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THE MICRO-HARDNESS ANISOTROPY OF FLUOR-OLIGOMERIC AND Fe-Co-W COATINGS

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Abstract – The influences of indenter micro-geometry on the micro-hardness performance in the film/substrate system are discussed. Experimental results verify the force required to produce hardness indents for thin films, the measurement of the size of plastic zone cross-sections of the indents, and the characterisation of the indenters. It was found that the deformation is highly localised beneath the indenter and failures in the corners of pyramidal indenters occurred.

Keywords: micro-hardness, thin films, failure.

1. INTRODUCTION

The conventional hardness testing is used among other methods in material research to retrieve corresponding data and to characterise specific materials [1]. The advantages of this method include many factors, and one of these, that only small volumes of material are required. Hardness determination of thin films by indentation is complicated because of extension of the plastically deformed zone. It is commonly stated that this zone extends 7-10 times the depth of the indentation. This plastically deformed zone extends up to different depths and we can conclude on the average hardness contribution of individual layers. However the interpretation of such results is difficult because practically we can separately determine the volumes of deformations of the two parts.

The traditional approach to the mechanical characterisation of coatings is (1) a measurement of hardness in which low loads and penetration depths (typically a tenth of the film thickness) are used to extract a film hardness while a higher loads are applied making an attempt to relate the film/substrate system response and (2) the measurement of toughness of film or interfacial fracture. These materials are often micro-structurally and mechanically heterogeneous due to local variations in thermo-mechanical history, which arise during the processing. As penetration progresses, the average stress in the coat increases, and generalised yield (large plastic zone directly under the indenter tip) is observed at depths of penetration approaching 1 diameter ahead of the tip face (fig. 1b).

Micro-indentation technique generally used to investigate the film hardness on the surface (current practice standards) can be applied also for investigations through cross-section of the layer and the study of fine-scale changes in hardness.

The aim of investigations is to present some explanations regarding the micro-hardness measuring of anisotropic solids in the thin film/substrate system.

2. TESTING THE MICRO-HARDNESS OF COATED SURFACES

Hardness normally implies the resistance of the material to local deformation and it is obtained by dividing the maximum indentation load by the projected contact area. However above mentioned definition of hardness does not describe precisely the resistance of the material to local deformation. Some authors suggested recently [3] that since the deformation is volume process and it takes energy to induce it, the energy related definition of the hardness is more descriptive particularly in the case of micro-hardness measurement of film/substrate system where the volume of deformed material is very small and mixed [4]. Dissipated indentation energy is calculated out of whole load displacement data (F-h curves) obtained during the testing by discrete integration of force being the function of displacement [5].

This approach considers that the on-load maximum indentation depth (h_{max}) is the sum of the plastic (h_p) and the elastic (h_e) components of indentation. For a Vickers indenter ($A = 24{,}5\ h_r^2$, where A is the projected area of indentation), the Meyer hardness values were derived from:

$$HM = \frac{F_{max}}{A} = \frac{F_{max}}{\alpha \cdot d^2} \qquad (1)$$

Where F_{max} is the maximum load applied, d - characteristic length scale of the resultant indentation impression, α - geometrical parameter of used indenter.

The ratio between the penetration depth and the coat thickness (t) always has to be kept below 10 % ($h_{max}/t = 1/10$) [5]. However this correlation covers in our experiments only narrow range of the F_{max} values. Volume of the indent is derived as an integral of the area of the indenter being function of penetration depth and then corrected by factor of final depth.

Previous experimental results of the fully plastic indentation regime [6] indicate that for identical spherical and Vickers indentation depths (i.e. $\delta_s = \delta_t$), the

corresponding hardness values are related by $H_s(\delta_s) \approx 0{,}7H_v(\delta_t)$. This relationship may be explained analytically relating the hardness with the work done by the indenter and the plastic zone volume for both types of indentation [7], and it is valid approximation at the end of the elastic-plastic indentation regime.

Deformation model assumes that that the volume of impression is proportional to the kinetic energy W of the indenter but is independent of its shape or tip angle 2Θ [6]. The volume of a rigid sharp indenter with an apex angle of 2Θ is:

$$V = \frac{\pi}{24} cot\,\Theta d^3, \tag{2}$$

where d is the diagonal, and:

$$W = V \cdot W_o = \frac{\pi \cdot W_o}{24} cot\,\Theta\, d^3 = W_o \cdot k \cdot d^3, \tag{3}$$

where W_o is the assumedly constant kinetic energy absorbed per unit volume of deformed metal and $k = \pi\, cot\, \Theta/24$ is a constant.

The total energy required to produce an indentation of depth h is given by:

$$W_t = \int_0^h F dh = H \cdot \frac{h^3}{3k}, \tag{4}$$

This is termed the "work of indentation" and, if measured (as could be readily achieved with continuos recording indentation technique) can be used to define an effective value of H which usefully describes the resistance to deformation over the penetration h.

Above a critical load, when the substrate starts to make itself felt, it is found that a wide range of films deforms by the shear of the coatings into the substrate (fig. 1).

For the same reason H in (4) may be considered as the plastic hardness value of the given material. Film effects become negligible in the deformation of the film/substrate system for large indentations.

All stress components in the region beneath the indenter are compressive and increase in magnitude with contact angle. The circumferential stress on the specimen surface (or radial stress along the indenter axis) attains a tensile peak at the elastic-plastic boundary.

The radius of the plastic zone is given by [8]:

$$R_{pl} = \varphi\left(\frac{E}{H}\right)^n cot^{1/3}(\Theta) h_{res}, \tag{5}$$

where R_{pl} is radius of the plastic zone; φ - for Vickers indenter is equal 3,5; E - Young's modulus; H - hardness; Θ - effective half-included angle; h_{res} - residual depth.

The radius R_{pl} was measured by averaging the horizontal size and the vertical size of the plastic deformation zone. The area of the imprint increases by nearly a factor of six with deeper penetration while the strain only increases by a factor of three.

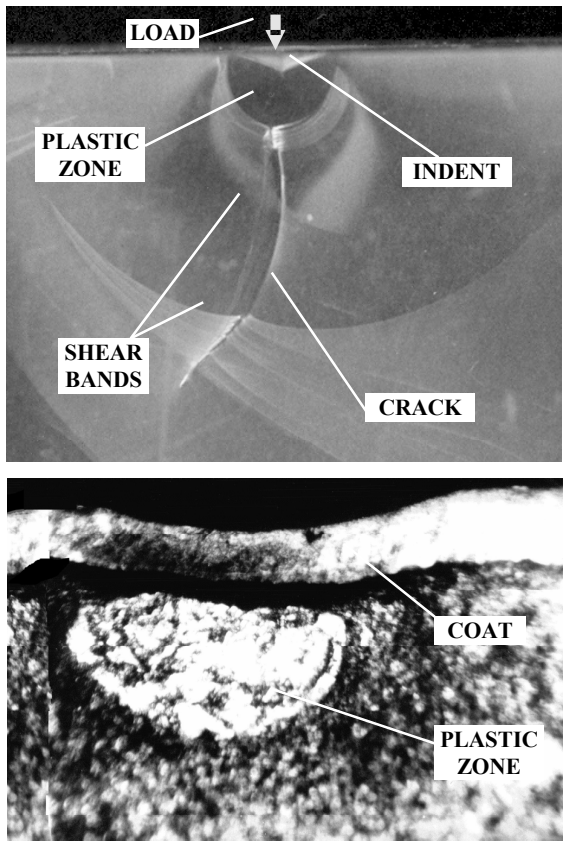


Fig. 1. Cross-sections of the hardness measurement specimens - evolution of shear band patterns on PMMA material (a) and plastic zone volume (b) in the film/substrate system with load beneath the Vickers indentation.

Moreover at small length scale additional factors like tip rounding or other size effects might influence the extension of the plastic zone. Depending on the strain limit, different sizes for the plastic zone can be defined. In this case, the radius of the plastic zone R_{pl} approximately equal: $R_{pl} \approx \gamma\, a_c$, where γ is a constant ranging from zero to ~ 3,5; a_c - contact radius.

3. EXPERIMENTAL METHODOLOGY

The fluor-oligomeric materials (FOM) - solutions of FOLEOX (0,5…10% concentration) were used for creating polymer coat on the metal surface. The specimen materials used are carbon steel utilised for machine structures (carbon content 0.45%). Cylindrical samples of 30x30 mm in size of medium carbon steel AISI 1045 (DIN 1.1186) composition in wt % (Fe, (0,37…0,44) C, (0,6…0,9) Mn, (0,19…0,23) Si) were cut, quenched and tempered state for various hardness levels (40<HRC<63). The samples were grounded and mechanically polished to a surface roughness R_a of 0,2 μm. They were than cleaned with acetone before testing.

After the surface is coated with fluor-oligomeric coat the chemosorbic bindings are created between metal surface and the film. The thickness of FOM layers was about 0,1…0,16 μm. Although the films allow water vapour diffusion, the

films both are hydrophobic and are not "wetted" when liquid waters contacts these layers.

The Fe-Co-W coatings were produced on roller specimens which could be adopted to tribological tests on according testing rig. Fe-Co-W containing films were electro-deposited on the mechanically polished tempered and non-tempered steels. Substrates were degreased and activated with dilute sulfuric acid immediately before plating and a seed-layer of Ni was electroplated within 1 min. from Wood's type solution containing $NiCl_2$-$6H_2O$ 240 g/l + HCl 80 g/l at 30 mA/cm^2. Then the Fe-Co-W-containing alloys were electro-deposited from the citrate-ammonia baths.

The buffer capacity of the plating bath solution was determined by titration with 15 M NaOH solution to avoid any dilution effects. Changes in pH were monitored by pH-meter ThermoOrion type 420. Buffer capacity values at certain pH were extracted after digital differentiation of titration curves.

The cross-sections of the samples were prepared by cutting, grinding, polishing to the sane level of roughness revealed by etching in aqua regia and observed by optical and SEM microscopy.

Hardness tests were carried out with a Vickers pyramid indenter, using a Fischer HP 100 XY-PROS ultra-micro-hardness tester [9]. A diamond indenter of standard geometry, typically a 136^0 square based pyramidal diamond (Vickers) is indented under a known load, into the surface of the sample. During tests, load – indentation depth – time data were recorded. Hardness measurements were performed under six different indentation loads, ranging from 0.1 to 1.0 N. At each load level, at least 10 measurements were made on the coatings. However, besides the properties of the coatings, the testing methods can also affect the performance of the coatings. Firstly, the fact that the response of the system depends significantly on the scale of contact, being dominated by the film hardness at small scales in comparison with the coating thickness and by the substrate hardness at large scales. Secondly, the stress-strain situation during indentation is triaxial.

4. RESULTS AND DISCUSSION

The figure 2 shows the loading-unloading cycle obtained using an micro-indentation tester operating with fluor-oligomeric film in the ramp mode and corresponding Vickers contact geometry. The load is incremented at constant speed up to the maximum load (F_{max}) and subsequently released at the same rate as in loading cycle.

Continuos depth-sensing recording does not give values of absolute micro-hardness value directly, because the area of indentation is not measured explicitly. However the indentation data can be processed on the basis of well-known assumptions [2].

The results show that only FOM film slightly reduced the micro-hardness value on the surface. It is likely attributed to the presence of pores in the coats and the reason could be Rebinder effect [10] and combination of factors: the real effect of native oxide at the surface or an effect of the coating procedure, and an artefact of the shape indenter tip for small indents.

As the deformed phase-transformed fluor-oligomeric layer of material tries to push in through the surrounding bulk material, internal stresses may be developed in the micro-volumes and it would help the relieving process of this excess internal stresses. Some much localised micro-cracking, particularly near the edges of the Vickers indenter, always occurs. In the case of FOM film large-scale brittle fracture which induces material removal, is essentially absent in these materials. The increase of hardness is achieved by accumulation of impurities in area of dislocations. The ductility increases with the mobility of dislocations. Fluor-oligomeric layer contributes to achievement of both effects.

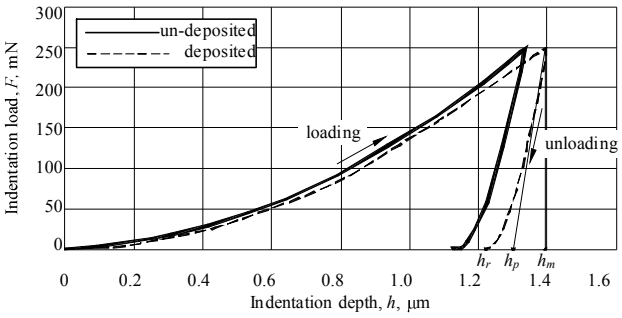


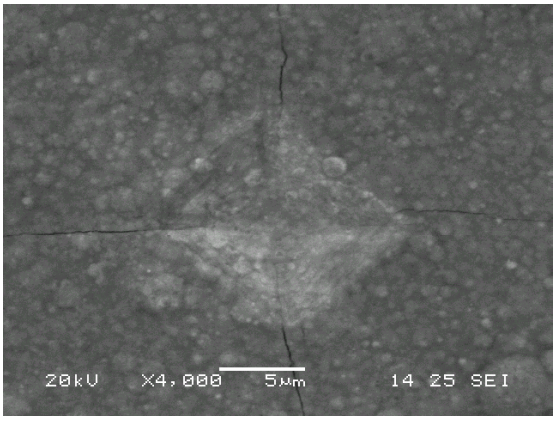
Fig. 2. Typical loading and unloading curves from a micro-indentation test cycle for fluor-oligomeric film. *F* is the loading force and h is the indentation depth. The depth of circle of contact h_p is obtained from the dotted extrapolation line.

The hardness of a material depends on several parameters such as the yield stresses σ_y, the Young's modulus *E* and the flow rule (plastic stress-strain relation) [7]. For small ratios σ_y/E, e.g. less than 0,002, the hardness values increase with increasing indentation angle. In fact in appears to depend on the evolution of plastic zone size with respect to the contact radius and the elastic behaviour does not influence the plastic flow for coating.

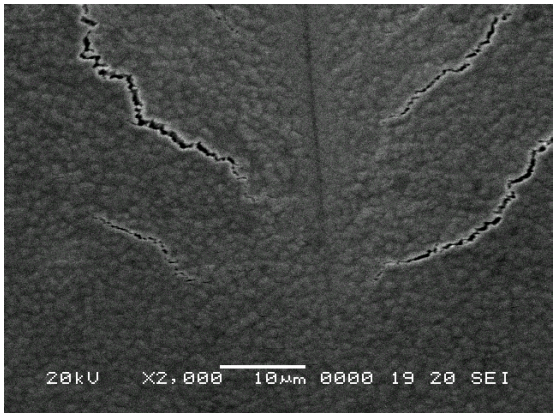
These results may be explained by assuming that in present experiments the coat adjusts initially to the elastic-plastic deformation of the underlying substrate during the indentation process until at a given deformation of substrate, the coat undergoes a cohesive-adhesive failure and that leads to film detachment. According to this interpretation for certain given film/substrate system characteristics (i.e. material, thickness, microstructure etc.) the failure will always occur when this critical deformation is reached, independently of the substrate hardness. SEM observations on indentation impressions demonstrate that the radial cracks are straight lines as seen in figure 3 (b,c).

Several factors may be responsible for the observed micro-cracking in Fe-Co-W coatings. It is highly probable, that the high interfacial friction between two adjacent surfaces and the deforming material may cause significant localised stress in the tip of indentation.

a)



b)



c)

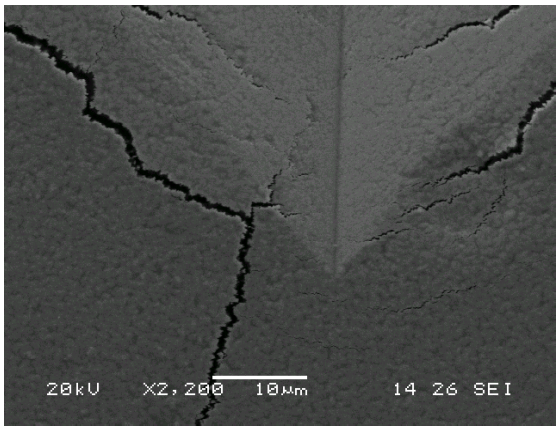


Fig. 3. Cracks development around a Vickers indent on Fe-Co-W coats showing general view of indentation (a), median (b) and lateral (c) vent cracks. The lateral cracks shows a marked anisotropy arising from the structure.

The hardness is described by the square of the diagonal ratio. Therefore is more sensitive to the precise diagonal values. Stress concentration effects on the corners of the pyramidal indenter enhance plastic deformation and failure and this may influence the measured area.

The observations suggest that while plastic deformation usually occurs in both coat and substrate (fig. 1b) - fracture also be possibly at larger loads (fig. 3a). Certain similarities also exist in the coat when deformation is dominated by cracking (fig. 3b,c). It is clear that they can occur at the indentation apex along the edges of the pyramid indenter, and in the form circumferential cracks around the indentation.

Plasticity and fracture for micro-hardness measurements must be considered separately, although the experimental results show some convergence and may be expressed by one formula. If the coating has been bent (fig. 3c) to displacements of the order of its own thickness, we identified the local plastic deformation at the points of maximum bending strain. There the true hardness value may reflect some other function of the yield stress of the coat rather than its conventional hardness.

The results of micro-hardness measurements of Co-W coats using different substrate are presented in fig. 4. They show how different could be surface strength if different substrate for coating is used. The coating of specimens with Co-W increases the micro-hardness of surface except when initial micro-hardness of substrate is higher as average.

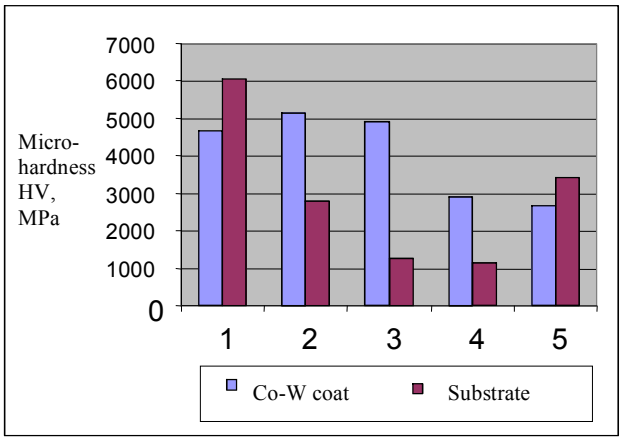


Fig. 4. Comparison of the micro-hardness of Co-W coats on different substrates: 1 – mechanically polished copper; 2 –brass mirror (the Cu-Zn alloy sprayed on the steel); 3 – steel „Stal 3“; 4 – chemically polished copper (micro-roughness); 5 – steel „Stal 3“.

5. CONCLUSIONS

The results obtained suggest that when indentations are performed in the fully plastic regime it is possible to establish a representative correlation between energetically defined complex hardness value and the substrate hardness. This result may be explained by considering the indentation size effect index values for the used substrate.

Surface modification by fluor-oligomeric film usually introduces a hardness gradient in the near surface region of the material. The fluor-oligomeric treatment decreases the micro-hardness of solid body till 15% at 0,02…0,03 mm deep because of chemosorbic interaction with steel.

It is necessary to estimate the arising of failures at the measurements of hardness and anisotropy. Several factors may be responsible for the observed micro-cracking in Fe-C-W coatings. Stress concentration effects on the corners of the pyramidal indenter enhance plastic deformation and failure and this may influence the measured area.

Film thickness and film hardness are relevant variables for determining the composite hardness and the deformation

behaviour of the film/substrate system at low indentation conditions.

In further investigations is necessary to understand why there is a difference between the calculated and measured hardness correction factors.

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