A New Method to Determine the Hardness of Thin Films

J. Lesage, A. Pertuz, D. Chicot

LML URA CNRS 1441 University of Lille – France
e-mail: jacky.lesage@univ-lille1.fr, didier.chicot@univ-lille1.fr

ABSTRACT

Measuring hardness of thin films, namely films of less than 10 µm thick, using standard microhardness testers is a very complicated task for several reasons. Among them, the most important one is due to the range of indentation loads that are available with these testers. These loads are too high to allow the determination of the hardness without involving a contribution of the substrate. In order to determine the hardness of the film it is necessary to separate the two contributions by means of a mathematical model. For that purpose, it is possible to use either one or the other models available in literature. Their application, though, requires the introduction of coefficients and data which have to be deduced from other experiments or from literature. The objective of the present work is to propose a new model, likely to avoid the knowledge of other data than that obtained easily from standard experimentation. As a general rule, all the models found in literature are based on a linear additive law expressing the measured apparent hardness (composite hardness) in function of the film and substrate hardness.

From the observation that any model for the composite hardness should allow the transition between a substrate hardness tendency and a film hardness tendency when applying decreasing loads, we propose to combine two types of additive laws, series and parallel, associated respectively to each of these behaviors. The ratio \((t/d)^n\) of the thickness \(t\) of the film to the diagonal \(d\) of the indent at a power \(n\), was found to be a pertinent parameter to express the variation of the composite hardness with the indentation load. A method was proposed to determine the value of \(n\), and finally, the procedure was applied to determine the hardness of various films Ti, TiN, TiNx, TiC, TiCN, Cr and DLC.

Keywords: thin film, hardness, model

1.INTRODUCTION

In order to improve the resistance to surface damage by mechanical actions, considerable research has been conducted to increase the hardness of the superficial zone of materials. This can be achieved for example by the deposition of hard thin films at the surface of materials.

In the objective of designing films possessing optimum mechanical properties, it is important to determine their hardness as precisely as possible. Unfortunately, direct determination of hardness, using a conventional micro-hardness tester, is not possible for a large range of indentation loads. This is because the substrate undergoes a part of the plastic deformation when the load is such that the depth of the indent exceeds one tenth of the film thickness [1-3]. As a consequence, the hardness number \(H_C\), which is calculated, is the result of contributions by both the substrate and the coating. Mathematical models are necessary in order to separate these two contributions and numerous authors have tried to construct such models by considering various hypotheses. Whatever the hypotheses, all the models available in literature assume a linear additive law to express the composite hardness \(H_C\):

\[ H_C = H_S + a (H_F - H_S) \]  \hspace{1cm} (1)

where \(H_F\) and \(H_S\) are respectively the film and the substrate hardness.

The differences between the models come from the more or less well-argued functions the authors have used to describe the variation of coefficient \(a\) with the applied load.

One of the earliest works was that of Bückle in 1965 [4], who defined empirically the coefficient \(a\) as a function of a weighting factor associated to the layers of an “influence zone” affected by the indentation. A more successful model was due to Jönsson and Hogmark in 1984 [5], who consider the load supporting
areas under the indent. Considering that these models could not represent the real deformation behavior during indentation, numerous authors have searched later to describe the volumes of the plastic zones developed under the indent. This was proposed originally by Sargent [6], followed by Bull, Burnett, Page and Rickerby [7-10] in 1987 who suggested to introduce a correction factor $\chi$ called the “interface parameter”. The development of depth sensing indentation tests allowed Ahn and Kwon [11] afterwards to propose a similar model requiring in addition the determination of the substrate and film yield stress.

In order to avoid the introduction of such a parameter $\chi$, we proposed in 1995 a model [12] based on the superposition of two hypothetic systems to represent the volumes of plastic deformation in the film and in the substrate under the indent. More recently, Ichimura et al. [13], basing their reasoning on the former model by Bull et al. [7-10] obtained a relation very similar to our model.

Korsunsky and Bull [14] have recently constructed a model based on the work of indentation associated to the deformation of the two materials and also of their interface. The model can describes very well the behavior of the coated system over a large range of indentation scales but fails to predict the hardness of the film when there is no sufficient data in the micro-indentation range.

As a rough estimation of the variation of the composite hardness between the two limits of film and substrate hardness, Fernandes [15] and Wang [16] have both proposed a linear relation to express coefficient $a$. Unfortunately these models lead to less accurate predictions than the Jönsson and Hogmark model and they will not be considered in the following.

Application of the models listed above requires the introduction of data that have to be deduced from other experiments or from literature. The objective of the present work is to propose a model which could avoid the knowledge of any other data than that obtained easily from standard measurements (e.g. thickness and apparent hardness). The basic idea on which we will now build this model, found its origin in the analogy between the variation of the Young modulus of reinforced composites in function of the volume fraction of particles, and the variation of the composite hardness between the hardness of the substrate and that of the film.

Although it is clear that there is no relation between the elastic deformation of composites and the elasto-plastic deformation of the film and the substrate during indentation, the mathematics used to describe the variations can be considered in a similar way.

In order to discuss the validity of the new model, calculated hardness of various films and substrates couples will be compared to the predictions given by a set of representative models applied to experimental values coming either from our laboratory or from literature.

2. HARDNESS MEASUREMENTS AND DATA COLLECTION

The films tested at the laboratory were prepared by an industrial vapor deposition process. Two types of films were deposited on a low carbon steel after careful polishing : TiN and DLC coatings of respectively 1,4 and 1,6 µm thick. Vickers indentations were then performed on the as-deposited samples using a Leco micro hardness tester with loads ranging from 0.25 to 20 N. Five tests were performed at each load in order to get a reasonable confidence in the calculated mean hardness value. Thickness of the film was measured directly either on a cross-section of a coated sample or using the ball cratering technique. Another set of data was collected from literature for films produced by different PVD or CVD techniques on various steel substrates. Table I resumes all the bibliographical data associated to the different films and also gives the Young modulus of the materials.

3. THE MODEL

Most of the models available in literature express the composite hardness $H_C$ under the form of a linear additive law in function of the film ($H_F$) and substrate ($H_S$) hardness (relation 1). This relation will be called "series relation" in the following. On the other hand, no model of the type :

$$\frac{1}{H_C} = \frac{1}{H_S} + a \left( \frac{1}{H_F} - \frac{1}{H_S} \right)$$

which could be qualified as "parallel relation", has been tried. However, similar relations deduced from very simple rheologic models have been used to represent the upper and lower bounds within which falls the elastic modulus of reinforced composites in function of the volume fraction of particles [19].
Therefore, a model for the Young modulus in function of the volume fraction of particles could be a combination of these two relations. We will examine how this very simple idea could be transposed to the composite hardness of thin films. Typical variation of the composite hardness in function of the ratio between the film thickness and the diagonal of the indent \((t/d)\) is shown on Figure 1.

![Figure 1. Typical variation of the composite hardness in function of the ratio t/d.](image)

It is seen that the variation of the composite hardness corresponds to a variation of \(t/d\) between 0 and a value near 1 (this was observed for a large variety of films and substrates). For higher indentation loads, \(d\) is high, \(t/d\) tends to 0 and the composite hardness tends to that of the substrate (the lower limit). On the contrary, when the indentation loads are lower, \(t/d\) tends to 1 and the composite hardness tends to that of the film (the upper limit).

If we consider the analogy with the elastic modulus of reinforced composites we may write two simple relations for the upper \((H_{CU})\) and lower bound \((H_{CL})\) of the composite hardness, where the coefficient \(a\) is expressed here as a function of \(t/d\):

\[
H_{CU} = H_S + f\left(\frac{t}{d}\right)\left(H_F - H_S\right) \tag{3}
\]

\[
\frac{1}{H_{CL}} = \frac{1}{H_S} + f\left(\frac{t}{d}\right)\left(\frac{1}{H_F} - \frac{1}{H_S}\right) \tag{4}
\]

The first one corresponds to the film tendency behavior for lower \(t/d\) and the second one to the substrate tendency behavior for higher \(t/d\). In order to allow the transition between substrate to film tendency we consider the following relation which combines the two previous relations:

\[
H_C = H_{CL} + f\left(\frac{t}{d}\right)\left(H_{CU} - H_{CL}\right) \tag{5}
\]

The problem is to give a form as simple as possible to the function \(f(t/d)\).
Consider first the relation known as Meyer’s law [20] which express the variation of the size of the indent \( d \) in function of the applied load \( P \):

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

(6)

Where \( n \) is called the Meyer index. When this index equals 2 the hardness number is a constant. That can be seen by replacing \( P \) by \( a d^2 \) in the expression of the Vickers hardness number:

\[
HV = \alpha \cdot a \left( \frac{d^2}{d^2} \right) = \alpha \cdot a = HV_0 = \text{Cste}
\]  

(7)

In some cases \( n \) differs from 2 and the hardness number is no more a constant but depends on the indentation load by the relation:

\[
HV = \alpha \left( \frac{1}{d} \right)^{2-n}
\]  

(8)

For the particular case of a film substrate couple, Figure 2 shows that the evolution of the measured diagonal and the applied load can be expressed by a similar relation than Meyer’s:

\[
P = a^* \cdot d^{n^*}
\]  

(9)

And the composite hardness number can be expressed by the following relation if it is introduced the thickness \( t \) of the film:

\[
H_C = \alpha' \left( \frac{t}{d} \right)^{2-n'}
\]  

(10)

**Figure 2.** Measured diagonal in function of the applied load in bi-logarithmic coordinates.
In this relation, it is seen that the variation part of the hardness number with load is represented by the factor $n^*$. In order to study the composite hardness, the choice for a $f(t/d)$ relation should involve that factor. After different attempts we adopted the following expression:

$$f\left(\frac{t}{d}\right)=\left(\frac{t}{d}\right)^n = f \quad \text{where} \quad m = \frac{1}{n^*} \quad (11)$$

In these conditions the composite hardness can be expressed by the following relation (12):

$$H_C = \left(1-f\right)\left(1/H_S + f \cdot \left(\frac{1}{H_F} - \frac{1}{H_S}\right)\right) + f \cdot \left(H_S + f \cdot \left(H_F - H_S\right)\right)$$

and the hardness of the film is the positive root of the equation (13):

$$A \cdot H_F^2 + B \cdot H_F + C = 0$$

with

$$A = f^2 \cdot (f - 1)$$

$$B = -2f^3 + 2f^2 - 1 \cdot H_S + (1-f) \cdot H_C$$

$$C = f \cdot H_C \cdot H_S + f^2 \cdot (f - 1) \cdot H_S^2$$

The value of $m$ is calculated by a linear regression performed on all the experimental points obtained for a given film substrate couple and deduced from the relation:

$$\ln d = m \cdot \ln P + b \quad (14)$$

The value of $m$ can be introduced in the model so that only the hardness of the films remains to calculate.

4. APPLICATION OF THE MODEL

For each load of indentation, the diagonal of the indent is measured and introduced in the general model in order to calculate the hardness of the film.

Figure 3 shows typical results obtained for the Titanium Nitride specimen [17]. Upper and lower bound, calculated using relations (3) and (4), are also shown on the figure. It is seen that the predicted values represented by the line agree well with the experimental points.
The same methodology was applied to all the coated materials. The results are collected in Table I. In order to validate the new model we decided to compare our predictions to those of some models chosen because of their different approaches: The Jönsson model with the two possible hypotheses, the model of Chicot, that of Ichimura and finally that of Korsunsky.

Whatever the model, the variations of the film hardness in function of the $t/d$ ratio, were found almost identical although the amplitude of the variations was different for each of them. Since all the models are based on very different assumptions, one may assume that the variations are not due to a bias of the models.

The best way to make useful comparisons is to consider the predictions of the different models at a given $t/d$ ratio. Since we have considered in our model that the composite hardness became that of the film when $t/d$ was approaching 1, we may extrapolate the values obtained for all the available $t/d$ to this value of 1. In these conditions one may expect the best predictions for the hardness of the film.

Table I summarizes all the data used for the calculation as well as all the results obtained using this procedure.

From a general point of view, the values calculated using the models of Chicot, Ichimura and Korsunsky are similar although some values predicted by the model of Korsunsky may be very different. This is observed when the number of experimental points is not sufficient in the domain of film influence. For the films tested here it seems that the model cannot applied satisfactorily for $t/d < 0.25$. In their paper Jönsson et al stipulate that the choice of the constant $C$, necessary to apply their model should be linked to the ratio $H_S/H_F$.

For high $H_S/H_F$ $C = 1$

and for low $H_S/H_F$ $C = 0.5$.

It could be difficult at first to decide what is low and what is high. For the films tested here a value of 0.2 seems to be a good indication of what value should be chosen for $C$. This is very clear on Figure 4 where we have compared the ratio $H_S/H_F$ to the relative difference between the Jönsson and Chicot model predictions ($H_F/H_{FC}$).
Figure 4. Relative difference between the Jönsson and Chicot model’s predictions in function of the substrate and film hardness ratio.

In order to test the validity of the predictions for the hardness of the films, we calculate the mean value of all the others models (Table 1). In accordance to the preceding remarks, the values shaded in gray for the Korsunsky model were not use for the calculation as for the Jönsson predictions which were chosen in accordance to the condition on the ratio $H_S/H_F$. Figure 5 gives an illustration of the good concordance between the predictions of the new model and mean prediction of the others models.
5. CONCLUSIONS

Starting from an analogy between the composite micro indentation behavior of thin films and the dependence of the Young modulus of reinforced composite on the volume fraction of particles, we proposed a new model. We have demonstrated here that this model is capable to give predictions as good as those given by other models. The main advantage of this model stands in the predictions which are obtained without any knowledge of the properties of either the substrate or the film. This is of great interest for the optimization of industrial processing and scientific knowledge of thin films as well.

6. REFERENCES


Table 1. Experimental systems used in the validation of the models.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Coating/ thickness (µm)</th>
<th>Substrate Coating</th>
<th>Jönsson HS E F (GPa)</th>
<th>Jönsson C = 0.5</th>
<th>Chicot</th>
<th>Korsunsky</th>
<th>Ichimura</th>
<th>$H_F$ mean value</th>
<th>m</th>
<th>$H_F$ (GPa)</th>
<th>new model</th>
</tr>
</thead>
<tbody>
<tr>
<td>[17]</td>
<td>TiN / 3.25</td>
<td>M-2 steel, 8.6/200</td>
<td>300</td>
<td>31.1</td>
<td>23.9</td>
<td>23.5</td>
<td>25.1</td>
<td>23.0</td>
<td>24.0 ± 1.0</td>
<td>0.62</td>
<td>25.3</td>
</tr>
<tr>
<td>[17]</td>
<td>TiCN / 3.25</td>
<td>M-2 steel, 8.5/200</td>
<td>255</td>
<td>57.3</td>
<td>42.6</td>
<td>39.9</td>
<td>51.5</td>
<td>39.0</td>
<td>47.0 ± 7.5</td>
<td>0.75</td>
<td>46.5</td>
</tr>
<tr>
<td>[9]</td>
<td>TiN / 2.5</td>
<td>Tool steel, 6.0/200</td>
<td>600</td>
<td>30.8</td>
<td>19.6</td>
<td>25.0</td>
<td>15.8</td>
<td>29.5</td>
<td>22.5 ± 5.0</td>
<td>0.59</td>
<td>29.5</td>
</tr>
<tr>
<td>[9]</td>
<td>TiN / 9.0</td>
<td>Tool steel, 6.0/200</td>
<td>600</td>
<td>3.1</td>
<td>19.7</td>
<td>21.1</td>
<td>28.9</td>
<td>23.7</td>
<td>23.5 ± 3.5</td>
<td>0.69</td>
<td>21.2</td>
</tr>
<tr>
<td>[9]</td>
<td>TiN / 2.0</td>
<td>Stainless steel, 1.6/200</td>
<td>600</td>
<td>2.2</td>
<td>13.6</td>
<td>22.3</td>
<td>9.6</td>
<td>22.9</td>
<td>22.5 ± 0.5</td>
<td>0.70</td>
<td>22.9</td>
</tr>
<tr>
<td>[9]</td>
<td>TiN / 5.5</td>
<td>Stainless steel, 1.6/200</td>
<td>600</td>
<td>8.8</td>
<td>13.4</td>
<td>18.9</td>
<td>17.2</td>
<td>18.8</td>
<td>18.5 ± 0.5</td>
<td>0.84</td>
<td>19.1</td>
</tr>
<tr>
<td>[11]</td>
<td>Ti / 4.0</td>
<td>High C steel, 2.0/200</td>
<td>120</td>
<td>0.9</td>
<td>5.5</td>
<td>7.0</td>
<td>5.1</td>
<td>6.8</td>
<td>6.0 ± 1.0</td>
<td>0.58</td>
<td>7.1</td>
</tr>
<tr>
<td>[11]</td>
<td>TiC / 4.0</td>
<td>High C steel, 6.4/200</td>
<td>460</td>
<td>7.4</td>
<td>19.5</td>
<td>21.3</td>
<td>18.8</td>
<td>23.7</td>
<td>21.0 ± 2.0</td>
<td>0.61</td>
<td>22.8</td>
</tr>
<tr>
<td>[5]</td>
<td>Cr / 1.0</td>
<td>BBS, 6.7/200</td>
<td>280</td>
<td>3.0</td>
<td>10.4</td>
<td>11.3</td>
<td>10.6</td>
<td>12.7</td>
<td>11.0 ± 1.0</td>
<td>0.55</td>
<td>11.8</td>
</tr>
<tr>
<td>[5]</td>
<td>Cr / 1.0</td>
<td>Stainless steel, 1.9/200</td>
<td>280</td>
<td>6.4</td>
<td>17.1</td>
<td>19.6</td>
<td>11.3</td>
<td>21.1</td>
<td>19.5 ± 1.5</td>
<td>0.59</td>
<td>28.9</td>
</tr>
<tr>
<td>[5]</td>
<td>Cr / 1.0</td>
<td>Stainless steel, 1.9/200</td>
<td>280</td>
<td>3.3</td>
<td>8.7</td>
<td>12.5</td>
<td>5.6</td>
<td>12.8</td>
<td>13.0 ± 0.5</td>
<td>0.61</td>
<td>11.3</td>
</tr>
<tr>
<td>[5]</td>
<td>Cr / 1.0</td>
<td>Copper, 0.9/130</td>
<td>280</td>
<td>2.2</td>
<td>7.2</td>
<td>12.4</td>
<td>3.8</td>
<td>12.5</td>
<td>12.5 ± 0.5</td>
<td>0.61</td>
<td>12.3</td>
</tr>
<tr>
<td>[18]</td>
<td>TiN0.55 / 3.0</td>
<td>316L, 2.7/200</td>
<td>600</td>
<td>5.5</td>
<td>12.7</td>
<td>15.4</td>
<td>19.8</td>
<td>16.3</td>
<td>16.5 ± 1.5</td>
<td>0.69</td>
<td>15.1</td>
</tr>
<tr>
<td>[18]</td>
<td>TiN0.65 / 3.0</td>
<td>316L, 2.7/200</td>
<td>600</td>
<td>0.5</td>
<td>16.9</td>
<td>19.7</td>
<td>22.7</td>
<td>20.2</td>
<td>21.0 ± 1.0</td>
<td>0.74</td>
<td>19.3</td>
</tr>
<tr>
<td>[18]</td>
<td>TiN0.75 / 3.0</td>
<td>316L, 2.7/200</td>
<td>600</td>
<td>7.8</td>
<td>24.1</td>
<td>27.3</td>
<td>43.3</td>
<td>28.1</td>
<td>31.5 ± 6.5</td>
<td>0.81</td>
<td>30.0</td>
</tr>
<tr>
<td>[18]</td>
<td>TiN / 1.4</td>
<td>Low C steel, 1.8/200</td>
<td>600</td>
<td>2.6</td>
<td>2.8</td>
<td>21.3</td>
<td>5.4</td>
<td>22.0</td>
<td>22.0 ± 0.5</td>
<td>0.56</td>
<td>21.8</td>
</tr>
<tr>
<td>[18]</td>
<td>DLC / 1.6</td>
<td>Low C steel, 1.9/200</td>
<td>440</td>
<td>8.0</td>
<td>6.1</td>
<td>27.0</td>
<td>9.5</td>
<td>27.8</td>
<td>27.5 ± 0.5</td>
<td>0.55</td>
<td>29.2</td>
</tr>
</tbody>
</table>

Where HF, EF and HS, EF are respectively the Hardness and Young Modulus of the film and of the substrates and C the constant used for the calculation when applying the model of Jönsson and Hegmark.