HEAT TREATMENT AND P EFFECT ON Ni-P/SiC COATINGS HARDNESS

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Ni-P/SiC coatings electrolytically deposed on mild steel having P contents up to 20at.% in the Ni matrix and a constant content of SiC reinforcing particles have been investigated in three heat treatment conditions. Having in view the small thickness of the coatings (a few tens of microns) a series of small loads F in the range 15 up to 300 g have been applied on the indenter during the Vickers microhardness testing. On account of the hardness dependence on load (ISE effect) not a unique hardness value but sets of H_V –F curves have been considered to have a meaning for revealing the composition, structure and heat treatment influence on the coating hardness. The precipitation hardening heat treatment at 420° C was shown to have a far larger influence in increasing the coating hardness than the increase of the P content in the Ni supersaturated solid solution.

INTRODUCTION

Electroplating or electrolytic deposition of a metal on a support material in conditions able to produce a definite structure and a smooth surface finish of the deposit is mainly used in decorative and anticorrosion purposes. Excepting hard chromium electroplating, electrolytic coatings are not hard enough to be recommended as wear resistant materials. Modern ideas have been applied in the last decades in electroplating processes for endowing the coating with antifriction properties without making recourse to the hard chromium plating that involves hexavalent chromium undesirable for ecological reasons. To this purpose Ni coatings are transformed into hard wear resistant composite materials by reinforcing them with finely dispersed oxide particles (TiO_2, ZrO_2, Al_2O_3) or carbide particles (SiC, WC, TiC).[1-3] Such coatings are interesting because they combine excellent corrosion resistance with high hardness and may be recommended for tribological applications in aggressive chemical environments. As hardness is involved in anti-friction applications[4] the coating may be hardened by rising the amount of hard particles in its matrix but at the expense of the coating toughness.

A different approach, adopted in this paper, for increasing the hardness of Ni/SiC coatings consists in increasing the hardness of the metallic matrix of the coating by introducing phosphorus in Ni during the electroplating process.[5-8] An additional increase in wear resistance for the metallic Ni-P matrix of such composite coatings is to be expected if a precipitation hardening heat treatment is applied and this approach has also been addressed in this paper. Because hardness is a very structure sensitive property the effect of phosphorus and of the heat treatment has been followed by indentation hardness measurements performed on Ni-P/SiC coatings having a constant amount of reinforcing SiC particles and variable contents of P.

EXPERIMENTAL

Investigated coatings

A series of Ni-P/SiC composite coatings electroplated on a mild steel support containing 0.17%C and 1.4% Mn have been investigated. These coatings have been obtained by a procedure described in a previous paper.[8] A complex aqueous electrolyte was used containing 210g/litre $NiSO_46H_2O$; 50g/litre $NiCl_2.6$ H_2O; 50 g/litre H_3PO_4; 50g/litre Na_2SO_4 and a variable amount of H_3 PO_3 and having its temperature maintained at 80° C and pH kept constant at 2. The amount of

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the active component for the co-deposition of phosphorous in the Ni matrix, namely H_3PO_3 was increased in steps in the electrolyte (5; 10; 20 g/litre H_3PO_3). A device was provided to keep in suspension the micronic SiC powder particles intended to be incorporated in the coating. The coatings have been symbolized $P_x S_y$ where x is the amount of H_3PO_3 dissolved in the electrolyte (in g/litre) and y is the amount of SiC particles in suspension in the electrolyte (in g/litre). A symbol $P_x S_y$ –(z)- t comprising the additional digits z (=at.%P in the Ni matrix of the coating) and t (=coating thickness in micrometers) have been used if needed.

Four Ni-P/SiC composite coatings have been selected for the hardness investigation which have been denoted P0S40; P5S40; P10S40; P20S40. The first coating P0S40 may be taken as a reference, its metallic matrix consisting of pure Ni. The values for the coating thickness have been evaluated from the optical micrographs viewed in transverse cross-section. The thickness of each coating appears to be uniform and the adherence of the coating to the support to be very good.

The correlation between the amount of H_3PO_3 in the electrolyte and the P content in the electroplated Ni coating was shown[9] to be a complex one as a result of the electrochemical mechanism of the cathodic reactions during the co-deposition of Ni and P as described by Lashmore:[10]

$$Ni^{2+} + 2e^- \rightarrow Ni \qquad (1)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (2)$$

$$H_3PO_3 + 6H^+ + 6e^- \rightarrow PH_3 + 3H_2O \qquad (3)$$

$$2PH_3 + 3Ni^{2+} \rightarrow 2P + 3Ni + 6H^+ \qquad (4)$$

The amount of H_3PO_3 in the electrolyte has an influence on the P content in the Ni matrix of the coating as a result of reactions (3) and (4) as well as on the amount of H_2 adsorbed in the coating as a result of reaction (2). As the amount of SiC in suspension in the electrolyte also interferes in this correlation the complete composition specification for the investigated Ni-P/SiC coatings was as follows: P0S40-(0); P5S40- (8.4); P10S40- (16.1); P20S40-(20).

Hardness characterization of the investigated coatings

Because of the small thickness of the coatings that was in the range of a few tens of micrometers, the hardness was characterized by a microhardness indentation method. A "Shimadzu HMV-2" microhardness apparatus equipped with a Vickers diamond indenter of square pyramidal shape having a 136° apex angle was used. Various loads have been applied on the indenter, namely 15g; 25g; 50g; 100g; 200g;300g. All indentations were made by applying the load F perpendicular to the smooth free surface of the coating. Five indentations have been made on the same sample to obtain a statistical average value for the hardness. The microhardness was calculated by means of relationship $H_V = 1854.4\ F/d^2$, where H_V is expressed in kg/mm², F in grams and the diagonal d of the indentation in micrometers.

RESULTS

Two types of heat treatment have been applied to the four investigated coatings, the first one consisting in 3 hours heating in air at 190° C and the second one consisting in 1 hour heating in N_2 at 420° C.

The first heat treatment was intended to produce the desorption of the hydrogen incorporated in the coating during the electroplating process as a result of the proton reduction at the cathode as indicated by eq.(2). Such dehydrogenation heat treatments are frequently applied if there is a risk of hydrogen embrittlement in electroplated coatings. The temperature of the dehydrogenation heat treatment we have applied to the investigated Ni-P/SiC coatings was selected by considering the results that point to a maximum volume of desorbed hydrogen located between 160^oC and 185^oC for Ni-P/SiC composite coatings electroplated from various electrolytes[9] containing from 0 up to 20g/litre H_3PO_3.

The second heat treatment was intended to produce precipitation hardening phase transformations and its temperature was selected according to the position of the exothermic peaks on the differential scanning calorimetry spectra (DSC) recorded at 10° C/min in N_2 atmosphere for Ni-P coatings reported in[9]. As the first exothermic peak starting around 320° C indicates the incipient precipitation of the metastable Ni_xP_y compounds and the second peak indicates the coalescence of the equilibrium Ni_3P phosphide (a transformation that goes to an end at 420° C) we have decided to carry out the precipitation hardening heat treatment at 420^oC.

The X-ray diffraction patterns we have recorded in Fig.1 on the composite coating having the highest phosphorus content P20S40-(20) agree with the above mentioned transformations. Fig.1a recorded in non-heat treated condition shows several low intensity peaks that point to the presence of the SiC phase and a high intensity broad peak that reveals the presence of a fine grain highly distorted phase having the face centered cubic lattice of Ni. No peaks revealing the presence of $Ni_x P_y$ compounds exist in the diffractogram. Because the Ni-P phase diagram indicates no solid state solubility of P in Ni one has to conclude that the Ni-P matrix in the coating is far from equilibrium consisting in a highly supersaturated solid solution of P dissolved in Ni. Such phenomena of solid state solubility extension are well documented in other deposition processes like rapid solidification of the melts.[9,10] By comparing Fig.1a with Fig.1b it is obvious that no phase transformations have been induced by the heat treatment at 190° C, the two X-ray diffraction patterns being alike. In contrast to this the heat treatment at 420° C has produced notable changes in the X-ray diffraction pattern of the coating pointing to transformations typical for a precipitation hardening heat treatment.
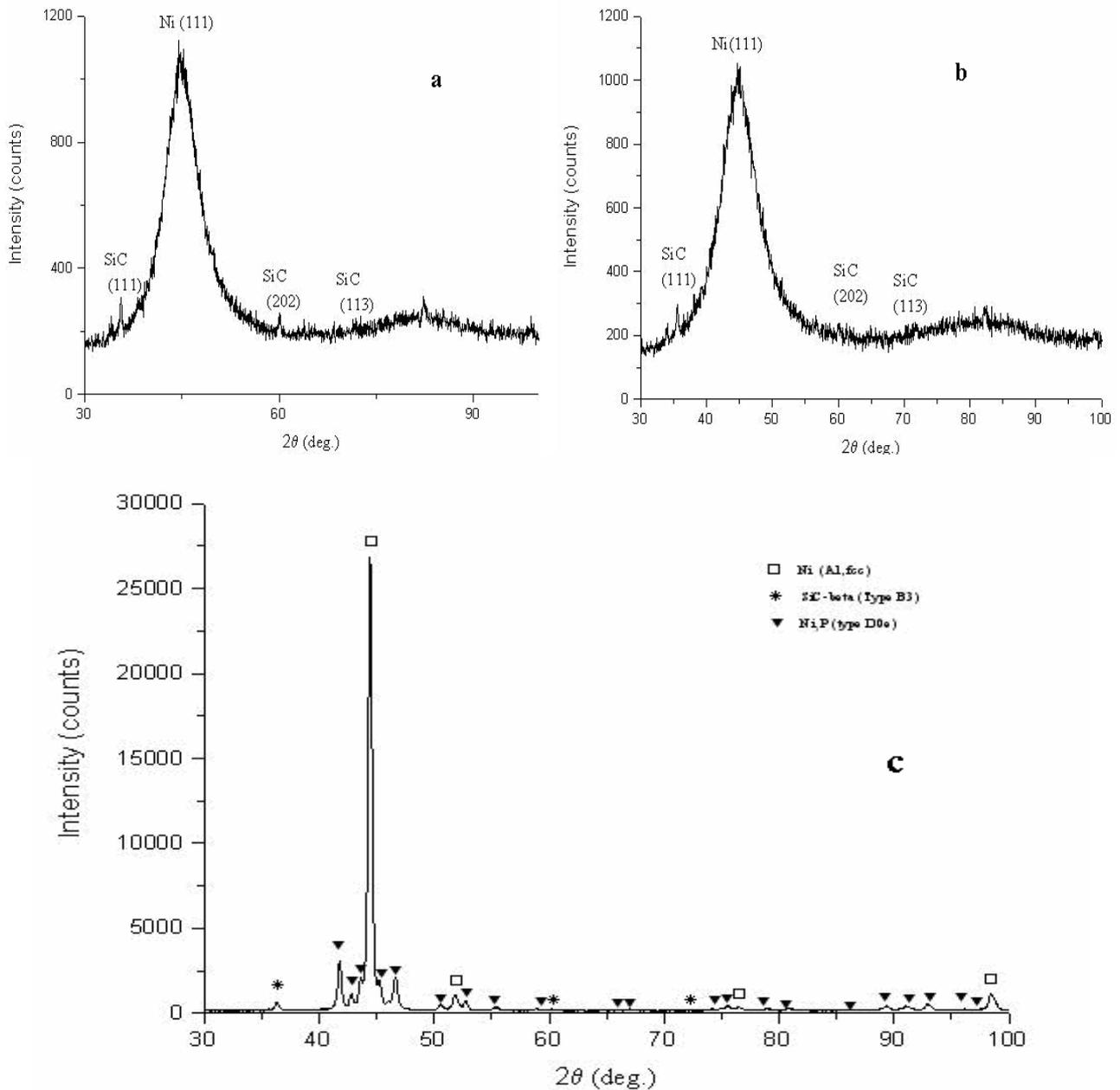
Fig. 1 – X-ray diffraction patterns of the P20S40-(20) composite coating in various conditions:
a) as-plated (not heat treated); (b) heat treated at 190°C; (c) heat treated at 420°C.

Indeed in Fig.1c new low intensity peaks have appeared that point to the presence of precipitated nickel phosphide particles, while the high intensity peak of the Ni based face centered cubic phase has become extremely narrow as a result of the drastic decrease of the lattice distorsions associated with the elimination of P from the supersaturated Ni based solid solution.

The hardness values we have obtained for the four investigated Ni-P/SiC composite coatings in various heat treated conditions are shown in Fig. 2–Fig. 6.

For the low loads we have applied on the indenter (having in view the very small thickness of the coatings of a few tens of micrometers) the measured microhardness values were dependent on the applied load F and this fact was more pronounced for the hardest coatings. As seen in Fig. 2– Fig.6 for all investigated composite coating this ISE effect (indentation size effect) consisted in an increase of the measured hardness when the load F applied on the indenter was diminished.

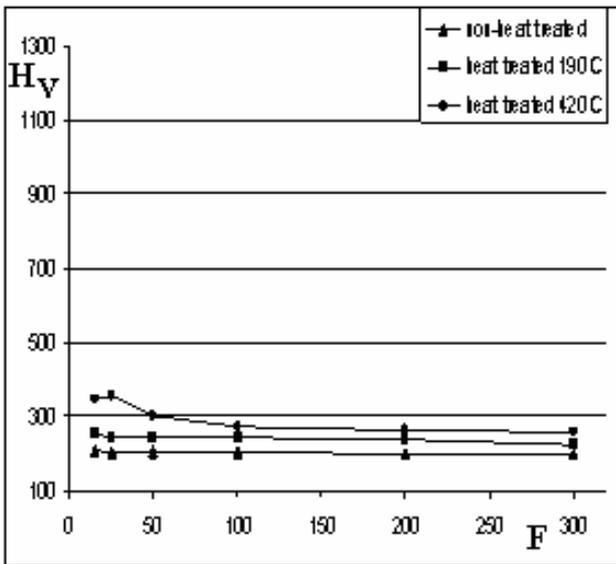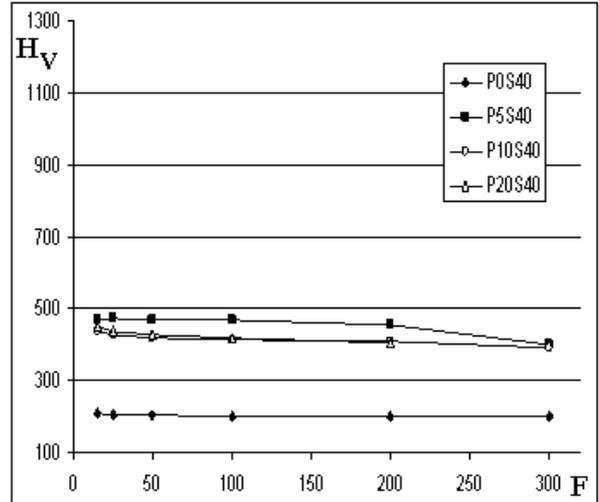Fig. 2 – Vickers microhardness H_V versus load F for the non heat treated composite coatings.
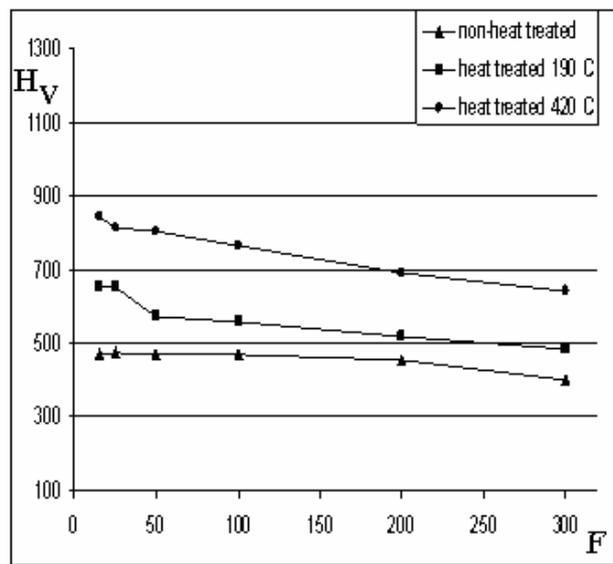

Fig. 3 – H_V dependence on F for the P0S40 coating.

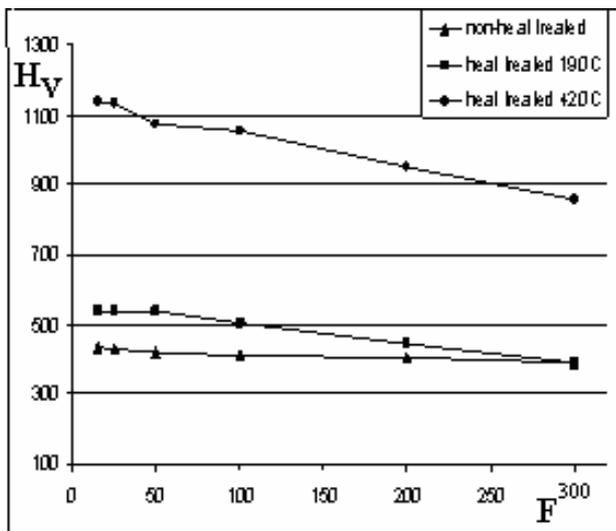

Fig. 4 – H_V dependence on F for the P5S40 coating.

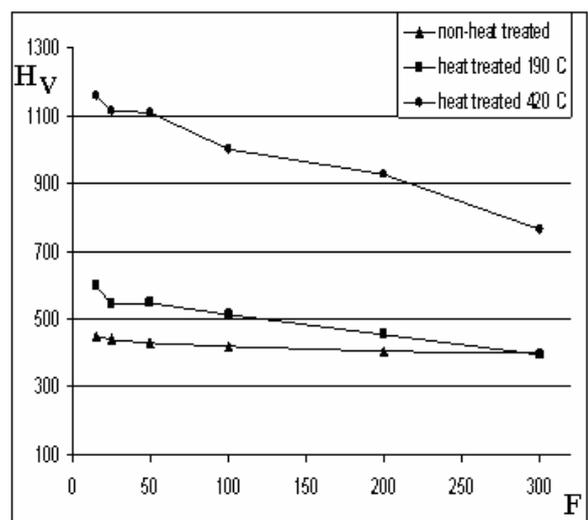
Fig. 5 – H_V dependence on F for the P10S40 coating.

Fig. 6 – H_V dependence on F for the P20S40 coating.

DISCUSSION

On account of the ISE effect no unique hardness value could be ascribed to each coating. In a next to come paper to be published in this journal we'll try to apply theoretical models to the measured microhardness values for the Ni-P/SiC coatings in view of eliminating the troublesome ISE effect and to obtain a unique true hardness value for each type of coating. For the moment we'll discuss the influence of the P content as well as of the heat treatment on the hardness of each coating by the series of $H_V = f$ (F) curves in Fig.2 to Fig.6.

Fig. 2 points to the increase in hardness promoted by increasing the P content in the coatings in non heat treated condition. It appears obvious that dissolving P in Ni increases the hardness of the coating and this is to be expected because a supersaturated highly distorted solid solution is formed (see the X-ray diffraction pattern in Fig.1a). As seen in Fig.2 this increase in hardness is the highest for the coating P5S40 -8.4 that is not the richest in P but it has a very fine nanometric grain size.[13] Hence one may infer that both the structural distorsions (produced by the fine grain size) and the chemical distorsions (produced by the supersaturation in P) are the source of hardness in the non heat treated coatings. By comparing Fig.2 with the subsequent figures (Fig.3– Fig. 6) one sees that the precipitation hardening heat treatment at 420° C is far more efficient in increasing the coating hardness as compared with the mere introduction of P in the Ni supersaturated solid solution. The hardness obtained after this heat treatment ranges in the expected sequence increasing as the P content increases. One may ascribe these facts to the structural transformations (attenuation of the grain size difference) that accompany the phase transformations (precipitation of the finely dispersed nickel phosphide particles put in evidence in the X-ray diffraction pattern in Fig.1c). Concerning the source of the rather modest modification in hardness that accompanies the dehydrogenation heat treatment at 190° C it may be put in connection with some structural transformations, such as a chemical and structural relaxation and a slight grain growth of the matrix as pointed in.[14]

CONCLUSIONS

The hardness of the Ni-P/SiC composite coatings produced by electrolytic co-deposition of P and Ni with simultaneous incorporation of a constant amount of SiC reinforcing particles was shown to depend not only on the P content in the metallic matrix of the coating but also on its structure and phase constitution that may be modified by a post-deposition heat treatment. A precipitation hardening heat treatment at 420^oC was shown to be far more efficient in increasing the coating hardness as compared with the mere introduction of P in the Ni supersaturated solid solution.

On account of the load size dependence of hardness (ISE effect) a meaningful evaluation of the composition, structure and heat treatment influence on the coating hardness was obtained if the whole H_V -F curve was considered instead of a single hardness value. In our opinion this procedure is to be preferred to the common practice consisting in specifying the microhardness value measured at an arbitrarily selected load, the latter practice being unsatisfactory because as demonstrated in this paper the extent of the ISE effect (expressed by the slope of the H_V –F curve) is not the same for different materials.

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