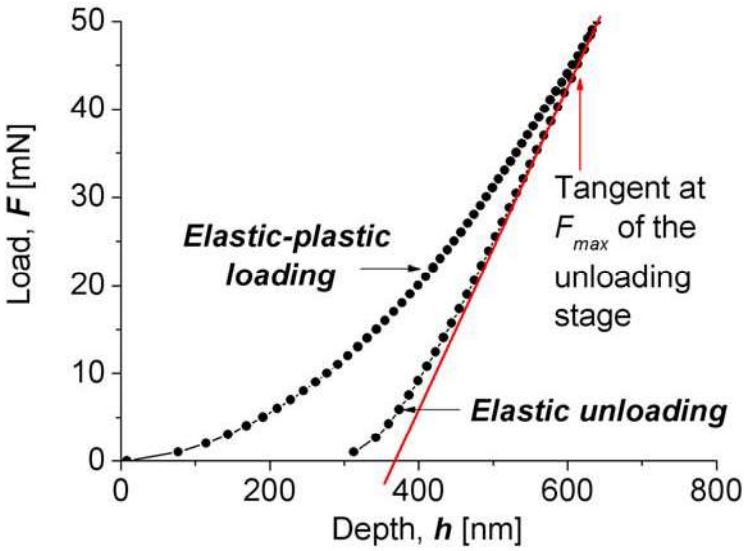
Part IV

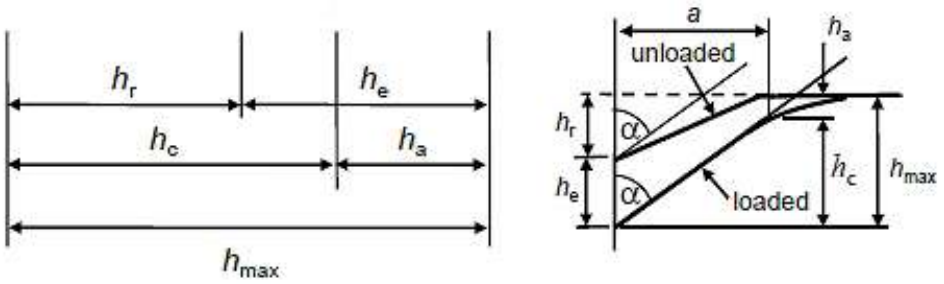
Theory of nanoindentation: Theoretical Analysis

IV.1) Stages of the indentation process, shown in the load-depth curve

During indentation the indenter is pressed into the surface of the specimen by a load, F which is usually increasing linearly with time to a maximum value, F_{max}. This is the loading stage. Then the indenter can be hold at the maximum load for a certain time period, this is the holding stage, which is followed by the unloading stage, where the load is decreasing linearly with time. There are the effects of both elastic and plastic deformations.

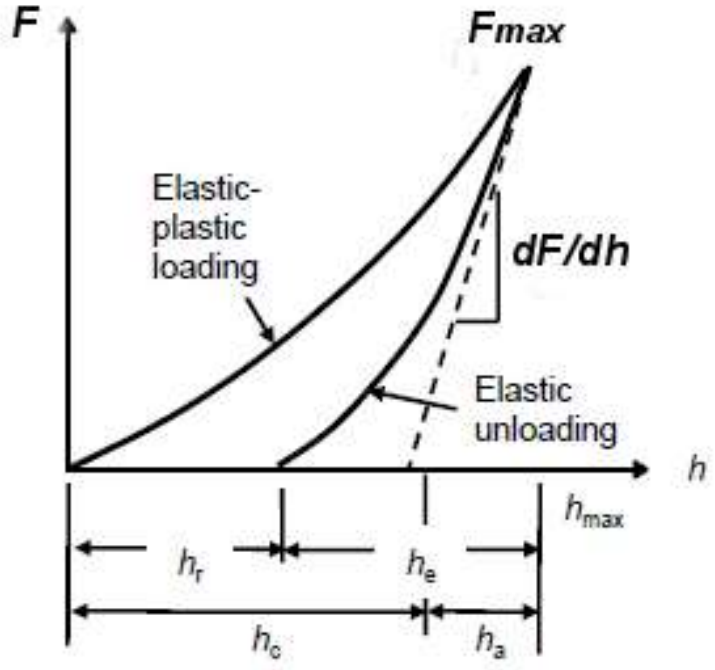
Both loading and unloading responses are recorded in the form of a load-displacement curve.





Although most nanoindenters are load-controlled machines, it is conventional practice to plot the load on the vertical axis and the displacement on the horizontal axis.

From the load-depth curve, we can read directly the maximum depth, h_{max}, the residual depth (h_r) and then the depth characterizing the elastic indentation, (h_e)

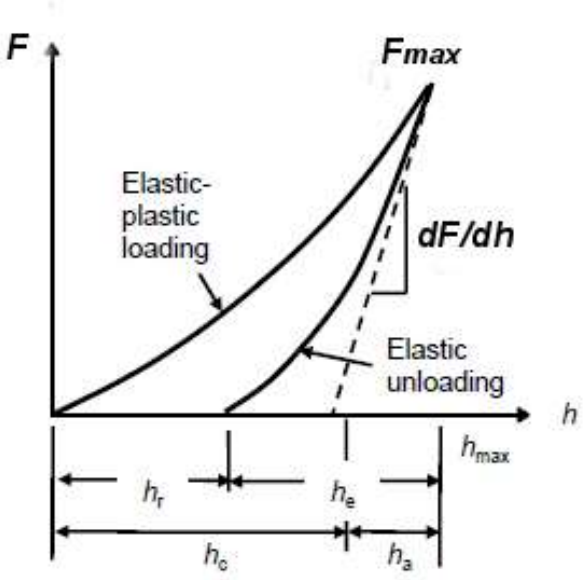


By analyzing also the slope of the unloading stage at the maximum load, the contact depth, h_c , and then, the projected area, A_p can be determined.

$$h_{\max} \; and \; \frac{dF}{dh} \; at \; h_{\max} \quad \rightarrow h_c, \; A_p$$

On the basis of these stages, we can do the analysis for the determination of Young' modulus, E and the hardness, H.

IV.*2) Theoretical determination of the hardness, H and reduced modulus, E^**



The load-depth curve is used to determine the depth of contact by using the elastic unloading data (even if the contact involves plastic deformation).

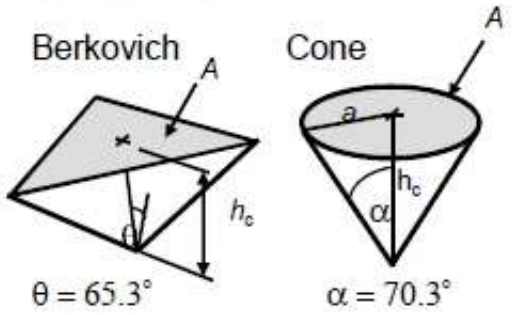
The actual indenter is conveniently modeled as an equivalent conical indenter.

The equations of contact were mentioned before:

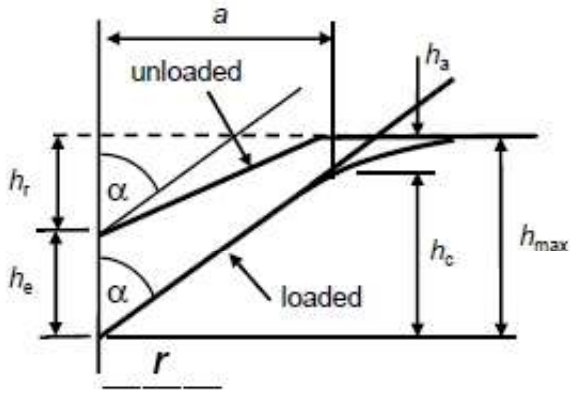
$$F = \frac{2}{\pi} \cdot E^* h^2 \cdot \tan\alpha' \qquad (1)$$

and

$$h(r) = \left(\frac{\pi}{2} - \frac{r}{a} \right) a \cot\alpha', \qquad r \le a$$



α' is the combined angle of the symmetric axis and the sides of the residual impression. (e.g. for cone $\alpha' = \alpha$, and for the Berkovich indenter $\alpha' = \theta$



$At \quad r = 0, h = h_e,$

$$h_e = \frac{\pi}{2} a \cot\alpha' \qquad \text{and}$$

$At \quad r = a, h = h_a,$

$$h_a = \left(\frac{\pi}{2} - 1 \right) a \cot\alpha'$$

From which we get:

$$h_a = \left(\frac{\pi - 2}{\pi}\right) h_e \quad and \quad h_{total} = h_c + h_a$$

Thus:

$$h_{total} = h_c + \left(\frac{\pi - 2}{\pi}\right) h_e$$

From the contact eq. (1):

$$F = \frac{2}{\pi} \cdot E^* h^2 \cdot \tan\alpha'$$

the derivative dF/dh can be given as:

$$\frac{dF}{dh} = 2E^* \frac{2}{\pi} h_e \tan\alpha'$$

and

$$F = \frac{1}{2}\frac{dF}{dh} h_e \quad \rightarrow \quad h_e = F\frac{2}{dF/dh}$$

Thus:

$$h_{\max} = h_c + \left[\frac{2(\pi - 2)}{\pi}\right]\frac{F}{dF/dh}$$

This is the most important formula for analyzing nanoindentation data.

$h_{\max}$, $F_{\max}$, *and* dF/dh are all obtained from measurements and also h_c can be determined.

$$Experimentally \quad h_{\max} , F_{\max} , and \; dF/dh \quad \rightarrow \quad h_c$$

Summary for the Calculation

of reduced (combined) modulus, E^*, and hardness, H

$$F = \frac{2}{\pi} \cdot E^* h^2 \cdot \tan\alpha'$$

$$\frac{dF}{dh} = 2E^* \frac{2}{\pi} h_e \tan\alpha'$$

$$h_e = \frac{\pi}{2} a \cot\alpha'$$

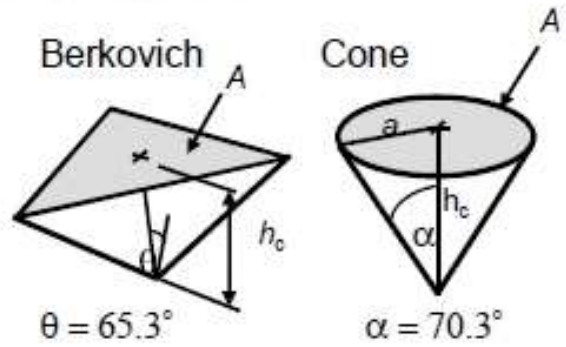
$$\frac{dF}{dh} = 2E^* \frac{2}{\pi}\frac{\pi}{2} a = 2E^* a$$

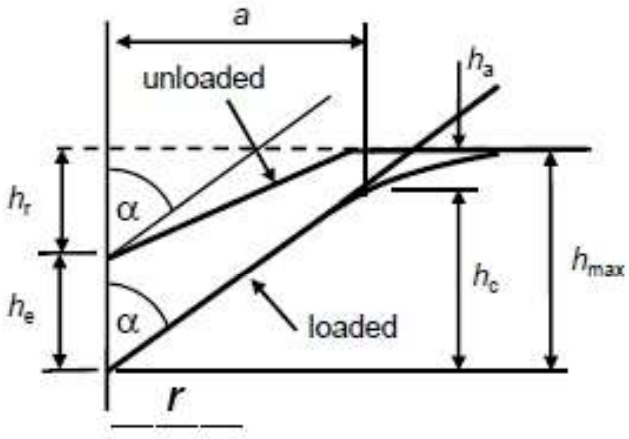
$$A = \pi \cdot a^2 \quad \rightarrow \quad a = \frac{\sqrt{A}}{\sqrt{\pi}}$$

$$\frac{dF}{dh} = 2E^* a = 2E^* \frac{\sqrt{A}}{\sqrt{\pi}}$$

$$h_c = h_{\max} - \left[\frac{2(\pi-2)}{\pi}\right]\frac{F}{dF/dh}$$

$$A_p = (3\sqrt{3}\tan^2\alpha')h_c^2 = 24.5\,h_c^2$$

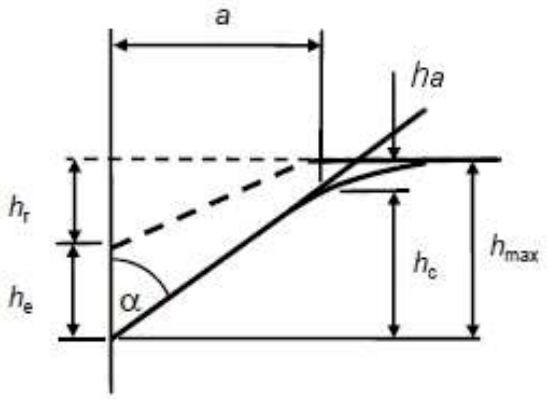




$$H = \frac{F}{A_p} \qquad and \qquad E^* = \frac{1}{2}\frac{\sqrt{\pi}}{\sqrt{A_p}}\frac{dF}{dh}$$

IV.3) Evaluation by Oliver and Pharr method

(***The most often used evaluating method***)

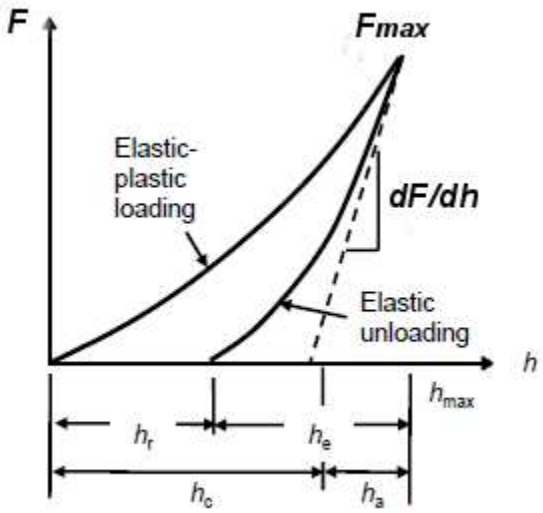


The theoretical analysis mentioned above is essentially discussed by Oliver and Pharr, who have shown that the slope at h_{max} of the unloading curve can be given in the mentioned formula:

$$\frac{dF}{dh} = 2E^* a = 2E^* \frac{\sqrt{A}}{\sqrt{\pi}}$$

Taking the results of finite element calculation of King

(R. B. King, Int. J. Solid Structures 23 (1987) 1657)



Oliver and Pharr corrected this formula by a term β:

$$\frac{dF}{dh} = 2E^* a = 2\beta E^* \frac{\sqrt{A}}{\sqrt{\pi}}$$

where the values of the constant β are:

$\beta = 1.000$ for conical

$\beta = 1.034$ for Berkovich

$\beta = 1.012$ for Vickers

$$h_c = h_{\max} - \varepsilon \cdot \frac{F}{dF/dh}, \qquad \varepsilon = \frac{2(\pi - 2)}{\pi} = 0.73$$

$$A_p = 24.5 h_c^2$$

The hardness:

$$H = \frac{F}{A_p}$$

The modulus:

$$E^* = \frac{1}{2}\frac{\sqrt{\pi}}{\sqrt{A_p}}\frac{dF}{dh}$$

V.6) Fitting the unloading curve:

When we analyze the depth-load data, the analyzing process is beginning with fitting the unloading stage to calculate the contact depth, h_c and then the contact area, A_c.

Note that before the fitting procedure, we have to check whether there is a creep or not at the beginning of the unloading stage. If yes, there is a creep, the data describing the creep should not be used for the fitting process.

Equation to fit:

1) Power-law function:

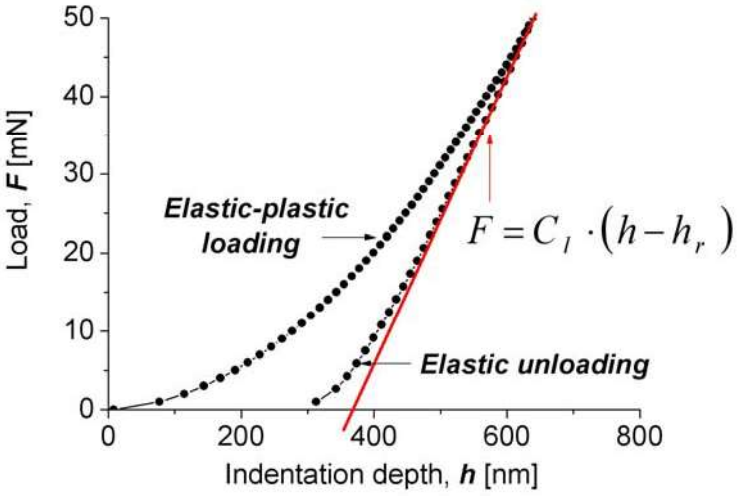
$$F = C_l \cdot \left(h - h_r\right)^m$$

2) Polynomial fit: $m = 2$:

$$F = C_2 h^2 + C_1 h + C_0$$

1) Most useful : linear $(m = 1)$

$$F = C_l \cdot \left(h - h_r\right)$$



But there is a problem, how much data we can use for the fitting process, because at low load, the indenter may not contact definitely to the surface of the sample, so the data at low load may not be correct, their use may lead to uncorrected fitting.

Part VII

Do's and Don'ts for making nanoindentation measurements

Do:

●Check that the sample is fixed well on the sample-holder

●Wait for thermal equilibrium before starting the test, rather than to try and correct for thermal drift later

●Be aware of the thickness of your samples (of the layer you want to indent) and select an appropriate minimum and maximum load.

●Apply corrections, if it is possible.

●Be aware that creep in the specimen, piling up, indentation size effects, etc, may affect your results.

●Remember to calculate the real modulus, E of the specimen from the reduced modulus E^* before quoting result for E

●Make a brief mention of the corrections applied and the test conditions when you quote your results in the literature.

Don't:

●Blindly analyze data without examining if the fit to the unloading is reasonable.

●Rush. Nanoindentation requires time and patience

●Do the measurements at the open air (open windows, open doors…etc).

●…

●…