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MECHANICAL PROPERTIES CORRELATED TO STRUCTURE FOR Ni-P/SiC COMPOSITE SURFACE COATINGS

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Abstract: *A complex research has been undertaken to obtain and investigate Ni-P/SiC surface coatings on mild steel and on pure Cu, electroplated from an electrolyte having various amounts of micron size SiC particles in suspension (0-80g/litre SiC) and various amounts of the electrochemically active component* H_3PO_3 *in the electrolyte (0-20g/litre* H_3PO_3*). Ni based solid solutions supersaturated in P have been obtained in the metallic matrix of the composite coating whose P content was increased in steps (0; 8.4; 16.1; 20at.%P). Two types of heat treatments have been applied to the Ni-P/SiC electroplated coatings, either a dehydrogenating annealing at* 190^oC *or a precipitation aging treatment at* 420^oC *whose structural effects were investigated by microscopy and X-ray diffraction examination. Various properties have been investigated in non heat treated and in heat treated condition: uniformity of coating thickness and adherence, friction coefficient, Vickers penetration hardness. A special attention was paid to the hardness testing of the coatings at low loads F applied on the indenter in order to avoid any influence from the substrate, and to take into consideration the ISE effect (indentation size effect). Reliable information on the effect of process parameters on the coating hardness have been obtained by considering either* H_V *versus F curves or by deriving a true hardness by means of a mathematical model applied to the experimental data. The precipitation hardening heat treatment was shown to be more powerful in increasing the coating hardness than the mere dissolution of P in the supersaturated Ni based solid solution. An interesting composition having 16.1at.%P and a medium amount of incorporated SiC particles was shown to exhibit the highest hardness in heat treated condition at* 420^oC*.*

Keywords: electroplated composite coatings, precipitation hardening, microsopy, X-ray diffraction, hardness.

INTRODUCTION

Modern surface coatings are very often required to combine tribological properties (either wear resistance or antifriction behavior) with chemical resistance to aggressive environments. A large variety of methods to obtain such coatings are nowadays available.

One of the simplest ways to obtain surface coatings is electrolytic deposition from aqueous solution of the protective metal, nickel and chromium being the most prized metals for such a purpose. In opposition to electrolytic Cr coatings that can be obtained in conditions that make them hard enough to offer wear resistance, Ni electrolytic coatings are not hard .(maximum 150 Vickers hardness). However in the last decades structural hardening mechanisms have been put at work to make Ni coatings wear resistant. On one hand alloying Ni with P or sometimes with B [1] from electrolytes transform the coating in a supersaturated crystalline or amorphous solid solution sensitive to precipitation hardening after a suitable heat treatment. On the other hand co-deposition of hard compounds particles (TiO_2 ,ZrO_2 , Al_2O_3 , SiC, WC, TiC) transform the electroplated Ni coating into a composite material hardened by the finely dispersed compound particles. By combining the two hardening mechanisms, namely precipitation of nickel phosphides by heat treatment and dispersing SiC particles in the Ni based layer interesting wear resistant anticorrosive coatings for tribological applications become available.

The mechanical properties of composite Ni-P based coatings are not limited to increased wear resistance. Indeed instead of incorporating hard compound particles as the above mentioned oxides and carbides, one may incorporate in the Ni-P matrix soft lubricating particles such as sulfides (MoS_2 ,

WS_2) or organic polymer particles. Interesting self lubricating coatings may be obtained in this way. Such a composite intended to minimize the friction coefficient consists in electroless Ni-P films in which *polytetrafluoroethylene (teflon) particles* of 0.4 microns nominal size have been incorporated in a content 15-25 vol.%. Such lubricant films are hydrofobic and are functional at temperatures up to 164°C. Fig.1 reproduced from reference [2] shows how the friction coefficient of Ni-P coatings is diminished by incorporating nanometric size WS_2 particles. The lowering of the friction coefficient of the Ni-P/ WS_2 composite coating by five times (from 0.25 to 0.05) depicted in Fig.1 shows how powerful this new technology of incorporating foreign particle in electroplated or in electroless deposited coating is.

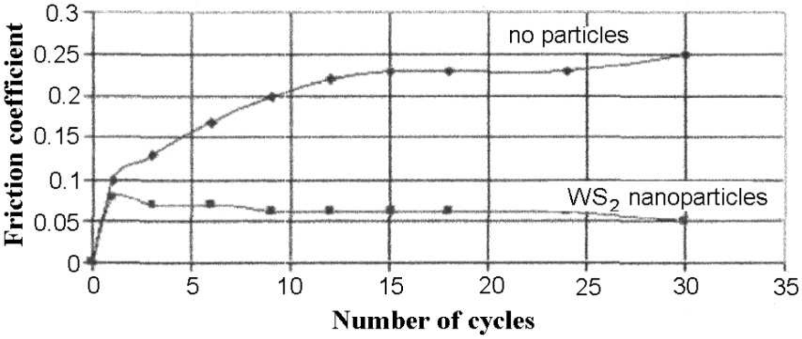


Fig. 1. Typical dependence of the friction coefficient vs. time for a Ni-P electroless coating on stainless steel, with and without soft lubricating particles incorporated (reproduced from reference [1]

Among these two groups of Ni-P based composite coatings (wear resistant or antifriction) our interest is focused in this paper on the wear resistant ones, more specifically on the electroplated Ni-P coatings reinforced with micronic size SiC particles. We have been interested in items such as how the increase of phosphorus content in the Ni matrix and the increase of SiC amount of incorporated SiC particles affect the mechanical properties. Additionally we have questioned how these properties are affected by phase and structural transformations induced by heat treatments.

Before presenting our results obtained on electroplated Ni-P/SiC composite coatings it is worth mentioning that the practical interest of Ni-P based surface coating as tribological materials is greatly increased by the possibility to apply an alternative procedure termed electroless plating which does not require electrical current. The deposition occurs in an aqueous solution containing nickel ions and sodium hypophosphite (as a reducing agent and source of phosphorus), chelates, complexing agents and stabilizers. Chemical reactions on the surface of the part being plated cause deposition of a nickel alloy, actually a dense alloy of nickel and phosphorus. The amount of phosphorus (3 up to 12%) is in the same range as for electrolytic coatings and results in the same type of structure, namely a Ni based solid solution supersaturated in P prone to undergo a precipitation hardening heat treatment. The deposition process is auto-catalytic and so very thick coatings can be applied, provided that the ingredients in the plating bath are replenished. Because all surfaces wetted by the electroless nickel solution are plated, the deposit thickness is uniform across the entire part giving the possibility to coat internal surfaces of pipes, valves a.s.o.. Excellent adhesion can be achieved on a wide range of substrates, including steel, Al, Cu and copper alloys. Such coatings are utilized on a wide variety of metallic components and unusual substrates to enhance wear resistance, corrosion resistance, durability, hardness, lubricity, solderability and weldability, uniformity of deposit regardless of geometries, nonmagnetic properties and for providing extended tool and component life.

EXPERIMENTAL INVESTIGATED MATERIALS; HEAT TREATMENTS APPLIED

Our research program,- from which a synthesis is presented here,- was an ample one including different support materials (either pure copper, or a mild steel), various amounts of the SiC reinforcing phase, various amounts of phosphorus co-deposed with Ni during the electroplating process and various heat treatments applied to the coatings.

To obtain the Ni-P/SiC composite coatings a complex aqueous electrolyte was used containing 210g/litre $NiSO_4.6H_2O$, 50g/litre $NiCl_2.6H_2O$, 50g/litre H_3PO_4 , 50g/litre Na_2SO_4 and a variable amount of H_3PO_3 .The active component in the electrolytic bath for the co-deposition of phosphorus was H_3PO_3 and its amount was either kept constant in a series of experimental runs or it was increased in steps (0; 5; 10; 20g/litre H_3PO_3) in a different series of experimental runs. According to [3] the temperature of the electrolytic bath was kept constant at 80^{o}C and the pH kept constant at 2.

The SiC particles intended to be incorporated in the Ni-P coatings were of about 1 micrometer in size and 10.4m^{2} /g specific surface as delivered by the Neyco Company; their purity was 99.9% (main impurities 0.03%Fe; 0.02%Al; 0.02%V). To incorporate the SiC particles in the coating a device was provided to maintain them in suspension in the electrolyte during the deposition process.

Two groups of coatings have been obtained and investigated:

(a) *constant SiC amount (namely 40g/litre), variable* H_3PO_3 *content in the electrolyte, mild steel support (plain carbon steel 0.17%C)* and

(b) *variable SiC amount, constant* H_3PO_3 *content in the electrolyte (namely 20g/litre), pure copper support (electrolytic copper).*

Each investigated coating has been identified by a symbol $P_x S_y$ where x is the content of H_3PO_3 in the electrolyte (g/litre) and y is the amount of SiC powder in suspension in the electrolyte (g/litre). The content x of H_3PO_3 in the electrolyte (g/litre) was shown to be correlated with a more meaningful value namely the content of phosphorus incorporated in solution in the crystal lattice of the Ni matrix of the coating as depicted in Fig. 2.

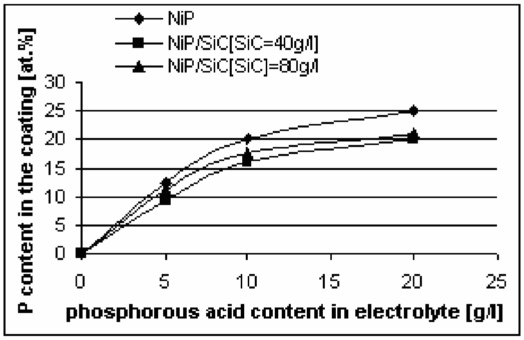


Fig. 2. Dependence between the P content in the coating and the amount of H_3PO_3 in the electrolyte

Two types of heat treatments have been applied to the Ni-P/SiC electroplated coatings: (i) a degasing annealing treatment at 190^{o}C intended mainly to eliminate the hydrogen incorporated in the Ni-P coating during its cathodic deposition and (ii) a precipitation aging treatment at 420 ^{o}C intended both to improve the adherence of the coating to the substrate by atomic diffusion and to promote the precipitation of fine nickel phosphides from the supersaturated Ni-P solid solution

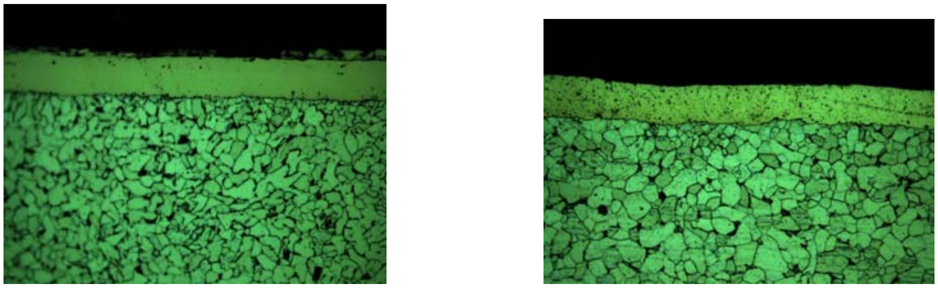
The type of the applied heat treatment was indicated (if needed) in the symbol of the specimen by specifying the temperature of the heat treatment as follows: $P_x S_y(0)$; $P_x S_y(190)$ and $P_x S_y(420)$.

RESULTS AND DISCUSSION

A wide variety of ***coating thickness*** have been obtained (depending on the electroplating conditions) covering the range from 5 up to 60 micrometers.

A first point of interest was the ***uniformity of the coating thicknes****s*. By recording optical micrographs in the transverse cross section of all investigated coatings we have put in evidence a very good uniformity of the coating thickness as illustrated in Fig.3. Inspection of the micrographs in Fig.3 also puts in evidence a good adherence of the coating to the substrate which was rendered even better by the application of the heat treatment

A second question of interest was how the ***topography of the surface of the coatings*** was affected by the presence of the embedded SiC particles. Optical micrographs, scanning electron micrographs and atomic force recorded micrographs (Fig.4) have all confirmed that the SiC particles have a levelling effect on the topography of the coating surface which may be ascribed mainly to the inhibitory action of these particles on the growth of the Ni-P metallic matrix grains during the electrolytic deposition (Fig.5)



P0S40 P5S40

Fig.3. Optical micrographs in transverse cross-section for two Ni-P/SiC coatings electroplated on mild steelc heat treated at 420^{o}C ; etching agent nital 2%; magnification x200

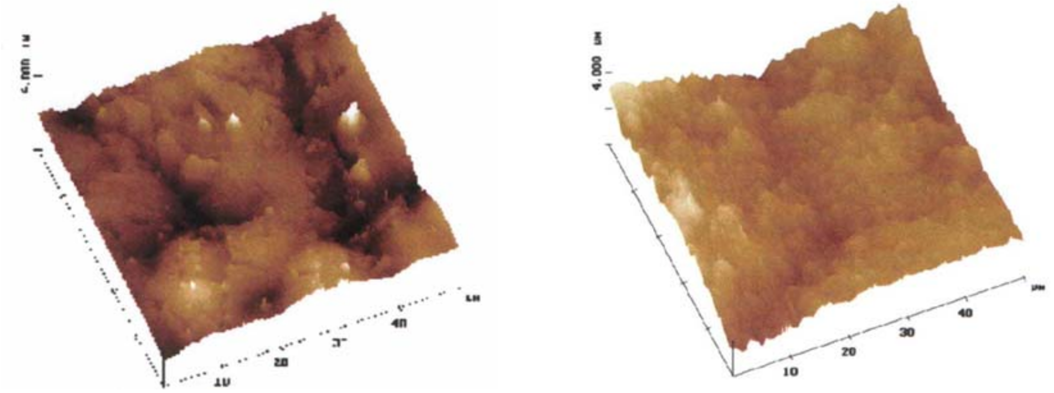
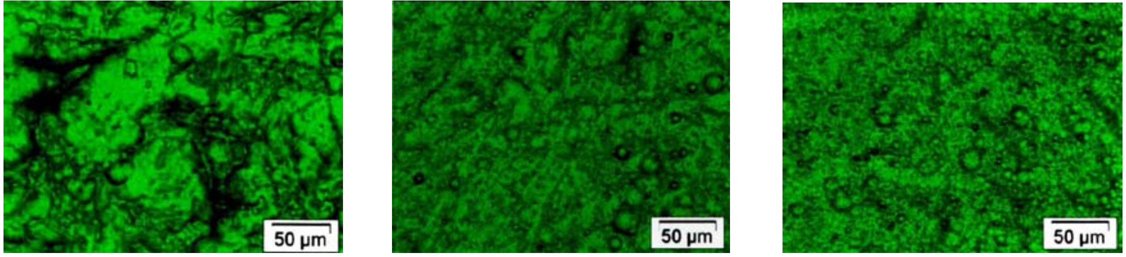


Fig.4. Atomic force microscopy images showing the surface topography of two coatings with the same P content in the Ni matrix and different amount of incorporated SiC particles in non heat treated condition: P20S0 (left) and P20S80 (right)



P20S0 P20S40 P20S80

Fig.5. Optical micrographs on the coatings surface showing the influence of increasing the amount of incorporated SiC particles on the grain size of the Ni-P matrix of the Ni-P/SiC composite coatings (non-heat treated condition)

Nanoscratching tests have been carried out in order to evaluate *the* ***friction coefficient*** of the coatings and their ***adherence to the substrate***. For each coating a series of 5 nanoscratch tests have been performed as depicted in Fig.6a; the aspect of a single nanoscratch is shown in Fig.6b and 6c at higher magnification. The variation of the friction coefficient along the scratch distance for all the five tests is represented on a single diagram for each investigated coating as depicted in Fig.7.

A closer inspection of the diagrams in Fig.7 shows for each coating a constant value of the friction coefficient along the scratch distance, thus pointing to a good adherence of the coating to the substrate material. Concerning the value of the friction coefficient the diagrams in Fig.7 clearly show that introducing SiC particles in the Ni-P metallic matrix of the coating has increased the average value of the friction coefficient from about 0.325 (sample P20S0) to 0.35 (sample P20S80).

a b c

Fig.6 (a) aspect of the five nanoscratches impressed on one of the investigated Ni-P/SiC coatings (P20S0 sample); (b) and (c): images of one scratch recorded at higher magnification

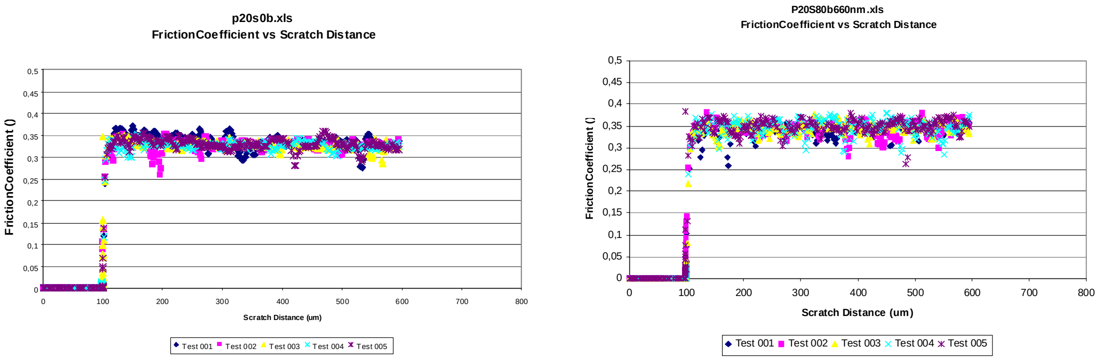
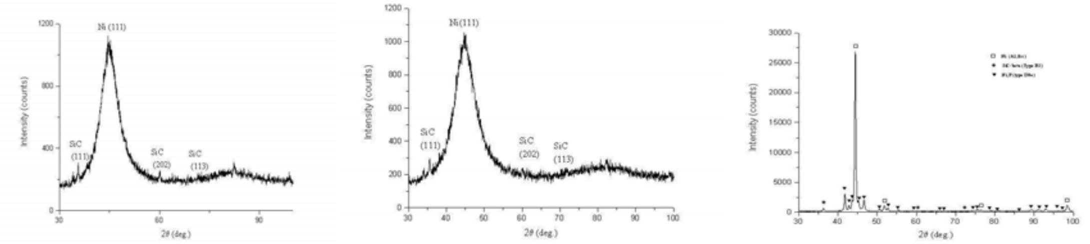


Fig.7 Friction coefficient versus scratch distance for two Ni-P/SiC coatings having the same content of phosphorus and different amount of incorporated SiC particles (non-heat treated condition): P20S0 (left) and P20S80 (right)

The ***fine structure of the coatings*** put in evidence by X-ray diffraction was another major point of interest in our research. The X-ray diffraction patterns we have recorded in Fig.8 on the composite coating having the highest phosphorus content P20S40 point to the nature of the phase transformations



a b c

Fig.8. X-ray diffraction patterns recorded for the coating P20S40 in different states: (a). non-heat treated; (b) heat treated at 190^{o}C; (c) heat treated at 420^{o}C

Fig.8a 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 [4] 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 crystal growth processes like rapid solidification of the melts [5]. By comparing Fig.8a with Fig.8b it is obvious that no phase transformations have been induced by the heat treatment at 190^o C, the two X-ray diffraction patterns being alike. In contrast to this the heat treatment at 420^o C has produced notable changes in the X-ray diffraction pattern of the coating (Fig.8c) pointing to transformations typical for a precipitation hardening heat treatment. Indeed new small intensity peaks have appeared pointing to the presence of Ni_xP_y precipitated Ni phosphides. At the same time the high intensity peak specific to the Ni based solid solution has become very slender, indicating according to the Sherrer relationship that all kind of lattice distorsions have been eliminated during the precipitation process when the P atoms leave their positions in the Ni lattice and give rise to precipitated Ni phosphide particles.

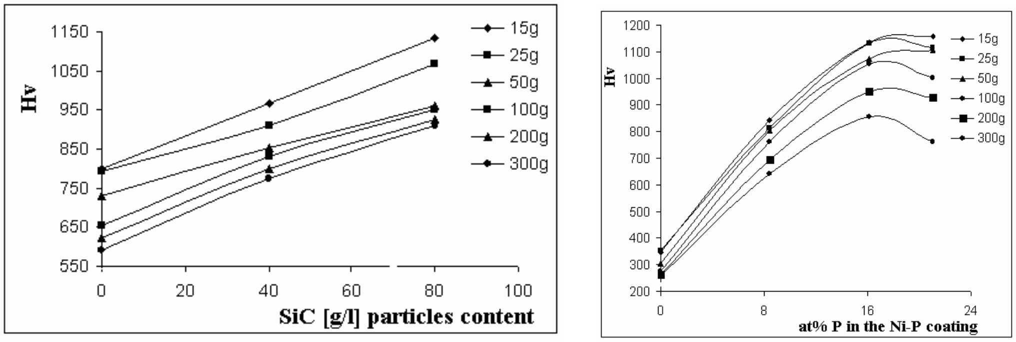
Because the phase transformations during the precipitation hardening heat treatment (indicated by the X-ray diffraction patterns in Fig,8) were governed by temperature dependent diffusion phenomena, the temperature of the heat treatment was critical for the resulting mechanical properties..This temperature was selected according to the position of the exothermic peaks on the differential scanning calorimetry spectra (DSC) recorded in reference [6] for Ni-P coatings.. 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 for all investigated coatings at 420° C.

Hardness, one of the most important mechanical property involved in the wear resistance of the surface coatings was thoroughly investigated in our research. All coatings have been characterized by their ***Vickers hardness*** measured by means of a Shimadzu HMV-2 microhardness tester equipped with a diamond pyramidal Vickers indenter (apex angle 136°) . Having in view the small thickness of the investigated coatings, in order to avoid any influence of the substrate on the measured hardness we have applied very low loads F on the indenter (15; 25; 50; 100; 200; 300 grams) that resulted in micronic size both for the depth of penetration and for the diagonal d of the the square indentation. According to the geometry of the Vickers indenter, the hardness H_V (in kg/mm^2) was calculated by means of the relationship $H_V = 1854.4\ F/d^2$, where d is in micrometers and F in grams.

At such low loads an ISE effect (indentation size effect) was manifest for each investigated coating, consisting in obtaining not a unique value for the hardness but a series of different values (each one specific for each applied load). In such conditions we have evaluated the influence exerted on hardness by the working parameters (amount of SiC particles incorporated in the coating, content of phosphorus in the metallic matrix of the coating, heat treatment applied) not by a single curve but by a family of curves obtained at various loads F, as depicted in the figures that follow.

For example inspection of the family of curves in Fig.9a shows a monotonous increase in hardness as the amount of SiC particles embedded in the coating increases.

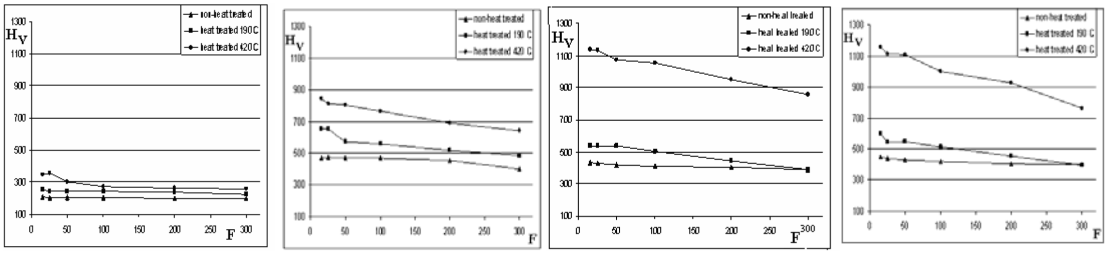
In contrast to this the family of curves in Fig.9b points to a more complex increase in hardness as the content of P in the Ni matrix of the coating increases. This more complicated dependence can be accounted for by different type of structures in the metallic Ni-P matrix of the coating promoted both by an increased P content and by application of the heat treatment.



a b

Fig.9. Family of hardness curves at various loads: a) depicting the influence of the variable amount of SiC particle incorporated in a Ni-P matrix (constant phosphorus content P20) and b) depicting the influence of the variable P content in the Ni-P matrix (constant amount of SiC particles S40) for Ni-P/SiC coatings heat treated at 420°C

As far as the influence of the heat treatments is concerned, our research has shown that it is strongly dependent on the initial content of P in the supersaturated Ni based solid solution obtained in the electroplating process, as clearly depicted in the series of figures 10. To make the diagrams comparable among them the scale of the ordinate was kept strictly the same.



P0S40 P5S40 P10S40 P2040

Fig.10. H_V versus F curves for four coatings having a constant amount of SiC particles and an increasing P content. For each coating the diagram has the H_V vs. F curves located in the following sequence: non heat treated (lower curve), heat treated at 190^{o}C (middle curve), heat treated at 420^{o}C (upper curve)

The first diagram in Fig.10 (sample P0S40) has the three hardness curves close together, that means no noticeable response to the heat treatment. This is to be expected because the metallic matrix contains no phosphorus consisting of pure Ni.

Inspection of the remaining diagrams in Fig.10 shows that the presence of P in the Ni matrix of the coating makes the precipitation hardening heat treatment at 420^{o}C more and more efficient in increasing the hardness as the P content increases. Indeed the upper hardness curves (420^{o}C treatment),- especially for high P content in the coating,- are far higher and are completel detached from the middle and lower curves that remain close together.

These results based on H_V versus F curves in spite of being quite relevant have not a complete meaning for reccomending a material for tribological applications. This is why we have gone further in our research and looked for a mathematical model enabling us to derive a unique hardness value characteristic to each coating instead of a multitude of values dependent on the applied load F. Details on the mathematical model we have applied to derive the true hardness for each coating from the ISE affected measured values have been given in a previous paper [7].

In what follows in Fig.11 we compare the true hardness values versus the P content in non heat treated condition (the lower curve in Fig.11) and in heat treated condition at 420^{o}C (the higher curve in Fig.11).

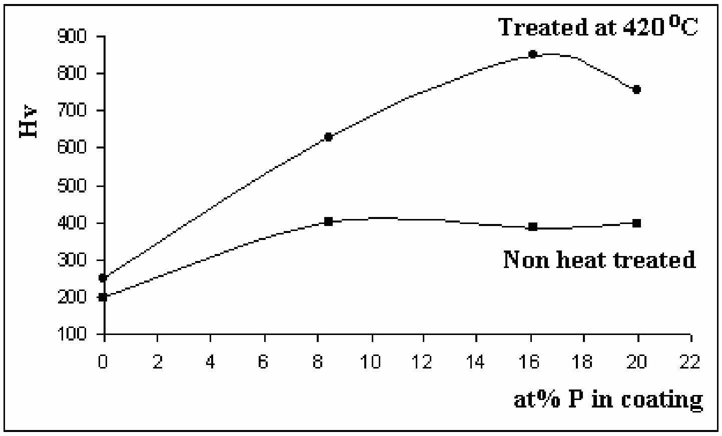


Fig.11. Effect on the true hardness of Ni-P/SiC composite coatings (electroplated from an electrolyte containing 40g/litre SiC particles) exerted by the combined effect of the precipitation hardening heat treatment and by the increase in P amount incorporated in the Ni based metallic matrix

The hardness values in Fig.11 may be considered as a corrollary of our researches on the hardness of the composite Ni-P/SiC coatings. Indeed they represent true hardness values (a unique value for each composite material), they have been obtained for composite coatings with a medium amount of embedded SiC particles (the value 40g/litre SiC particles in the electrolyte being located in the middle of the investigated interval 0-80) and they point to the effect of P in various amounts and in different structural distribution in the Ni based matrix.

It is obvious from Fig.11 that introducing phosphorus in the crystal lattice of the Ni matrix of the coating in non-heat treated condition has a hardening effect that may be accounted for by the large difference in atomic radii (r_{Ni} =0.124 nm and r_P =0.212 nm, respectively) and by the high degree of supersaturation. This degree of supersaturation is large for the investigated compositions (0-20at.%P,) because in equilibium condtion P is completely insoluble in Ni [4]. However a far larger hardening effect is brought about by the precipitation hardening heat treatment at 420°C which at the optimum P content succeeds to increase the hardness of the coating by more than twice as compared to the hardness in non-heat treated condition (from 385 up to 850 kg/mm^2 for 16.1at.%P).

Another striking trait of the true hardness dependence on P content in Fig.11 consists in its slight dependence in non heat treated condition. Indeed in the composition range 8.4- 20at.%P the true hardness of the Ni based solid solution supersaturated in P seems to be not much influenced by the degree of supersaturation.

In contrast to this after the precipitation hardening heat treatment at 420°C the true hardness is very sensitive to the P content, the upper curve in Fig.11 showing not a monotonous dependence. We believe that the upward branch of the hardness curve in heat treated condition (upper curve in Fig.11) may be ascribed to an increasing amount of precipitated nickel phosphides from the supersaturated solid solution, while the downward branch may be the result of an overaging phenomenon during which the precipitated nickel phosphides start to grow in size and diminish their hardening effect. So one may say that the applied heat treatment temperature of 420°C is the optimum aging temperature for the 16.1at.%P supersaturated Ni based solid solution but not for the 20at.%P supersaturated Ni based solid solution, for which it represents an overaging temperature.

CONCLUSIONS

To conclude one may say that our research has arrived at a good end in indicating an interesting wear resistant surface coating able to work in an aggressive chemical environment, namely the Ni-P/SiC coating electroplated from an electrolyte containing 40g/litre SiC particles and having 16.1at.%P in its Ni based metallic matrix. After an optimized precipitation hardening heat treatment at 420°C this coating manifest the highest true hardness.

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