The small thickness of thin surface coatings may create difficulties in the characterization of their properties. This is true irrespective of the nature of the substrate material either metallic or polymeric. In this study an attempt is made to have a deeper insight in the characterization of thin coatings by indentation hardness tests. Attention was focused on the indentation size effect (ISE)- manifest at low loads applied on the indenter, that makes the hardness dependent on load. Two groups of materials with different chemistry have been investigated. For the first group consisting in eight sulfide compounds available as bulk minerals both ISE affected hardness values and ISE free hardness values (true hardness) were recorded. For the second group consisting in electroplated Ni-P/SiC composite coatings with variable P content no ISE free hardness region could be recorded. The true hardness of the coatings was obtained from the ISE affected values by means of a mathematical model.

Key words: microhardness, sulfide compounds. Ni-P/SiC coatings, ISE effect

Surface engineering is a continuously increasing field of interest in chemical engineering as it tries to functionalize industrial products (polymeric, ceramic or metallic) by changing the chemistry, structure and properties of the outer layer of the product so that to meet more and more pretentious demands required by modern technological applications. These demands may concern a variety of surface properties, either chemical (catalytic, anticorrosive, decorative), physical (heat conducting, heat dissipation, electromagnetic shielding, antistatic, protection against UV radiation) or mechanical (wear resistance, antifriction). It is worth to mention that even for polymeric products there is nowadays an increasing interest in the mechanical behaviour of metallic outer coatings [1-3] and in their characterization. Surface coatings of micronic or even nanometric thickness are nowadays produced by a variety of chemical or physicochemical procedures involving electrodeposition, electroless deposition, CVD (chemical vapor deposition), PVD (physical vapor deposition) etc. Outer layer coatings may become even more interesting if they are made as composite materials consisting in a matrix and a dispersed phase of different chemical nature. For example the Ni-P/SiC composite coatings investigated in this paper combine the anti-corrosive properties of Ni with the hardness imparted by the phosphorus incorporated in the Ni matrix and also by the reinforcing SiC dispersed particles. Various other compounds may be introduced in the Ni-P matrix of the coating to induce high hardness and wear resistance such as (WC, B4C) or (TiO2, ZrO2, Al2O3) [4,5]. Opposite properties, namely antifriction behaviour, may be obtained if solid lubricant particles such as sulfides (MoS2, WS2) or even polymeric particles such as polytetrafluorethylene are embedded in the metallic matrix [6].

A convenient way to characterize surface coatings and to check that their properties are reproducible is to carry out an indentation microhardness test. The test is nondestructive and easy to be performed. For thin coatings there is however a risk to have the indenter penetrating the coating and to record an altered hardness value that is influenced by the substrate material. If the substrate is a polymer product that is always softer than the metallic coating the altered recorded value will be lower than the true hardness of the coating. To avoid this inconvenient one has to make recourse to very small loads applied on the indenter, but this introduces another risk, namely to have the recorded microhardness values load dependent (the ISE effect). To eliminate the ISE effect and to obtain the true hardness of thin coatings a mathematical model is applied in this paper that is verified by the experimental data obtained on electroplated Ni-P/SiC composite coatings as compared to the data obtained for bulk chemical compounds selected among sulfide minerals. The substrate of the investigated coatings was metallic but the solution proposed may be valid as well for polymeric substrates.

Experimental part

Investigated samples

Large bulk polycristalline mineralogical samples were used to measure the hardness of the investigated sulfide compounds. Each mononimeral mineralogical particle was considered to represent a sulfide compound in pure chemical state.

The composite Ni-P/SiC coatings were electroplated on a mild plain steel support (0.17 wt% C) at 80°C from an aqueous electrolyte of the following composition: 210g/L NiSO4.6H2O; 50g/L NiCl2.6H2O; 50 g/L Na2SO4; 50g/L H3PO4; the content of the active component for phosphorus co-deposition namely H3PO4 was modified in steps as follows 5, 10, 20g/L. The pH equal to 2 in the electrolyte was kept constant. The SiC particles intended to be incorporated in the coating during the electroplating process were maintained in suspension by stirring the electrolyte. The metallic matrix of the composite coating was the result of the co-deposition of Ni and P. The SiC particles were about 1μm in size and 10.4m2/g specific area.
Hardness characterization

Indentation tests were carried out by means of a micro-Vickers diamond indenter of square pyramidal shape with 136° apex angle.

For the sulfide mineral compounds the tests were carried out by means of an Epitetype-Zeiss optical microscope equipped with the Vickers microindenter incorporated in a Hanemann lens. The polished surface of each polycrystalline sulfide sample was indented at various loads applied on the indenter as follows: 5; 10; 20; 40; 65; 80; 100g. Ten indentations were imprinted at each load and the average of the ten diagonals used to calculate the hardness by means of relationship $H_V = \frac{1854.4F}{d^2}$.

For the electroplated Ni-P/SiC composite coatings a Shimadzu HMV-2 micro-Vickers tester was used by applying the load perpendicular on the smooth free surface of the coating. Various loads were applied on the indenter as follows: 15; 25; 50; 100; 200; 300g. Five indentations were imprinted at each load on each coating and the average of the five diagonals used to calculate the hardness $H_V$.

Results and discussions

Hardness and ISE effect in bulk chemical compounds

In a previous research [7-9] we have performed a thorough study on the ISE effect in a large group comprising 24 pure mineral compounds belonging to the sulfide class, selected according to their crystallography and chemistry [10].

As the investigated samples were bulk polycrystalline no restrictions concerning the size of the indentation diagonal or the depth of penetration existed. So the span of the selected applied loads was large enough to encompass both the load values range where the ISE effect (hardness dependence on applied load) was manifested as well as the load values range where the hardness maintained itself constant (load independent) as depicted in Fig.1 for eight of the investigated compounds. In what follows we have denoted by $F_c$, the minimum load value located on the horizontal branch for which the hardness value becomes constant ($H_{Vc}$) or load independent. Of course $H_c$ may be considered to be the true hardness of the substance.

For six among the eight investigated sulfides in figure their value $F_{c}$ appears to be the same, namely about 40 g. This was true for FeS (pyrophyllite), ZnS (wurtzite), CuS (chalcomite), PbS (galena), MoS$_2$ (molybdenite), Ag$_2$S (acanthite). By admitting that hardness is an external expression of the strength of the chemical interatomic bonds, this fact seems to be a consequence of the common chemical nature of the investigated sulfides that are ionic-covalent compounds.

However exceptions appear for the remaining two compounds in Fig.1, namely a higher $F_{c}$ value (~65 g) for Cu$_x$S$_y$ (enargite) and a lower $F_{c}$ value (~20 g) for Cu$_2$S$_2$ (chalcopyrite). We have looked for the reasons of these exceptions in some peculiarities in the chemistry of the corresponding compound. For instance Cu$_x$S$_y$ (enargite) is out of the rule because it is not a true sulfide but rather a sulfo-salt belonging to a semi-group in which the semi-metals Sb, As or Bi play the role of cations, in contrast with their anionic role in true sulfide-type compounds such as Fe$_x$As$_y$ (arsenopyrite), Ni$_x$S$_y$ (gersdorffite), and Co$_x$S$_y$ (cobaltite).

On the other hand the case of Cu$_2$S$_2$ (chalcopyrite) is also special. In spite of the fact that the structure of chalcopyrite was fully established since 1973 [11] there is still a debate concerning the valency state of the constitutive metallic atoms. There are arguments [12] that plead in favor of the resonance between two states. One of them corresponds to the formula Cu$^{+}$Fe$^{2+}$S$_2$ while the second corresponds to the formula Cu$^{2+}$Fe$^{3+}$S$_2$ resulting from a hybridization type $sp^3$ that endows the substance with strong covalent bonds.

If one is interested to apply Vickers microhardness tests to characterize thin coatings instead of bulk substances what matters is not only to know a priori the value for $F_c$, in order to make use of loads $F \geq F_c$, for obtaining the true hardness of the coating but also to make sure that such loads will result in a size of the indentation (diagonal $d$ and depth of penetration $p$) that is compatible with the coating thickness $t$ in order to avoid any influence from the substrate material.

Relationship (1) derived from the definition of the Vickers microhardness and the general relationship $p/d$, may be used to calculate the critical depth of penetration $p_{cr}(\text{in } \mu m)$ below which the ISE effect is manifested:

$$p_{cr} = \left(\frac{1854.4 F_{c}/H_{Vc}}{2}\right)^{1/2}$$

For sake of illustration, for the hardest bulk crystalline substance in figure 1, namely for Fe$_x$S$_y$ (pyrophyllite), one obtains the values $p_{cr} = 2 \mu m$ and $d_{cr} = 14.3 \mu m$. On the other hand for the softest bulk crystalline substance in figure 1, namely for Ag$_2$S (acanthite), one obtains the values $p_{cr} = 8.1 \mu m$ and $d_{cr} = 56.8 \mu m$. All values lie in the range of microns or tens of microns.

Hardness and ISE effect on thin metallic coatings

If one intends to obtain in a direct way the true hardness of a coating (unaffected neither by the ISE effect nor by the substrate material) one has to apply a load $F > F_{cr}$ and on the other hand one has to make sure that the thickness $t$ of the coating is large enough to observe either the condition $t > p_{cr}$ (if the indenter is applied perpendicular on the free surface of the coating) or the condition $t > d_{cr}$ (if the indentation is performed in transverse cross-section perpendicular on the thickness of the coating). For relatively thick coatings the above mentioned conditions are not difficult to be met.

However problems arise when thin coatings are intended to be characterized by microhardness indentation tests. The problems that may arise in this instance and a solution proposed to solve them will be exemplified in what follows by using the results of the researches we have performed on composite thin coatings consisting in a Ni-P alloy reinforced with micronic SiC particles.
The technique we have applied to obtain such coatings has been described in detail in a previous paper [13]. The metallic matrix of the Ni-P/SiC composite coatings consisted in a supersaturated Ni based solid solution whose phosphorus content increased as the content of H 3PO 3 in the electrolyte was increased. The content of incorporated SiC reinforcing particles in the coating also increased as the content of SiC particles maintained in suspension in the electrolyte was increased.

An index \( t \) was used to indicate the coating thickness in micrometers that was dependent on the time of the electrolytic deposition process.

In what follows we have considered only the coatings having the highest phosphorus content \( (20\text{at.}\%\text{P}) \), electroplated from an electrolyte containing 20 g/L H 3PO 3 and 40 g/L SiC.

Because of the metastable state of the as plated coatings heat treatments proved to be effective in changing the properties of the composite Ni-P/SiC coatings, as shown in a previous paper [14].

As depicted in the optical micrographs in figure 2 the integrity and the good adhesion between the coating and the substrate material were preserved or even improved during the heat treatments.

A first heat treatment we have applied consisted in heating for 3 h in air at 190°C and it aimed at producing the desorption of the hydrogen incorporated in the coating during the electroplating process. The temperature of the dehydrogenation treatment was selected at 190°C by considering the results in paper [15] that point to a maximum volume of desorbed H 2 in the temperature range 160-185°C for Ni-P/SiC coatings electroplated from various electrolytes containing from 0 up to 20 g/L H 3PO 3. A second heat treatment consisting in heating for 1 h in N 2 at 420°C aimed at producing phase transformations in the Ni-P matrix of the coating by precipitating submicronic particles of Ni P 3 compounds. The temperature of the precipitation hardening treatment was selected at 420°C by considering the results in one of our previous papers [17], since this model starts from the fact that the Kick law \( F=Kd^2 \) is observed only in the absence of the ISE effect. In the presence of the ISE effect the linear dependence of \( F \) on \( d^2 \) is distorted. To make the Kick law valid even in presence of the ISE effect the model supposes that the effective force \( F_2 \) responsible for the plastic deformation during indentation is less than the applied force \( F \) by an amount \( W \) (representing the elastic deformation prior to plastic flow).

The results of the Vickers microhardness tests in figure 3 show that the precipitation hardening heat treatment (upper curve in fig. 3) has a notable effect in increasing the hardness of the composite Ni-P/SiC coating. Indeed the upper hardness curve corresponding to the heat treated condition at 420°C is completely detached from the lower hardness curves (non heat treated condition or heat treated condition for dehydrogenation at 190°C).

Concerning the ISE effect revealed by the \( H_v \) versus \( F \) curves in figure 3, it appears obvious that it is manifested in opposite direction in comparison with the sulfide pure compounds in figure 3. This is to be ascribed to the different chemical nature of the ionic-covalent sulfide compounds as compared to the metallic character of the Ni-P matrix of the composite investigated coatings.

Even more important is the fact that the \( H_v \) versus \( F \) curves in figure 3 do not exhibit a horizontal branch allowing one to obtain directly the true hardness of the coating (especially in heat treated condition). This is true at least up to the largest applied force \( F=300g \) in spite of the fact that \( 300g \) is a relatively high load for microhardness measurements.

In these circumstances in order to eliminate the ISE effect and obtain the true hardness of each coating we have made recourse to a mathematical model proposed many years ago [16] but not very popular as yet. As explained in detail in one of our previous papers [17] this model starts from the fact that the Kick law \( F=Kd^2 \) is observed only in the absence of the ISE effect. In the presence of the ISE effect the linear dependence of \( F \) on \( d^2 \) is distorted. To make the Kick law valid even in presence of the ISE effect the model supposes that the effective force \( F_2 \) responsible for the plastic deformation during indentation is less than the applied force \( F \) by an amount \( W \) (representing the elastic deformation prior to plastic flow). So one may write:

\[ F_2 = F-W \quad (2) \]

or

\[ F=W+F_2 \quad (3) \]

According to this supposition one has to write the Kick law in terms of \( F_2 \) (the effective force involved in indentation) as follows:

\[ F_2 = Kd^2 \quad (4) \]

In terms of \( F \) (the experimental applied force) the linear dependence on \( d^2 \) will contain the free term \( W \)

\[ F=W+Kd^2 \quad (5) \]

Fig.2. Optical micrographs in transverse cross-section (at different magnification) for the Ni-P/SiC coated samples obtained from an electrolyte containing 20 g/L H 3PO 3 and 40 g/L SiC, in non heat treated condition and after applying the heat treatment at 190°C and at 420°C, respectively. Coating thickness indicated in \( \mu \text{m} \) (etching agent: 2% HNO 3 in ethylic alcohol solution)

Fig.3 \( H_v \) versus \( F \) curves for the Ni-P/SiC coatings obtained from an electrolyte containing 20 g/L H 3PO 3 and 40 g/L SiC, in non heat treated condition \( (t=24 \mu \text{m}) \), respectively after applying the heat treatment at 190°C \( (t=27 \mu \text{m}) \) and at 420°C \( (t=27 \mu \text{m}) \)
As shown in the graphs in figure 4, equation (5) was validated by our Vickers indentation hardness tests. Indeed the confidence coefficient \( r^2 \) when processing the experimental \( F \) versus \( d^2 \) data was higher than 0.99.

In order to calculate the true hardness one has to take into account the definition of the Vickers microhardness, namely

\[
HV = 1854.4 \left( \frac{F}{d^2} \right)
\]

(6)

where the coefficient 1854.4 takes into account the geometry of the Vickers indenter as well as the correspondence between the different units, namely \( HV \) (in kg/mm\(^2\)), \( F \) (in grams) and \( d \) (in \( \mu \)m).

Because \( F/d^2 \) in eq.(6) is the slope of the \( F \) versus \( d^2 \) plot in figure 4 we have calculated the true hardness of the investigated Ni-P/SiC coatings simply according to eq.(7)

\[
HV = 1854.4 K
\]

(7)

in which \( K \) was the slope of each straight line in the graphs in figure 4.

As specified earlier this heating is actually a precipitation heat treatment by aging.

We have ascribed the peculiarity clearly manifested on the upper curve in figure 5a consisting in a decrease in hardness at too high \( P \) content by taking into account the
aging mechanism of the precipitation hardening heat treatment. In our opinion this may be due to an overaging phenomenon at 20 at.% P. Actually one may suppose that heating at 420°C is the right temperature for precipitating fine submicronic particles of NiP compounds in the 16 at.% P coating, but it may be not the appropriate aging temperature for the 20 at.% coating inducing in the latter coating a coalescence of the NiP particles or even a change in their chemistry.

For sake of comparison we have also given in figure 5b the set of H versus P content in the Ni-P/SiC coatings heat treated at 420°C measured at various loads applied on the indenter (values affected by the ISE effect).

The comparison between figure 5a and figure 5b results in two main conclusions. First, the mathematical processing of the microhardness data gives the possibility to characterize a thin coating by a single hardness value (the true one). Indeed in figure 5a a single „H versus at.%P” has replaced the bundle of curves in figure 5b. Second, if one adopts the common procedure consisting in characterizing a thin coating by the microhardness value measured at a low load F, even if one specifies the load, as for example H(15) (the hardness value measured at 15g in fig.5b), the measured value is misleading being in a large error in comparison with the true value (fig.5a) on account of the ISE effect.

Conclusions
The comparative investigation of indentation microhardness measured on bulk ionic-covalent mineral sulfide compounds and on electroplated Ni-P/SiC composite coatings has revealed the difficulties that may arise in the characterization of thin coatings properties. Penetration hardness tests of thin coatings are known to be subject to contrary constraints: a small load applied on the indenter is required for avoiding any influence from the substrate, but large loads are necessary for eliminating the troublesome hardness dependence on load (ISE effect).

For bulk mineral sulfide compounds both the range of high F values for which the hardness was load independent (true hardness) as well as the range of low F values for which the hardness was load dependent were possible to be recorded. Value F(15) that separates the two regions proved to be sensitive to modifications in the chemistry of the compound.

For thin coatings (a few tens of μm thick) consisting in electroplated Ni-P/SiC composite layers all microhardness Vickers tests performed up to a relatively high value for F proved to be ISE affected and so misleading in respect to the true hardness. A mathematical processing of the ISE affected experimental values, based on a model involving the modification of the Kick law, was demonstrated to allow one to obtain meaningful true hardness values. The mathematical model demonstrated to be valid for coatings on metallic substrates may be valid as well for polymeric substrates.

References

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