CHARACTERIZATION OF HARDNESS AND ELASTICITY OF COPPER AND CERAMIC USING NANOINDENTATION

D. Milani, *NTNU Nanomechanical Lab*

Nanoindentation technique is very useful to detect nanohardness and elastic properties of the materials. Experimental measurements on copper and ceramic are presented, that show the different characteristics of ductile and brittle materials. A series of tests is conducted using a TriboIndenter equipped with a Berkovich tip. The calculation of the parameters has been performed, according to the Oliver and Pharr analytical model; this method has important implications on how to determine reduced Young's modulus and hardness. A specific procedure must be followed, to find the best fit of the load-displacement unloading curve. The relationships between force and displacement are shown and analyzed, focusing on the deformation process of the materials; data are also compared with Hertz contact model. The procedure and the results confirmthe accuracy of the Oliver and Pharr model.

1 Introduction

Since many technologies have begun to investiagate ever small scales, the characterization of the mechanical properties of the materials has become more difficult. One tool that is widely used for such measurements is nanoindentation. It's a technique suitable for testing small volumes of material, that consists of loading a specimen with an indenter. The operating principle is as follows: the tip is pushed in the sample perpendicular to the surface by applying an increasing the load, up the desired value. The load is then decreased until you get a full or partial relaxation of the material. The resulting load-depth curve is then used to calculate the mechanical properties such as hardness and Young's modulus. In the following analysis, the procedure described in the famous article by Oliver and Pharr [1] is adopted. The importance of this publication for the nanoindentation is the introduction of several innovative solutions and a measurement technique that does not require vision systems for the calculation of the imprint of indenter.

The first studies on topics related to the contact between elastic bodies, were made by Hertz [2]. Considering a sphere of radius R pressed on an elastic half-space, the load and the displacement can be related by the following equation:

$$P = \frac{4}{3} E_r R^{\frac{1}{2}} h^{\frac{3}{2}} \tag{1.1}$$

where P is the load, h the elastic displacement, R the sphere radius and E_r is the reduced elastic modulus, which is defined as

$$E_r = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_i^2}{E_i} \tag{1.2}$$

which describes the system as if it consists of two springs in series: the i refers to the indenter and s to the specimen. A generalization of this concept was given by Sneddon work [3], that investigated the relation between load and indentation depth for indenters with other shapes in addition to the spherical. So the new formula, valid for tips described by the revolution of a smooth function (paraboloid, conical, cylindrical) is as follows

$$P = \alpha h^m \tag{1.3}$$

that with the value of $m = 2$ can be traced back to the case already studied by Hertz.

The Young's modulus is a very important parameter to characterize a material. In order to find it, it is necessary to use the expression of the stiffness, which is the derivative of the curves in the first part of the unloading [4]. It is given by

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A} \tag{1.4}$$

The problem is then moved to find the shape of the unloading curve P and area A. According to Oliver and Pharr method, it is possible to describe very well the unloading curves with a power law relation:

$$P = \alpha \left(h - h_f\right)^m \tag{1.5}$$

With a least square fitting procedure the parameters α, m and h_f can be found. In this way it is possible to calculate accurately the derivative of the unloading curve and get the stiffness. The values α and m depend on the shape of the curve, and h_f is the value of the displacement of the surface after load removal (as shown in Figure 1.1). Theorically this value is the final depth on the load-displacemente diagram; but the final unloading data have a significant deviation. For this reason h_f must be calculated numerically omitting these data.

Another advantage of using the method presented by Oliver and Pharr is to consider the shape of the indenter, to calculate the contact area at maximum load without having to use other techniques such as microscopy. The expression of A is a functional that depends on the value of h_c, the contact depth; for the Berkovich geometry is

$$A(h_c) = 24.5h_c^2 + C_1 h_c^1 + C_2 h_c^{\frac{1}{2}} + C_3 h_c^{\frac{1}{4}} + \ldots + C_8 h_c^{\frac{1}{128}} \tag{1.6}$$

where the C_i coefficients describe deviation from ideal geometry because of blunting at the tip. The contact depth can be evaluated from the difference between the maximum displacement reached h_{max} and the displacement of the surface at the perimetr of the contact h_s:

$$h_c = h_{max} - h_s \tag{1.7}$$

The latter parameter can be calculated from

$$h_s = \epsilon \frac{P_{max}}{S} \tag{1.8}$$

where ϵ is a geometric constant that for the Berkovich tip is equal to 0.75, P_{max} is the peak load and S the stiffness.

Therefore it is possible to calculated the two target parameters of this analysis: the reduced elastic modulus, from the Equation 1.4

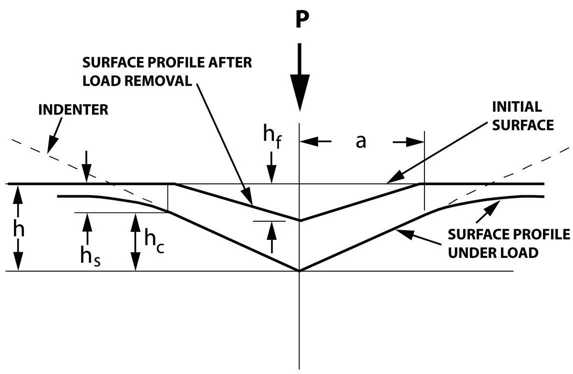

Figure 1.1: Different depths reached by the indenter

$$E_r = \frac{1}{\beta}\frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}} \tag{1.9}$$

in which β is a small correction for the nonaxisymmetric indenter shape (for Berkovich indenter is $\beta = 1.034$) [5, 6].

The other mechanical parameter is the nanohardness, defined as the mean pressure the material supports under load:

$$H = \frac{P_{max}}{A} \tag{1.10}$$

where the area is evaluated from Equation 1.6.

2 Method

The tests have been performed using Hisytron TRIBOINDENTER, in the NTNU Nanomechanical Lab, in a room with controlled temperature and humidity. The machine is provided with a vibration isolation table and an enclosure to ensure a good accuracy and stability. The axis movement is managed in 3 stages: for large displacements electrical step motors operate; for smaller and precise movements there are piezo-devices and the capacitive transducer.

A peculiar feature of this instrument is the three plate capacitive transducer that is used as both the actuator and sensor of the instrument (see Figure 2.1). The force is applied electrostatically while the displacement is simultaneously measured by the change in capacitance; this allows to get very accurate measurements.

A Berkovich-shaped diamond indenter is installed on the machine. Its area function is know:

$$A(h_c) = 24.5h_c^2 + 4.19e3h_c^1 - 1.92e5h_c^{\frac{1}{2}} + 1.52e6h_c^{\frac{1}{4}} + -3.19e6h_c^{\frac{1}{8}} + 1.84e6h_c^{\frac{1}{16}}$$

The materials that have been tested are copper, a notoriously ductile metal, and a

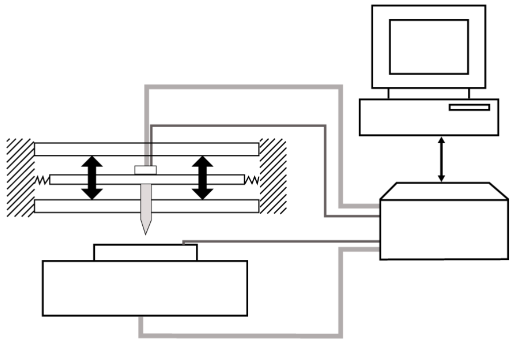

Figure 2.1: TriboIndenter scheme

brittle ceramic, whose chemical composition is $La_{0.8}Ca_{0.2}CoO_{3-5}$. In order to guarantee stability, the specimens can be fixed magnetically on the testing machine.

The first phase of the test consists in the positioning of the tip with an optical sensor; with the aid of the CCD sensor of the TriboIndenter, the probe position is refined. Afterwards the indenter detects precisely the distance from the sample on the vertical axis, applying a pre-load of $1\mu N$ on the surface. Then the second phase begins: the load starts to increase until the set value, it is kept constant for a period of time and finally it decreases detaching from the sample. In the Figure 2.2 the curves of loading and unloading for the two materials are shown: the load increases linearly and it reaches the maximum value after $t_1 = 5\,s$; at $t_2 = 9\,s$ it starts to decrease and at $t_3 = 12\,s$ it returns to zero. During this process the displacement of the tip is monitored: hence the TRIBOINDENTER provides data for the load and the depth.

For the copper specimen three indentations have been conducted, at the maximum load of $1500\,\mu N$, $1000\,\mu N$ and $500\,\mu N$. Instead for the ceramic sample only two indentations have been performed, but at higher loads: at $5000\,\mu N$ and $2000\,\mu N$.

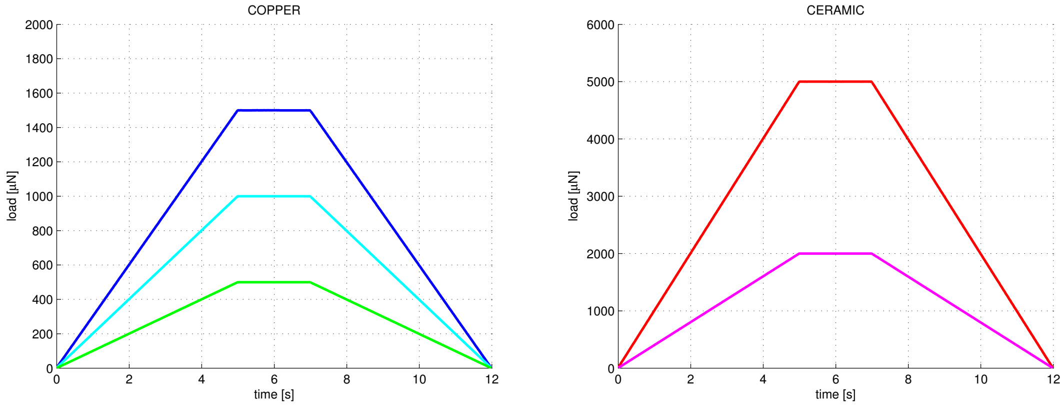

Figure 2.2: Copper and ceramic loading and unloading curves

3 Results

In the following experimental results and their processing are presented. As mentioned, the TRIBOINDENTER test machine provides output values of depth and load. The Figure 3.1 and Figure 3.2 represent the cycle of loading and unloading for the nanoindentation. Notice how in the case of copper, a ductile material, the final value of the depth of the indenter is much higher when compared to that of ceramics. This means that only a small portion of the deformation is elastically recovered during the unloading, but there is still an plastic deformation. However the curves of brittle material, especially in the second test, are virtually identical, and this is indicative of the good elasticity of the material.

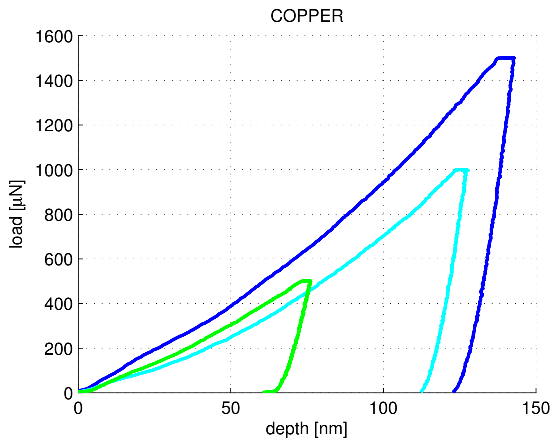

Figure 3.1: Loading and unloading curves for copper

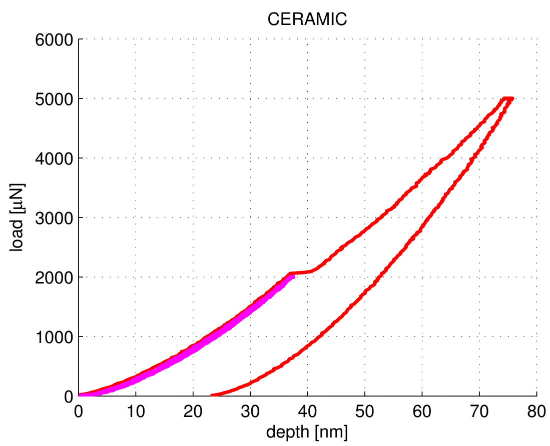

Figure 3.2: Loading and unloading curves for ceramic

In order to understand the elastic part of the diagrams only the unloading curves are considered in the analysis. As shown by Equation 1.5, the purpose is to describe the data with an exponential law. To do this it is necessary to shift the unloading branch of the parabola, so that it starts from the origin; then it is possible to interpolate and find a value of α and m that satisfactorily describe this curve. The Figure 3.3 and 3.4 show the curves with the axes in logarithmic scale, because assuming Equation 1.5 in a logarithmic plot the unloading equation becomes:

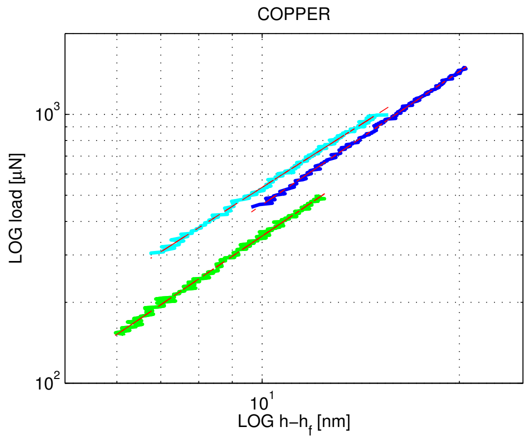

Figure 3.3: Interpolation of the unloading curves for copper indentations in logarithmic scale

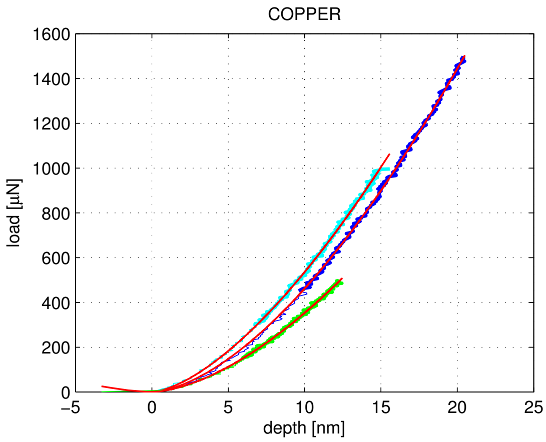

Figure 3.5: Comparison between unloading curves of copper

$$\log P = m \log(h - h_f) + \log \alpha \qquad (3.1)$$

In this way the interpolation of the data can be realized with a first degree polynomial (a line).

An important consideration is that concerns the final part of the unloading curve: it can be seen that these data deviate significantly from the ideal shape. This leads to two consequences: the first is that is not correct to assume the last experimental datum of the depth as the value of h_f. So this parameter is to be considered in the interpolation algorithm, and therefore the best fitting curve is characterized by the values of h_f, m and α. In the Appendix, the MATLAB code used to process the data is explained. Particular attention should be given to the algorithm for the curve fitting, based on least squares method, that interpolates the data to get the best approximation, using the minimization of the norm of residuals.

Moreover, as previously mentioned, the interpolation is performed considering the experimental data up to 10.5 s (70% of the unloading curve) and the rest are ne-

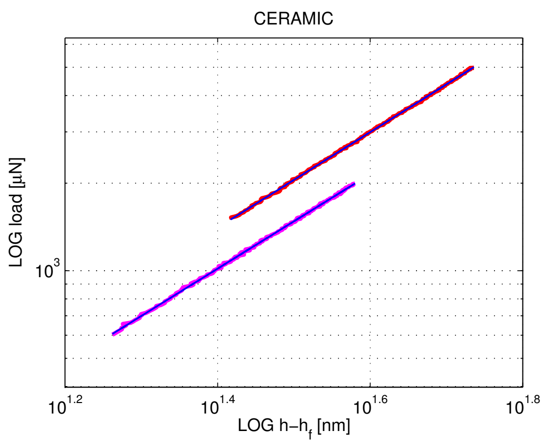

Figure 3.4: Interpolation of the unloading curves for ceramic indentations in logarithmic scale

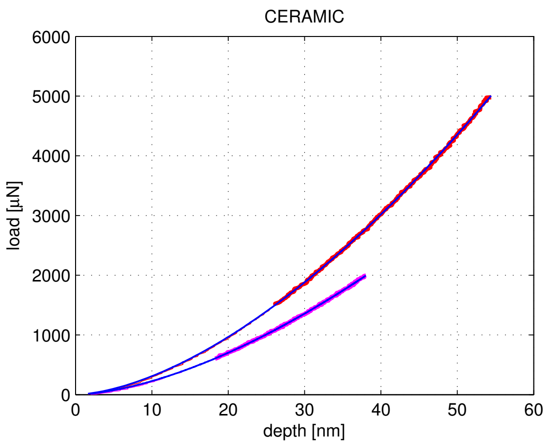

Figure 3.6: Comparison between unloading curves of ceramic

glected. In the Figure 3.3 and Figure 3.4 it is possible to see the linear approximation in a logarithmic scale.

The Table 1 presents the numerical values from the fitting and a value of the estimator R^2, the coefficient of determination for the statistical model. Note that for the second indentation of the ceramic, the negative value of h_f has no physical sense, but it is merely the result of the interpolation. It arises from the fact that the recovery is fully elastic and the curve returns to the origin. The foregoing is graphically illustrated in Figure 3.5 and Figure 3.6. Note the cut-off in the plot of the curve: when the line becomes thinner, these data are not considered in the analysis.

The next step of data processing is to find the slope of the curve at the load peak (Figure 3.7 and Figure 3.8). The tangent of the the parabola at the maximum point has to be calculated, whose angular inclination is the value of the stiffness, according to the equation:

$$S = \left. \frac{dP}{dh} \right|_{h=h_{max}} \tag{3.2}$$

Once the stiffness value has been calculated, it is possible to obtain the depths h_s and h_c, which are the displacement of the surface at the perimeter of the contact and the contact depth respectively, how presented in Equation 1.8 and Equation 1.7.

	α	m	h_f [nm]	R^2
copper #1	10.23	1.651	122.23	0.9981
copper #2	15.73	1.538	112.27	0.9967
copper #3	8.58	1.624	63.79	0.9954
ceramic #1	7.29	1.635	21.60	0.9997
ceramic #2	5.33	1.628	-0.78	0.9996

Table 1: Parameters describing power law fits of unloading curves and relative coefficients of determination

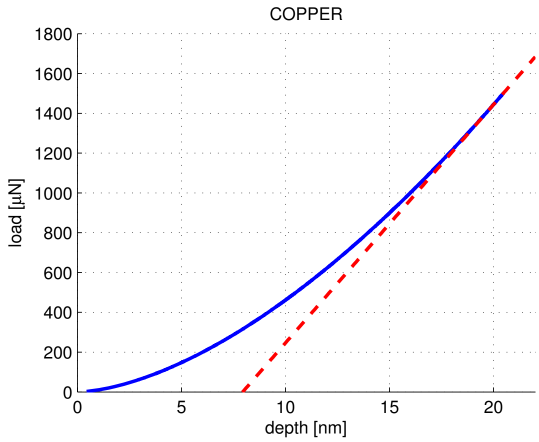

Figure 3.7: Stiffness calculation using the slope of the unloading curve at h_{max} for copper (indentation 1)

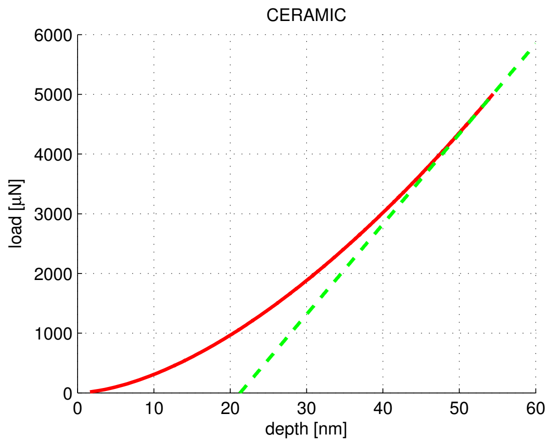

Figure 3.8: Stiffness calculation using the slope of the unloading curve at h_{max} for ceramic (indentation 1)

Hence it is simple to compute the area using the functional presented above. The numerical values for these parameters are shown in Table 2.

Finally, it is possible to calculate the two parameters object of this paper, the reduced elastic modulus and the nanohardness, according to the following equations [6]:

$$E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \tag{3.3}$$

$$H = \frac{P_{max}}{A} \tag{3.4}$$

	$h_c\,[nm]$	$A\,[10^4\,nm^2]$
copper #1	133.17	55.99
copper #2	120.68	46.71
copper #3	70.24	17.91
ceramic #1	51.08	10.64
ceramic #2	19.77	2.89

Table 2: Contact depth and area

The numerical results are given in Table 3.

4 Discussion and conclusion

The above analysis has been performed following the guidelines of the article by Oliver and Pharr. This has led to significant results.

It is possible to make a comparison with the hertzian contact model [2]. In the tests a pyramidal shape of indenter was used. Hertz's theory applies to a body with a spherical shape; furthermore, it is valid only in the hypothesis perfect elasticity. So the cycle of loading and unloading degenerates on a single line, whose equation is as follows

$$P = \frac{4}{3} E_r R^{\frac{1}{2}} h^{\frac{3}{2}} \tag{4.1}$$

which is quite similar to Equation 1.5, where $\alpha = \frac{4}{3} E_r R^{\frac{1}{2}}$, $m = 1.5$ and $h_f =$ 0. To find the unknown radius, which is the round of the indenter tip, the best fitting for a set of data among those examinated has to be considered (Figure 4.1). The choice is to interpolate data from the second indentation in ceramics, which has a cycle almost perfectly elastic. Using the value of the reduced elastic modulus found previously (see Table 3) it is possible to obtain the value of $R = 239.92\,nm$.

	$E_r\,[GPa]$	$H\,[GPa]$
copper #1	137.17	2.67
copper #2	132.22	2.13
copper #3	134.00	2.78
ceramic #1	396.21	46.81
ceramic #2	430.09	68.97

Table 3: Reduced elastic modulus and hardness

Now each of the nanoindentation load curves can be compared with that assumed by the Hertz model, as shown in Figure 4.2 and Figure 4.3.

As can be seen the approximation is acceptable only for the first part of the line, and even the first values of the experimental data could be influenced by the plasticization due to the roughness of the surface of the specimen [8].

The Hertz model best describes the ceramic material, which has a more elastic behavior; instead copper is a very ductile metal. The difference lies in the way of deformation: as can be seen from Figure 4.4, in ceramic there is not an appreciable plastic deformation; the displacement after the unloading is completely restored. But in the case of copper, because of the particular structure of the crystal lattice, the disloca-

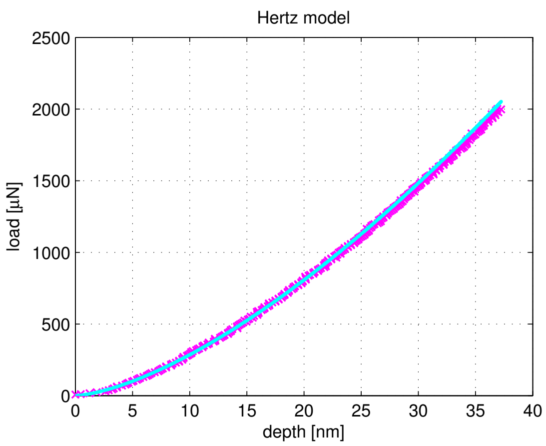

Figure 4.1: Interpolation of loading curve of ceramic indentation according to Hertz model

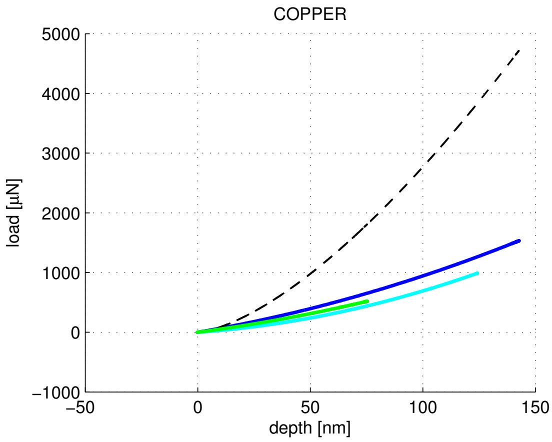

Figure 4.2: Comparison between copper loading curves and Hertz model (black line)

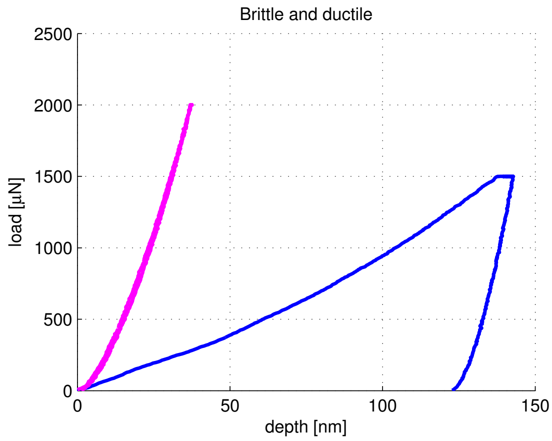

Figure 4.4: Differences in the curves of brittle and ductile materials; for ceramic there is no plastic deformation

tions can reach the grain boundaries, and allow a permanent deformation which remains even when the value of the load returns to zero.

Particular attention should be paid to the loading curve of the first indentation in ceramics (Figure 4.5). There is a plateau in this plot: the material deforms elastically in the initial stage, followed by plastic deformation of which the onset is characterized by an evident displacement shift in the loading curve. This phenomenon is called pop-in. It can be explained by different causes: by a phase transition, a film breaking or also by dislocations slip. In this case, it is reasonably assume that it deals with the latter reason. The pop-in is the first stage of plastic deformation during nanoindentation. This phenomenon is ascribed to the nucleation and further propagation of interstitial loops of dislocations beneath the indenter [7]. After the pop-in the material is in a elasto-plastic phase. For this reason, it deviates from the ideal elastic behavior predicted by the Hertz theory.

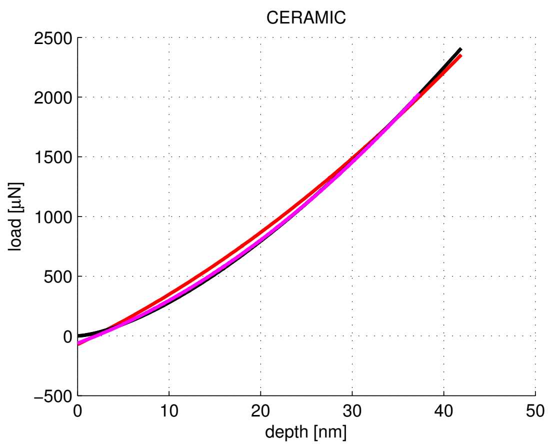

Figure 4.3: Comparison between ceramic loading curves and Hertz model (black line)

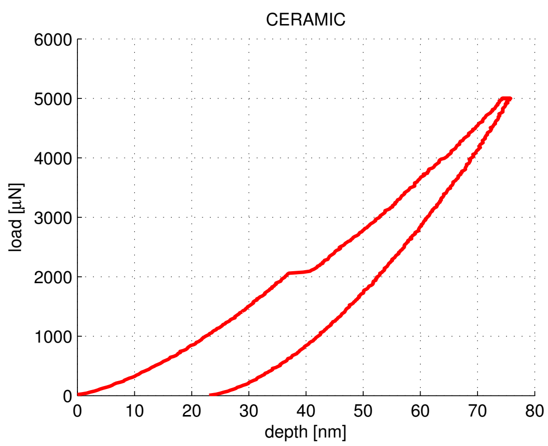

Figure 4.5: Pop-in phenomenon in ceramic indentation, when a critic load is reached

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Appendix

To process the data is useful to use a programming language such as MATLAB. The following is the script used for data processing. It should be looked into the iterative loop for calculating the best fitting of the unloading curves. The software uses a non-linear convergence method to estimate the values for k, h_f and m that best fit the unloading data. From the interpolated curve, the slope is calculated by differentiating dP/dh at the maximum displacement. Then it is possible to consider the slope as a measure of the stiffness (Equation 1.4).

```
%% Nanomechanics
% Damiano Milani
%%%%%%%%%%%%%%%
close all
clear all
clc

choice=input('Choose the dataset> ');

% load copper data file
cu0=importdata('data/Cu_000 LC.txt','\t',3);
cu1=importdata('data/Cu_001 LC.txt','\t',3);
cu2=importdata('data/Cu_002 LC.txt','\t',3);

% load ceramic data file
cer0=importdata('data/ceramic_000 LC.txt','\t',3);
cer1=importdata('data/ceramic_001 LC.txt','\t',3);

RESULTS=zeros(5);

%% Hertz model
%%%%%%%%%%%%%

% Radius from ceramic indentation #2
cer1.data(:,1);
cer1.data(:,2);

[peak j]=max(cer1.data(:,2));

% loading curve only
up_depth_cer=cer1.data(1:j,1);
up_load_cer=cer1.data(1:j,2);


% Hertz fitting
jj=0;
Km=up_load_cer(2:end)./up_depth_cer(2:end).^1.5;
Km=mean(Km);

K=0.5*Km;
buff=inf;

while (K<2*Km)
    jj=jj+1;
    dx=0.01;
    K=K+dx;
```

```
    dist=sum((K.*up_depth_cer.^1.5-up_load_cer).^2);
    d_(jj)=dist;
    if dist<buff
        flag=jj;
        buff=dist;
    end
end

K=0.5*Km+dx*flag;

figure(10)
plot(up_depth_cer,up_load_cer,'mx','linewidth',1)
hold on
plot(up_depth_cer,Km.*up_depth_cer.^1.5,...
    'c-','linewidth',2);
title('Hertz model')
xlabel('depth [nm]')
ylabel('load [\muN]')
grid on

E_cer=430.087/1000;

%hertz radius
R=(K*3/4/E_cer)^2;



%% Choice cycle
%%%%%%%%%%%%%%%

for ch=choice
switch ch
    case 1
        file=cu0.data;
        colore='b';
        titolo='COPPER';
    case 2
        file=cu1.data;
        colore='c';
        titolo='COPPER';
    case 3
        file=cu2.data;
        colore='g';
        titolo='COPPER';
    case 4
        file=cer0.data;
        colore='r';
        titolo='CERAMIC';
    case 5
        file=cer1.data;
        colore='m';
        titolo='CERAMIC';
end

depth=file(:,1);
load=file(:,2);
time=file(:,3);


%% Interpolation
%%%%%%%%%%%%%%%%

% peak
i=find(time==7);
hmax=depth(i);
pmax=load(i);

hfo=depth(end);

% unloading curves
un_load=load(i:end);
un_depth=depth(i:end);

n=find(time==10.5)-i;

k=0;
z=-1;
hf0=hfo*z;
buff=1;

% fitting algorithm
while (hf0<2*hfo)
    k=k+1;
    dx=0.5;
    hf0=hf0+dx;
    h_hf=un_depth-hf0;
    [coeff S]=polyfit(log(h_hf(1:n)),...
        log(un_load(1:n)),1);
    s_(k)=S.normr;
    if S.normr<buff
        flag=k;
        buff=S.normr;
    end
end

hf=hfo*z+dx*flag;
h_hf=un_depth-hf;

% interpolation
coeff=polyfit(log(h_hf(1:n)),log(un_load(1:n)),1);
interpol=polyval(coeff,log(h_hf));

% statistical parameters
r2(ch)=corr2(interpol(1:n),log(un_load(1:n)))^2;

[fitc,gof]=fit(log(h_hf(1:n)),log(un_load(1:n)),'poly1');
R2(ch)=gof.rsquare;

% fitting coefficients
m=coeff(1);
a=exp(coeff(2));


%% Plots

% load vs time
figure(1)
title(titolo);
xlabel('time [s]')
ylabel('load [\muN]')
grid on
hold on
plot(time,load,colore,'linewidth',2);

% load vs depth
figure(2)
hold on
plot(depth,load,colore,'linewidth',2);
title(titolo);
xlabel('depth [nm]')
ylabel('load [\muN]')
grid on

% LOG load vs depth
figure(3)
loglog(depth,load,colore);
hold on
title(titolo);
xlabel('LOG depth [nm]')
ylabel('LOG load [\muN]')
```

```
grid on

% LOG load vs dh
figure(4)
loglog(h_hf(1:n),un_load(1:n),colore,...
    'linewidth',2.5);
hold on
loglog(h_hf(1:n),exp(interpol(1:n)),'b-',...
    'linewidth',1);
title(titolo);
xlabel('LOG h-h_f [nm]')
ylabel('LOG load [\muN]')
grid on
axis([10^1.2 10^1.8 10^2.6 10^3.8])

% unloading vs depth + fitting curve
figure(5)
plot(h_hf,un_load,colore);
hold on
plot(h_hf(1:n),un_load(1:n),colore,...
    'linewidth',2.5);
plot(h_hf,a.*h_hf.^m,'b','linewidth',1);
title(titolo);
xlabel('depth [nm]')
ylabel('load [\muN]')
grid on


%% Output
%%%%%%%%%

eps=0.75;
beta=1.034;

% Stiffness (derivative)
S=a*m*(hmax-hf)^(m-1);


% plot with slope
figure(6)
hold on
plot(h_hf,a.*h_hf.^m,colore,'linewidth',2);
plot(h_hf,S.*h_hf+a.*(hmax-hf).^m-S.*(hmax-hf),...
    'g--','linewidth',2);
xlabel('depth [nm]')
ylabel('load [\muN]')
grid on


hs=eps*pmax/S;

hc=hmax-hs;

% area function
A=24.56*hc^2+4.19e3*hc-1.92e5*hc^(1/2)+1.52e6*hc^(1/4)...
    -3.19e6*hc^(1/8)+1.84e6*hc^(1/16);

% HARDNESS
H=pmax/A*1000;

% REDUCED ELASTIC MODULUS
Er=1/beta*sqrt(pi)*0.5*S/sqrt(A)*1000;


RESULTS(ch,:)=[hf m a H Er];
res2(ch,:)=[hc,A];

Ei=1141;
nui=0.07;
nu(1:3)=0.34;
nu(4:5)=0.4;

E(ch)=-Er*Ei*(1-nu(ch)^2)/(Er*(1-nui^2)-Ei);


%% Hertz contact
%%%%%%%%%%%%%%%%

[peak j]=max(file(:,2));

up_depth=file(1:j,1);
up_load=file(1:j,2);


P_hertz=4/3*Er/1000*R^0.5.*up_depth.^1.5;
figure(11)
hold on
plot(up_depth,P_hertz,'k-','linewidth',2);

err_tot=sum(sqrt(real((P_hertz-up_load).^2)));


cf=polyfit(up_depth,up_load,2);
aprx=polyval(cf,up_depth);

for kk=1:length(up_load)
    perc=0.01;
    err=abs(aprx-P_hertz)./P_hertz;
    if (err>perc)
        kk=kk-1;
        break
    end
end

% Hertz-data comparison
figure(11)
plot(up_depth,aprx,colore,'linewidth',2)
title(titolo);
xlabel('depth [nm]')
ylabel('load [\muN]')
grid on


end
tilefigs

%% save results
display(datestr(now))
RESULTS
dlmwrite results.dat _ -append
save results.dat dx RESULTS -ascii -append
```