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Research Article

DETERMINATION OF ABSOLUTE HARDNESS OF THIN FILMS BY MODEL APPLICATION

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ABSTRACT

In order to determine the absolute hardness of film or coating, it is necessary to separate the different contributions. It is known that, depending on the thickness of the film and on the applied load, indentation measurements give apparent hardness values which are the results of contributions by both the substrate and the film. There is a need therefore to separate these two contributions in order to determine the true hardness of the film. Numerous authors have worked on this subject during the past and a large number of models who are written under an additive linear function are available in the literature. This study is to determine the absolute hardness of nitride thin layers obtained by two activation rate plasma of 50 and 65%. A series of classical Vickers indentation at several loads were applied at the surface of the specimens. The true hardness of these thin films was determined by using monolayer model of Jonsson and Hogmark which gives in general cases the concluded results.

Keywords: Hardness, coatings, thin film, monolayer, iron nitride.

1. INTRODUCTION

During the last decades, the use of nitride films to improve the chemical and mechanical resistance of machine parts made of steels has shown an extensive development [1]. Iron nitride films produced by plasma nitriding treatment, in particular, have high hardness and resistance to wear and corrosion at high temperature [2]. Owing to these properties, they are used for many applications such as cutting tools made of high-alloy steel intended for machining wood [3].

Generally, the nitriding process consists of treating the parts in a medium capable of giving nitrogen to their surface at a temperature conducive to the diffusion of the atoms towards the core of the parts. Several studies have focused on the kinetics of nitrogen diffusion in ferrite [4, 5], on the formation of nitrides in the combination and diffusion areas [6-8].

The objective of the present study was to obtain the absolute hardness of thin iron nitride films obtained by plasma nitriding on low steel substrate. This work requires the application of monolayer models in order to separate the contribution of the substrates to the measurement of hardness [9-1, 14]. Because of its simplicity, we chose the Jönsson and Hogmark model that is based on the deformed areas and gives in most cases good results [10].

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2. MODELS OF THIN FILM HARDNESS

During the measurement of the film hardness, the substrate undergoes a plastic deformation when the indentation exceeds one tenth of the thickness of the film. As a result, the number of H_C hardness, which is measured, is the result of the contributions of the substrate and the coating. In this case, the composite hardness H_C is given by:

$$H_C = aH_F + bH_S \quad (1)$$

where H_F and H_S are respectively the hardness of the film and substrate, $a + b = 1$ and a varied from 0 to 1.

Mathematical models are needed to separate these two contributions and many authors have attempted to construct such models based on linear additive laws by considering the mixture of deformed areas and volumes during indentation as hypotheses.

2.1. Bückle Model

During the indentation test, a plastically deformed area is generated in the immediate vicinity of the imprint. For Bückle [9], this zone of influence can be subdivided into sub-layers parallel to the surface and of the same thickness equal to the depth of penetration of the indenter. Under these conditions, the measured value of the hardness results from the contributions of each layer by their own hardness and their distance to the surface. These contributions are taken into account by attributing to each layer a weight Pi, the measured hardness is written:

$$H = \frac{\sum_{i=1}^{n} Hi.Pi}{\sum_{i=1}^{n} Pi} \quad (2)$$

In the case of a homogeneous coating of hardness H_F and thickness e, deposited on a substrate of hardness H_S, Bückle proposes to express the thickness of the coating in multiple of the penetration depth D which is proportional to the thickness of the layer e. Under these conditions, the composite hardness is then written:

$$H_C = \left(\frac{\sum_{i=1}^{K} Pi}{\sum_{i=1}^{12} Pi} \right) \cdot H_F + \left(\frac{\sum_{i=K+1}^{12} Pi}{\sum_{i=1}^{12} Pi} \right) \cdot H_S \quad (3)$$

From the numerical values indicated in figure 1, it is possible to calculate the coefficient of influence a as a function of the ratio of the depth of impression on the thickness of the coating (D/e =1/k). Figure 1 shows the calculated points as well as the more general curve of smoothing that the author deduces.

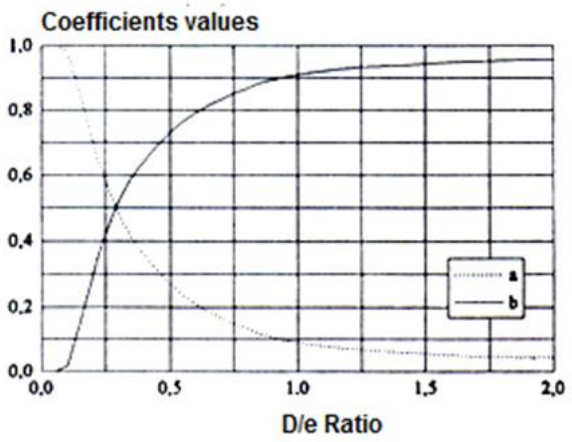

Figure 1. Evolution of the parameters *a* and *b* with the ratio of D/e [9]

In this figure, it is noted that the calculated points correspond to values of D/e ratio less than or equal to 1. As a result, the choice of parameters for the construction of the smoothing curve will strongly determine the shape of the curve for values of D/e greater than 1 and possibly lead to variations in the application of the model

2.2. Jönsson and Hogmark Model

To separate the substrate and coating contributions on measured hardness a simple geometric approach was used [10]. The coefficient of influence *a* is represented by the ratio of the deformed areas under the imprint of indentation, the relation (1) is written:

$$H_C = H_S + \left(\frac{A_F}{A}\right)\cdot(H_F - H_S) \tag{4}$$

where A_F is the area over which the H_F pressure is applied and A the total deformed area.

The hypothesis adopted is that the deformation of the layer is in coherence with that of the substrate under the indentation imprint and that the power dissipated by the deformation is localized on the blanks of the imprint. To express the A_F area, the authors consider two different geometries related to the mode of deformation of the film. Figure 2a and 2b show respectively the geometry retained when the thin film under the indenter (case of ductile materials) and when the thickness film remained constant during the indentation (case of fragile materials).

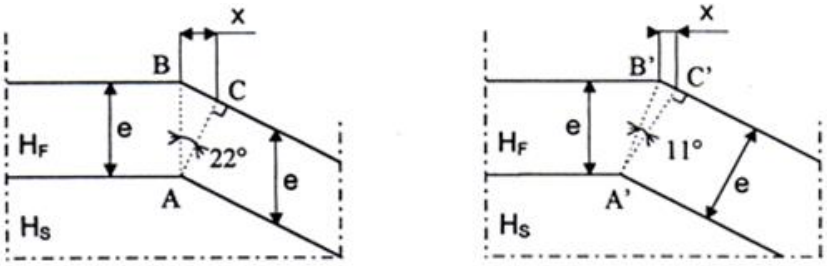

Figure 2. Geometric representation of the model of Jönsson and Hogmark [10].

Under these conditions, the coefficient of *a* witch equal A_F/A is expressed as a function of the diagonal impression d and the thickness of the film e:

$$a = \frac{A_F}{A} = 2C\frac{e}{d} - \left(C\frac{e}{d}\right)^2 \tag{5}$$

Which leads to:

$$H_C = H_S + \left(2C\frac{e}{d} - \left(C\frac{e}{d}\right)^2\right)\cdot\left(H_F - H_S\right) \tag{6}$$

2.3. Burnett and Rickerby Model

In their parts, Burnett and Rickery [11-12] have proposed a mixing law based on volume deformation, the composite hardness H, is given by:

$$H_C = \left(\frac{V_F}{V}\right)\cdot H_F + \left(\frac{V_S}{V}\right)\cdot H_S \tag{7}$$

Figure 3 presents the volumes of plastically deformed zones, V_F and V_S respectively in the film and in the substrate

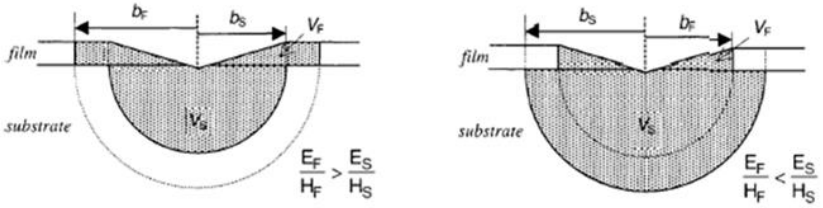

Figure 3. Plastic zone morphologies from (Burnett and Rickerby model) [11]

It is generally accepted that the plastic zone is assimilated to the hemisphere where its radius b is expressed as a function of the diagonal of impression d. According to Lawn et al. [13], this ray is written:

$$b = \frac{d}{2}\cdot\left(\frac{E}{H}\right)^{1/2}\cot^{1/3}\xi \tag{8}$$

E is the Young's modulus, *H* is the hardness and ξ (74 °) is the half-angle at the apex of the indenter taken between the edges.

In order to obtain a better correlation with their model, Burnett and Rickerby [11,12] introduce a correction factor χ called interface parameter. The authors justify the introduction of this factor to reflect the fact that there is an adhesion between the substrate and the film during indentation.

$$H_C = \frac{H_F V_F}{V} + \chi^3\frac{H_S V_S}{V} \qquad \text{for} \quad H_S < H_F \tag{9}$$

$$H_C = \chi^3\frac{H_F V_F}{V} + \frac{H_S V_S}{V} \qquad \text{for} \quad H_F < H_S \tag{10}$$

V_S and V_F are plastically deformed volumes calculated by the relation (7). V is the total volume plastically deformed ($V = \chi 3V_F + V_S$ or $V = V_F + \chi 3V_S$), and χ is an empirical parameter which represents the variation of the volume of the plastic zone as a function of the adhesion of the interface. Since χ was varied according to the mechanical characteristics of the film and the substrate.

$$\chi = \left(\frac{E_F \cdot H_S^{'}}{E_S \cdot H_F^{'}} \right)^q \tag{11}$$

where q varies theoretically between 1/2 and 1/3 [16], H'_S and H'_F are the hardness of the film and the substrate for a fixed diagonal.

2.4. Chicot and Lesage model

In order to avoid the introduction of such a parameter, Chicot and Lesage [14] presented a model based also on volumes plastically deformed but which implicitly takes into account the interaction between the substrate and the coating. This model is also based on a volume law of mixture for the plastic zone. Plastic deformation related to the applied load is assumed to be continuous between the coating and substrate. As indicated in figure 4, the contribution of the coating and the substrate was considered as both hypothetical systems.

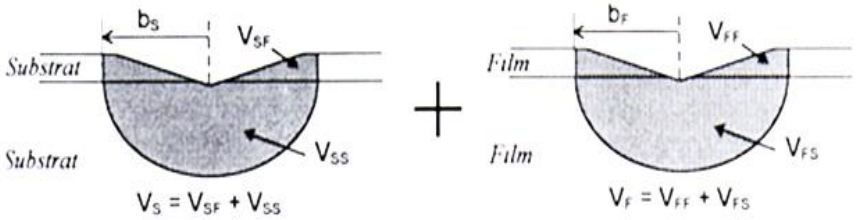

Figure 4. Plastic zone morphologies from (Chicot and Lesage model) [14]

Under these conditions, the composite hardness is written:

$$H_C = \alpha_1 \left(\frac{V_{FF}}{V_F} + \frac{V_{SF}}{V_S} \right) \cdot H_F + \alpha_2 \left(\frac{V_{FS}}{V_F} + \frac{V_{SS}}{V_S} \right) \cdot H_S \tag{12}$$

In this relation, the hardness H_C shows a term relating to the influence of the substrate in the deformed volume in the film and, in the same way, the influence of the film is taken into account in the deformation of the substrate. The condition on the constants a and b ($a + b = 1$) imposes $\alpha_1 = \alpha_2 = 1/2$. In the expression of the volumes Vij, the indication i refers to the constitution of the material considered and the j refers to the zone of the deformation. The deformed volumes can be approximated by a hemisphere of radius bi for the total volume and by a cylinder of radius bi, height e, for the volume deformed in the film area.

$$a = \frac{1}{2} \left(\frac{\pi b_F^2 e}{(2/3)\pi b_F^3} + \frac{\pi b_S^2 e}{(2/3)\pi b_S^3} \right) \tag{13}$$

Applying the relation (8) in the simplified form of a, this factor become

$$a = \frac{3}{2} tg^{1/3} \xi \frac{e}{d} \left\{ \left(\frac{H_F}{E_F} \right)^{1/2} + \left(\frac{H_S}{E_S} \right)^{1/2} \right\} \tag{14}$$

3. MATERIALS AND METHODS

The material used is an AISI 4140 steel whose chemical composition is 0.40% C, 0.85% Mn, 0.70% Si, 1% Cr and 0.30% Mo. The samples are circular pellets with a diameter of 30 mm and a thickness of 2 mm. To ensure uniformity of nitriding, the samples are ground and polished with diamond paste to a particle size of 1 micron. The ion plasma nitriding treatment is carried out under an atmosphere composed of a gas mixture of 80% nitrogen and 20 % hydrogen at a pressure of 5.4 mbar for a treatment time of 6 hours and polarization of 450 volts. The structures of films were observed using an Inel diffractometer with a monochromatic Co (Kα) radiation. Morphology and thickness of the layers were performed using an optical microscopy of type Nikon. In order to determine the hardness of the films in each situation, we perform first Vickers indentation for loads ranging from 0.1 to 10 N and at least three indentations for each load using a Leco microhardness tester.

4. RESULTS AND DISCUSSIONS

4.1. Structure

The figure 5 shows the presence of nitrides γ' (Fe_4N) and ε ($Fe_{2-3}N$) and ferrite. We notice that the diffraction peaks corresponding to the phase γ' are exalted to those corresponding to the phase ε. This confirms that nitride γ' predominates the combination layer.

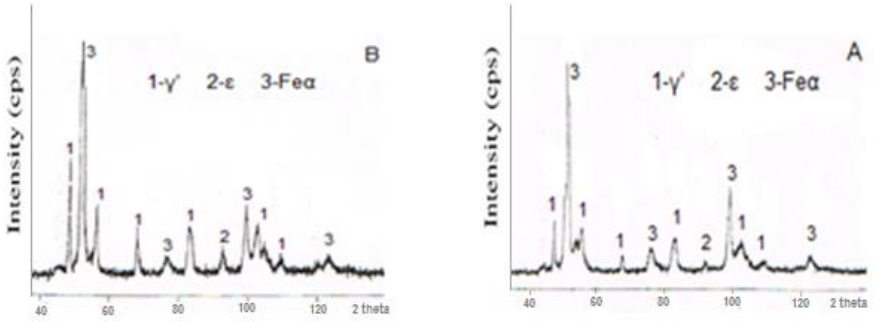

Figure 5. Structure of nitride layers obtained activation rate of (A) 50% and (B) 65%

Figure 6 shows the microstructure of the plasma iron nitride layer for two activation rates 50 and 65%. For an activation rate of 50% an irregular combination layer is observed with a thickness of 3µm (fig. 6A). The relative variation of the thickness of the combination layer is all the more accentuated for a high activation rate (fig. 6B). The layers formed corresponding to the levels of 50 and 65% are respectively in the vicinity of 3 and 8 microns. The both films were essentially constituted from iron nitride of γ'-Fe_4N and ε-$Fe_{2-3}N$.

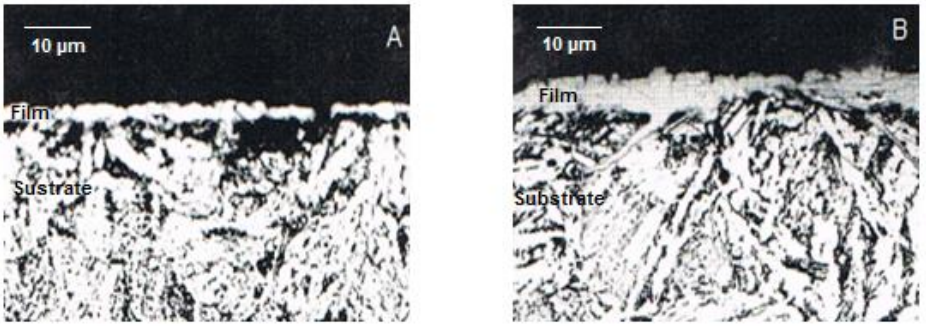

Figure 6. Microstructure of nitride layers obtained for activation rate of (A) 50% and (B) 65%

4.2. Hardness

It is known that, depending on the thickness of the film and on the applied load, indentation measurements give apparent hardness values which are the results of contributions by both the substrate and the film. There is a need therefore to separate these two contributions in order to determine the true hardness of the film. Numerous authors have worked on this subject during the past and among predictive models that of Jonsson and Hogmark is still widely used because it is very simple to employ.

Before presenting the results of film hardness determination by the model of Jonsson and Hogmark it is necessary to clarify this important point. The model of Jonsson and Hogmark involves a parameter C which can takes two different values depending on the toughness of the film: *C = 0,5* for brittle material, *C = 1* for ductile material.

Table 1. Results of the Vickers hardness tests

P(N)		0.1	0.25	0.5	1	2	3	5	10
50%	H_C (MPa)	6,7	5,7	5	4,4	3,9	3,6	3,2	2,8
	d (µm)	5	9	13	20	30	39	53	81
65%	H_C (MPa)	7,9	6,8	6,1	5,5	4,6	3,8	3,4	3
	d (µm)	4	8,2	12	18	27	39	52	78
Substrate	Hs (MPa)	2,7	2,6	2,7	2,6	2,6	2,6	2,6	2,5
(50, 65%)	d (µm)	8	13	18	26	37	45	59	85

The discussion of the brittle or the ductile behavior of hard films is rather difficult a priori. We will present the results of the calculation for the two values of C. Table 1 collects the results obtained for indentations at the surface of the films and also the results of indentations performed on the substrate.

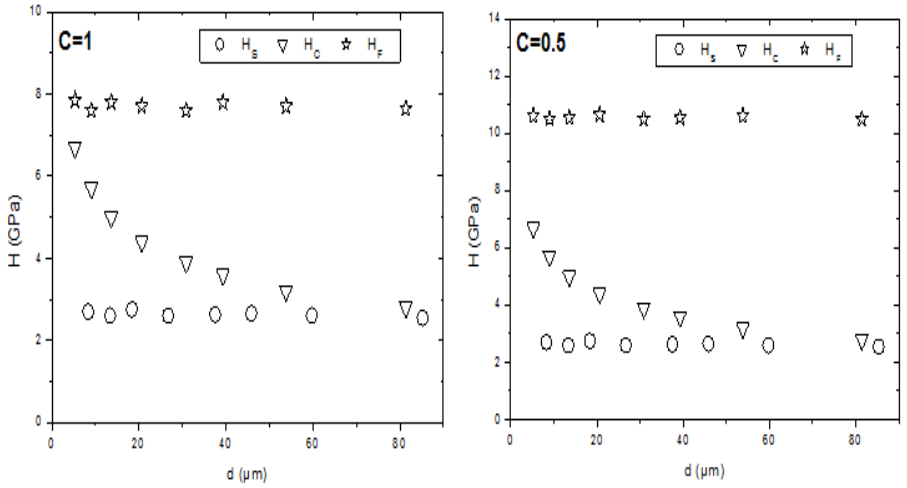

Figure 7. Calculated values of the film hardness according to J&H model nitride at activation rate of 50%

Fig. 7 and 8 summarize the results of the calculation of steel nitrided by two activation rates of 50 and 65% following the model of Jonsson and Hogmark for *C=1* and *C=0.5.* The hardness of substrate for different samples takes a value almost of 2.5 GPa.

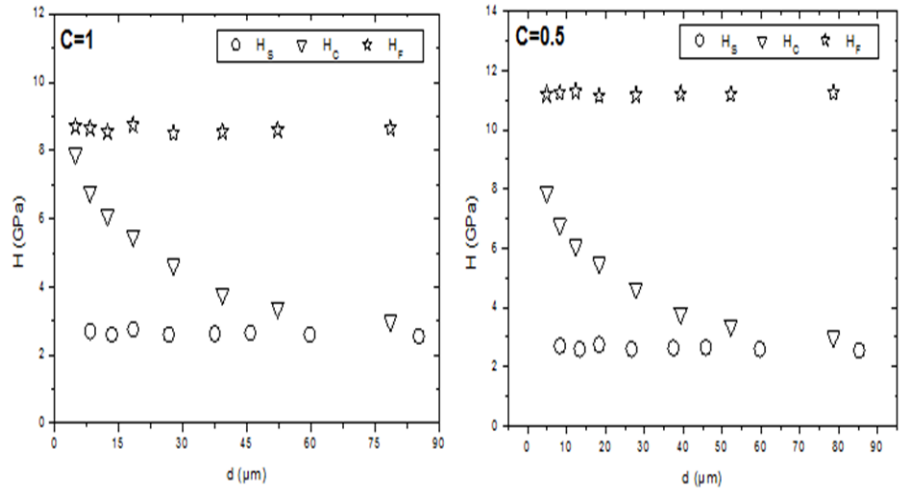

Figure 8. Calculated values of the film hardness according to J&H model nitride at activation rate of 65%

The both figures show that the film hardness is very different depending to activation rate on the chosen value for C in the Jonsson and Hogmark model. We notice that the hardness of film take the low values for the coefficient *C=0.5* relative to the other value of *C*. The mainly observation is that for *C=0.5* the model of Jonsson and Hogmark gives a hardness value of 11.2 GPa for nitriding steel produced by activation rate of 65% similar estimations to our model. This

estimation of hardness is in accordance with that of nitride steel obtained by Zdenek Pororny et al [15].

5. CONCLUSION

The nitriding treatment of AISI 4140 steel was carried out for two activation rates of plasma. The thickness of layers was depended to the used conditions. The nitride films presented two solid solutions of γ'-Fe_4N and ε-$Fe_{2-3}N$. According to the analysis by XRD, the compound of γ' has an important part from the layers. The goal of this study is to determine the hardness of layers by using a monolayer model of Jonsson and Hogmark wich is easy relative to the other models.
The calculated hardness of the nitriding film notably by using the coefficient C=0.5 have high values compared to the measured values which corresponds to the composite hardness (film and substrate). The layer produced by the activation rate of 65% gives a high thickness and a strong hardness relative to the second one.

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