Measurements of some mechanical properties of ceramics by indentation methods
Principles and applications

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Contents of the presentation

Introduction

Part 1 : The hardness
• the different hardness numbers
• influence of the test load : the ISE
• hardness for thin coatings

Part 2 : The elastic modulus
• with Knoop indentation tests
• from Instrumented Indentation Test IIT
• Elastic modulus for thin films

Part 3 : The Toughness

Part 4 : The adhesion of thick coatings
Why using indentation methods to characterize properties of ceramics?

Heterogeneous ceramics

Hertzian contact

Multi phases

Porous ceramic

Thin and thick coatings

What is indentation test: PRINCIPLE

CLASSICAL TEST

INSTRUMENTATION

Geometrical analysis of the residual indent
Instrumented Indentation Test

**Mechanical properties by indentation**

1. **Hardness:** $H$
2. **Elastic modulus:** $E$, $K$
3. **Toughness:** $K_C$
   - Adhesion of coating: $K_{CA}$

**Yield stress:** $\sigma_y$
- Strain-hardening factor: $n$
- Creep parameter: $\eta$ (Viscosity)
- Fatigue behavior
HARDNESS

A first problem: hardness number definition

\[ H = \frac{F}{A} \]

- Vickers
  - True contact area: \( \frac{1.8544F}{d^2} \)
  - Maximal depth: \( \frac{F}{26.43h_{\text{max}}} \)
  - Contact depth: \( \frac{F}{26.43h_C} \)

- Projected contact area
  - \( \frac{2F}{d^2} \)
  - \( \frac{F}{24.5h_{\text{max}}} \)
  - \( \frac{F}{24.5h_C} \)

Hardness in Microindentation
Hardness in Nanoindentation

Oliver & Pharr (HR1)
Knoop hardness: Projected surface

\[
KHN = \frac{P}{A_P} = \frac{P}{L^2 \cdot \tan \left( \frac{\varphi}{2} \right) / 2 \cdot \tan \left( \frac{\theta}{2} \right)}
\]

Projected contact area \( (A_P) \)

Length of the large diagonal \( L \)

MPa

The specific problem for ceramics: brittleness

- Bioglass – load: 500g
- Bioglass – load: 50g

- An important part of indentation energy is participating to cracks formation
- the indent measurement is not easy

- Indentation Size Effect (ISE)
- high results discrepancy (optical measurements)
- very sensitive to heterogeneities

Very low loads
An example on a bioceramic

### Martens hardness
- calculated from a depth measurement
- low load indents: no cracks

<table>
<thead>
<tr>
<th>Density</th>
<th>Vickers hardness</th>
<th>Martens hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H with</td>
<td>H with</td>
</tr>
<tr>
<td>50%</td>
<td>5.75 / 0.11</td>
<td>1.01 / 0.19</td>
</tr>
<tr>
<td>50%</td>
<td>5.75 / 0.11</td>
<td>1.01 / 0.19</td>
</tr>
<tr>
<td>95%</td>
<td>5.75 / 0.11</td>
<td>1.01 / 0.19</td>
</tr>
<tr>
<td>90%</td>
<td>5.75 / 0.11</td>
<td>1.01 / 0.19</td>
</tr>
<tr>
<td>100%</td>
<td>5.75 / 0.11</td>
<td>1.01 / 0.19</td>
</tr>
</tbody>
</table>

Martens hardness number is preferable to Vickers number for ceramics

**Low loads**: ISE

### Indentation Size Effect: ISE

**MACRO-indentation**

- \( H_0 = \) Macrohardness
MICRO-indentation

Hot pressed silicon nitride

NANO-indentation
What is the origin of ISE?

EXPERIMENTAL

MATERIAL

- Dislocations network
- Cracks
- Sinking-in, Pile-up
- Heterogeneity, Impurities Gradient
- Work hardening during indentation
- Structure change

INSTRUMENT MEASUREMENT

- Vibration
- Loading rate
- Dwell-time
- Positioning
- Accuracy
- Indenter shape
- Tip rounding

SPECIMEN

- Polishing
- Oxidation
- Pollution
- Residual stress
- Roughness

Mathematical expression of ISE

Two approaches

1st group: Descriptive approach

Meyer (1908)

\[ P = A_1 \cdot d^n \]

\( n = 2 : \) no ISE

2nd group: Dislocations theory

Nix & Gao (1998)

\[ \frac{H}{H_0} = \sqrt{1 + \frac{h}{t}} \]

Li & Bradt (1998): PSR model

Proportional Specimen Resistance

\[ P = a_1 d + a_2 d^2 \]

Gong (1999)

\[ P = P_h + a_1 d + a_2 d^2 \]


\[ P_{\text{max}} = a_1 + a_1 h_a^2 + a_2 h_a^2 \]

Instrumented Indentation Tests

Surface polishing, roughness, residual stresses, indenter tip...
Example of ISE for bioceramic $\beta$-TCP

Fully dense bioceramic obtained by Sintering + High Isostatic Pressure (HIP)

$H_0 \sim 4.5$ GPa

PSR model

$H\beta-TCP\text{ 100\% - PSR model}$

$P = -0.02395 \times 10^{-6} + 1499.29 \times 10^{-6} \ h \ c^2$

$H(0&P) = 4.59 +/- 0.49 \ GPa$

Nix&Gao model

$H = \frac{h}{1 + \frac{h}{h_0}}$ 

$H^* = H_0^{*}(1 + \frac{h}{h_0})$

$H(0&P) = 4.59 +/- 0.49 \ GPa$

$H(0&P) = 4.09 +/- 0.16 \ (4.33 \ HV)$

$H(0&P) = 4.31 +/- 0.17 \ GPa$
Hardness measurements for thin hard coatings

Influence of the substrate and the load on the hardness measurement.

\[ f(HV) \]

\[ f(1/d, 1/h) \]

\[ H_C = H_S + a \cdot (H_F - H_S) \]

Some examples models


\[ A_F \]

\[ A_S \]

Total area

\[ A = A_S + A_F \]

\[ H_C = \frac{A_S}{A} H_S + \frac{A_F}{A} H_F \]

\[ H_C = H_S + \frac{A_F}{A} (H_F - H_S) \]

Ductile

\[ C = 1 \]

Brittle

\[ C = 0.5 \]
KORSUNSKY et al. (1998) : *Work of indentation model*

\[ \beta = \frac{h}{t} \]

\[ H_C = H_S + \frac{H_F - H_S}{1 + k \cdot \beta^2} \]

**Reasen II**
- Comportement uniquement élastique du système

**Reasen I**
- Comportement élasto-plastique du film, comportement du substrat d'abord totalement élastique (I), puis élasto-plastique (II)

**Reasen IIIa**
- Figur du film et déformation plastique du substrat

**Reasen IIIb**
- Figuration complète du film et déformation plastique du substrat

**Reasen III**
- Comportement du film négligeable comparé à la déformation plastique d'approche dans le substrat

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**Application of Korsunsky model to DLC film**

HM is calculated from the loading curve in DSI

Influence of the substrate at 3% of thickness!
ELASTIC MODULUS


Important elastic recovery during unloading for materials with high H/E

\[ \frac{w'}{L} = \frac{w}{L} - \frac{\alpha KH}{E} \]

0.45

Ceramics
Depth-sensing indentation analysis

**Flat punch indenter**

- Load, $P$
- Depth, $h$
- Elastic unloading
- Reduced modulus
- Contact area
- Contact stiffness

**Material + Indenter**

$E_R = \left( \frac{1 - V_m^2}{E_m} \right)^{-1}$

**Reduced modulus**

$S = \frac{dP}{dh} = 2E_A \frac{A}{R^2}$

**Contact area**

$\alpha = \frac{4\pi A}{R^2}$

**Flat cylindrical indenter**

- Load, $P$
- Depth, $h$
- Elastic unloading
- Reduced modulus
- Contact area
- Contact stiffness

**Depth-sensing indentation analysis**

**Pyramidal indenter (Berkovich – Vickers)**

- Load, $P$
- Depth, $h$
- Equivalent « punch » unloaded surface
- Creep

**True surface profile after load removal**

**Initial surface**

**Contact surface profile under maximum load**

**Equivalent « punch » unloaded surface**
Vickers indenter : Oliver and Pharr method (1992)

True surface profile after load removal

Equivalent « punch » unloaded surface

Oliver and Pharr : pyramidal indenter is equivalent to a « punch » indenter at the beginning of the unloading

\[
C = \frac{1}{S} = \left(\frac{dh}{dP}\right)_{h = h_{\text{max}}} = \frac{1}{\beta \gamma} \frac{1}{2} \frac{1}{\sqrt{A} E_R}
\]

\[
A = 24.5 h_C^2
\]

Compliance (inverse of the Contact stiffness)

Material + Indenter

Spherical indenter

Hertz’s theory

\[
h_{\text{max}} = 2 \cdot h_C
\]
Problem!

The instrument deformation

$$ C = \frac{1}{S} = \frac{1}{S_{\text{measured}}} = \frac{1}{S_{\text{theoretical}}} = \frac{1}{S_{\text{frame}}} $$

$$ C = C_f + C $$

$$ E = 161.3 \text{ GPa} $$

Application for bioceramics $\beta$-TCP

by spherical indentation (0.01 N – 5 N)

WC Spherical indenter ($E = 540 \text{ Gpa, } \nu = 0.2$)

$D = 200 \mu m$

Hertz’s theory not verified

Hertz’s theory

$$ h_{\text{max}} = 2 \cdot h_c $$
Annual Meeting of the Belgian Ceramic Society - Mons, 7th February 2011

\[
\frac{dh}{dP}_{h=h_{\text{max}}} = C_f + \frac{1}{2 \cdot \gamma \cdot E_R \cdot \sqrt{D}} \frac{1}{\sqrt{h_C}}
\]

\[E = 162.4 \text{ GPa}\]

by Knoop indentation (15 tests – 5 N)

\[W' = 15.95 \pm 0.25 \mu m\]

\[L = 124.8 \pm 1.7 \mu m\]

\[E = 160 \text{ GPa} \pm 26 \text{ GPa}\]

Vickers indentation : \[E = 161.3 \text{ GPa}\]

Spherical indentation : \[E = 164.4 \text{ GPa}\]

Knoop indentation : \[E = 160 \text{ GPa}\]
Elastic modulus of thin films

Materials
PACVD TiCN on steel substrate

Influence of the substrate as soon as indentation depth is higher than 1% of thickness (Chudoba et al. 2002, Cleymand et al. 2005)

Substrate properties must be taken into account

Available models: Linear additive law

\[ E_c = E_s + a(hc) (E_f - E_s) \]

where \( a(hc) \) is an "influence" function of the contact indentation depth (hc)

Doerner and Nix (1986)
Mencik et al. (1997)
Mencik et al. (1997)
Antunes et al. (2007)
Gao et al. (1992)
Antunes et al. (2007)

<table>
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<td>[ E_c = \frac{E_s}{1 + \frac{t}{h_s}} ]</td>
<td>[ E_c = \frac{E_f}{1 + \frac{t}{h_f}} ]</td>
<td>[ E_c = \frac{E_s}{1 + \frac{t}{h_s}} ]</td>
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</tr>
</tbody>
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Problem: The equations does not consider the compliance and the asymptotical behavior of the property
The new model

Non asymptotical behaviour

The influence factor should tend asymptotically
1) to the elastic modulus of the film (low loads)
2) to the elastic modulus of the substrate (high loads)

Existing models

New model

H_i = H_s + \left( H_f - H_s \right) \left( \frac{1}{1 + K\beta^2} \right)

\beta = \frac{h}{t}

Dureté : Korsunsky 1998

Hardness : rule of the tenth
On massive material:

\[
\frac{1}{S} = C_f + \frac{1}{\beta \gamma} \frac{1}{24.5} E_R h_c 
\]

(\text{Oliver and Pharr})

On thin film:

\[
\frac{1}{S_c} = \frac{1}{S_f} + a(h_c) \left( \frac{1}{S_f} - \frac{1}{S_c} \right) \quad \text{with} \quad a(h_c) = \frac{1}{1 + k h_c^2}
\]

(Korsunsky)

Substrate influence

\[
\frac{1}{S_c} = C_f + \left( \frac{1}{2\beta} \left( \frac{1}{24.5} \right) \right) \frac{1}{h_c} + \frac{1}{h_c (1 + k h_c^2)}
\]

Film influence

Which can be simplified as follows:

\[
\frac{1}{S_c} = \frac{P_0}{h_c} + \frac{P_1}{k h_c^2} + \frac{P_2}{(1 + P_1 h_c^2)}
\]

Microindentation results (0.1N – 20N)

<table>
<thead>
<tr>
<th>Film Type</th>
<th>E_f (GPa)</th>
<th>E_s (GPa)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCN-1</td>
<td>484</td>
<td>232</td>
<td>0.999</td>
</tr>
<tr>
<td>TiCN-2</td>
<td>461</td>
<td>215</td>
<td>0.985</td>
</tr>
<tr>
<td>TiCN-3</td>
<td>681</td>
<td>227</td>
<td>0.998</td>
</tr>
</tbody>
</table>

470 GPa – 610 GPa (Karlsson et al. 2000)  
486 GPa – 621 GPa (Bull et al. 2003)
**Nanoindentation: correction of tip**

In practice, the indenter presents defects at its extremity. This is the rounded tip.

\[ h_b = R \left( \frac{1}{\sin \psi} - 1 \right) \]

\[ A = \pi \tan^2 \Psi (h_c + h_b)^2 = 24.56(h_c + h_b)^2 \]

\( R = 350 \text{ nm} \)
\( h_c = 22 \text{ nm} \)
\( \Delta = 20 \text{ nm} \)

**Berkovitch**

Rounded tip

Troyon (2005)

**Nanoindentation: much less sensitive to substrate influence**

The influence of the substrate is low for the nanoindentation load range.

The new model results in inaccurate \( E_s \) values.

\( E_s = 200 \text{ GPa} \)

No connection between micro and nano indentation experimental points.
Nanodentation results (5mN – 300mN)

| TiCN-1 | 274 (GPa) | 200 | 0.999 |
| TiCN-2 | 326 (GPa) | 200 | 0.999 |
| TiCN-3 | 390 (GPa) | 200 | 0.999 |

486 GPa – 621 GPa (Bull et al. 2003)
470 GPa – 610 GPa (Karlsson et al. 2000)

Results in nanoindentation and in microindentation are not comparable

Nanoindentation is very sensitive to:

- tip rounding
- Roughness
- surface pollution
- chemical composition gradient
- …
TOUGHNESS

Vickers Indentation Fracture *VIF* method

Principal: pushing a Vickers indenter into the ceramic to generate cracks

Radial-Median cracking mode

Palmqvist cracking mode
More than 20 equations to calculate \( K_c \) in the literature (Ponton et al. 1989)

Chicot et al. 2009: two mean relations

\[
K_{c(R-M)} = 0.0154 \left( \frac{E}{H_v} \right)^{1/2} \frac{P}{c^{3/2}} \quad \quad \quad K_{c(P)} = 0.0089 \left( \frac{E}{H_v} \right)^{2/5} \frac{P}{a^{1/2}}
\]

Identification of the cracking mode?

\[
c \propto P^{2/3} \quad \quad a l^{1/2} \propto P
\]

Material constants

Radial-Median cracking mode

Palmqvist cracking mode
Problem: $a$ is load depending (Indentation Size Effect (ISE))

\[ al^{1/2} \propto P \]

Meyer's relation:

\[ l \propto P^{2(1-1/n)} \]

\[ P = A_t (2a)^n \]

\[ n \propto \ln(P) \ln(2a) \]

Meyer's index

Radial-Median cracking mode

\[ c \propto P^{2/3} \]

Slope: 0.66

Palmqvist cracking mode

\[ l \propto P^{2(1-1/n)} \]

Slope: 2(1-1/n)
Application for bioglass $55\text{SiO}_2\cdot13.5\text{CaO}\cdot31.5\text{Na}_2\text{O}$

Loads: 100g – 500g

Calculation of the Meyer's index $n$

\[ l \propto P^{2(1-1/n)} \]

Meyer's index: 1.8832

\[
\text{Meyer's index } = 1.8832
\]

\[
l \propto P^{2(1-1/n)}
\]

\[
0.938
\]
The intermediate cracking mode (Lube et al. 2001)
New relation for intermediate cracking mode (Miranzo et al. 1984 - Chicot et al. 2009)

\[ Kc_{(I-M)} = (\alpha - \beta \cdot q) \cdot f \left( \frac{E}{HV} \right) \cdot \frac{P}{a_q c^{(1.5-q)}} \]

\[ f \left( \frac{E}{HV} \right) = \left( \frac{\beta_{exp}}{\delta} \right)^{-1.5} \]

\[ \alpha \text{ and } \beta \text{ are two constants} \]

\[ \delta = \frac{2}{3} \left( 1 + \ln \beta_{exp} \right) \]

\[ \beta_{exp} = 0.768 \left( \frac{E}{HV} \right)^{0.408} \]

\[ q = \left( \frac{1.5 \cdot s - 1}{s} \right) \cdot n \]

\[ \text{Slope of } \ln (c) / \ln (P) \]

\[ \text{Meyer's index} \]

\[ \text{Constant between 0 and 1} \]

Calculation of the two constants \( \alpha \) and \( \beta \): two limit conditions (\( q = 0 \) and \( q = 1 \))

\[ Kc_{(I-M)} = (\alpha - \beta \cdot q) \cdot f \left( \frac{E}{HV} \right) \cdot \frac{P}{a_q c^{(1.5-q)}} \]

\[ Kc_{(R-M)} = 0.0154 \left( \frac{E}{HV} \right)^{1/2} \frac{P}{c^{3/2}} \]

\[ Kc_{(P)} = 0.0089 \left( \frac{E}{HV} \right)^{2/3} \frac{P}{a^{1/2}} \]
Results on nitrogen incorporated glasses

nitrogen is incorporated into glass networks by substituting for oxygen to give a more highly linked network.

$K_{IC(M-M)} = 1.005 \text{ MPa.m}^{1/2}$

One N is bonded to 3 silicons

The oxygen is linked to two silicons

INTERFACIAL TOUGHNESS
Interfacial Indentation Toughness

\[ K_{CA} = 0.015 \frac{P_C}{d^{3/2}} \left( \frac{E}{H} \right)^{1/2} \]

with

\[ \frac{E}{H} = \frac{E_a}{H_a} + \frac{E_c}{H_c} = \frac{E_a}{H_a} + \frac{E_c}{H_c} \]

Example on a plasma coating TiO₂

\[ P_c = 7.5 \text{ N} \]
\[ d_c = 35 \mu m \]
\[ K_{ca} = 4.66 \text{ MPa.m}^{1/2} \]

Example on a plasma coating NiCrBSi

\[ P_c = 15.8 \text{ N} \]
\[ d_c = 78 \mu m \]
\[ K_{ca} = 3.15 \text{ MPa.m}^{1/2} \]

\[ P_c = 63 \text{ N} \]
\[ d_c = 194 \mu m \]
\[ K_{ca} = 4.27 \text{ MPa.m}^{1/2} \]
Stellite onto stainless steel

Influence of the residual stresses: As-received coated systems.

Influence of the residual stresses: Annealed coated systems.

A unique critical point: \( K_{ca_0} = 6 \text{ MPa.m}^{1/2} \)
Discussion and conclusion

Indentation Methods (Instrumented or classical tests) can be used to achieve to almost all mechanical properties: Hardness, Young’s Modulus, Toughness

Advantages:
- easy to prepare the testing specimens
- several measures with one single apparatus
- results are in accordance with results in literature

Disadvantages:
- non standardized methods (need mathematical models)
- measurements are local measurements problems of discrepancy
- Influence of the surface (residual stresses, roughness…..)
- Influence of the tip for very low loads (nano indentation)

Many thanks for your attention