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TRUE HARDNESS OF Ni-P/SiC COATINGS DERIVED BY A MATHEMATICAL MODEL

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The experimental Vickers microhardness values for electroplated Ni-P/SiC composite coatings in three conditions of heat treatment obtained by applying a series of small loads on the indenter have been processed according to a mathematical model in order to eliminate the troublesome ISE effect (load dependence of hardness) and obtain a unique value representing the true hardness for each coating. The true hardness values for Ni -P/SiC coatings compared with the values for Ni/SiC coatings point to a four times hardness increase produced by incorporating P in the crystal lattice of Ni and by precipitating it as a finely dispersed Ni-P compound during a subsequent heat treatment.

INTRODUCTION

In a previous paper[1] the hardness increase produced by the co-deposition of P in electroplated Ni-P/SiC composite coatings and by a subsequent precipitation hardening heat treatment at 420° C was characterized by series of $H_V = f(F)$ curves each of them affected by the ISE effect (microhardness H_V dependence on the load F applied on the indenter). This ISE effect was unavoidable at the low loads F (in the range 15-300 g) imposed by the small thickness of the coatings (in the range 24 to 38 μm).

The usual practice to elude the troublesome ISE effect is to characterize thin coatings by the microhardness measured at a unique small load for all coatings. We consider this practice unsatisfactory because the extent of the ISE effect (expressed by the slope of the H_V–F curve) is not the same for different materials as shown by the results in our previous paper.[1] In what follows we try to obtain a unique true hardness value for each coating by making recourse to a theoretical model based on the physical causes of the ISE effect.

THE ISE EFFECT AND THEORETICAL MODALITIES TO ELIMINATE IT

Indentation microhardness appropriate for thin coatings can be made by means of various diamond indenters.[2,3] The most commonly used is the Vickers square pyramid indenter with apex angle 136° and the Knoop elongated pyramid indenter. Indentation hardness tests have become microhardness tests in 1940 when Hanneman and Bernhardt have introduced a Vickers pyramid indenter of very small size (base square diagonal equal to 0.8 mm) in the objective lens of an optical microscope equipped with a device to apply the loads and with a micronic scale for measuring the diagonal of the indentation. If the geometry of the indenter is considered the Vickers microhardness H_V (in kgf/mm^2) defined as the ratio between the load F (in grams) and the area of the indentation calculated by means of the indentation diagonal d (in micrometers) is as follows:

$$H_V = 2\sin(136^\circ/2)\,(F/d^2) = 1854.4\ F/d^2 \qquad (1)$$

As the hardness H_V is constant for a given material eq.(1) indicates the size of the indentation

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d^2 to be proportional to the load F according to the well known Kick law expressed by eq.(2):

$$F=Kd^2 \tag{2}$$

However at low values of the applied load the Kick law is no more observed[4] and the measured hardness begins to be dependent on load (see our results in Table 1). This is the troublesome ISE effect whose explanation has to be looked for in the mechanism of the plastic deformation during the indentation process.

Previous researches performed by one of the authors[5] on a large number of mineral substances have ascertained the theoretical model proposed by Hays and Kendall for metallic materials[6] as the best suited to eliminate the ISE effect and to derive the true hardness of the material, in comparison with other theoretical models.[7] In this paper we try to apply the Hays-Kendall model to composite materials as those represented by Ni-P coatings reinforced by micronic SiC particles. The Hays-Kendall model states that the Kick law would be obeyed at whatever load if one admits that the force F_2 which effectively produces the plastic deformation during the indentation process is smaller than the applied force F by an amount W equal to the force required to initiate the plastic deformation in the material. Hence the Kick law should be written as follows:

$$F_2 = F - W = Kd^2 \tag{3}$$

or

$$F = W + Kd^2 \tag{4}$$

A regression statistical treatment applied to all pairs of values F and d^2 experimentally obtained for a given material at various values of the applied load F enables one to calculate the two constants W and K in eq. (4). Constant K (equal to the slope of the straight line obtained by the regression statistical treatment) is further used to calculate the true hardness of the material by means of eq.(5)

$$H_V = 1854.4\ K \tag{5}$$

obtained by combining eq.(3) and eq.(1).In so doing one has to use the effective force F_2 instead of the applied force F in the latter equations namely $F_2 = Kd^2$ for eq.(3) and $F_2 = H_V d^2 /1854.4$ for eq.(1).

When the Hays-Kendall model is applied to the experimental hardness measurements performed on thin coatings it is important to make sure that the experimental data are not affected by the hardness of the underneath support. This means to take into consideration only the data obtained at penetration depths for which the indenter is in the layer. If the geometry of the indenter is taken into account the depth of penetration h is correlated with the size d of the diagonal of the indentation as follows:

$$h = (d/2)\ \mathrm{tg}\ (90^\circ - 136^\circ/2) = 0.187d$$

or

$$\text{roughly} \quad h \sim 0.2\ d \tag{6}$$

EXPERIMENTAL

As specified in our previous paper[1] Vickers microhardness measurements have been carried out for four Ni-P/SiC coatings in three conditions (as plated; heat treated at 190°C in view of dehydrogenation; heat treated at 420°C in view of precipitation hardening). The investigated coatings were denoted as follows:

P0S40-(0) ; P5S40-(8.4) ;
P10S40-(16.1); P20S40-(20)

where x in the symbol $P_x S_y$–(z) indicates the amount of H_3PO_3 in solution in the electrolyte (g/l); y is the amount of SiC powder in suspension in the electrolyte from which SiC particles are co-deposited in the coating (g/L) and z is the resulting phosphorus content in the coating (at.%P). If needed an additional index t (representing the thickness of the coating in μm) is introduced in the symbol P_x S_y –(z)-t. A Shimadzu HMV-2 Vickers microhardness tester was used. The load F was applied perpendicular on the smooth free surface of the coating and a series of loads were applied for each sample as follows: F= 15; 25; 50; 100; 200; 300 g. The H_V value was taken as the average of five indentations for each sample and each load.

RESULTS

Table 1 summarizes the experimental data obtained by the Vickers microhardness test for all investigated samples. The heat treatment applied and the coating thickness t (in μm) are indicated in column 2 for each sample. By comparing the values for the coating thickness t with the penetration depth h (calculated by means of eq.(6) it appears obvious that no influence from the underneath support material (a mild steel) was exerted on the hardness for forces F applied on the indenter ranging below 300 g. The data in Table 1 show that the hardness measured for a given sample has not a unique value but is dependent on the load F (the ISE effect).

Table 1

Results on microhardness (H_V in kgf/mm^2) measured at various loads F for all investigated samples

Sample	Heat treatment	F, [g]	15	25	50	100	200	300
P0S40	None; t=33μm	H_V	210	205.5	203	201.1	200	198.2
		d^2	132.5	225.5	456.7	922	1854.1	2806.6
	190° C; t=36 μm	H_V	254.5	245	242.5	241	237.5	223
		d^2	109.3	189.2	382.3	769.5	1561.6	2494.7
	420° C; t=36 μm	H_V	347	354	303	274	261.5	258
		d^2	80.2	131	306	677	1418.3	2156.3
P5S40	None ; t=36μm	H_V	469	473	470	468	454	402
		d^2	59.3	98	197.3	396.2	816.9	1383.9
	190° C; t=38 μm	H_V	649.5	648.5	571	557	518.5	482.5
		d^2	42.8	71.5	162.4	332.9	715.3	1153
	420° C; t=38 μm	H_V	841.5	813.5	803	763	692	643
		d^2	33	57	115.5	243	536	865.2
P10S40	None; t=21μm	H_V	435	429	418	412	407	391
		d^2	64	108.1	221.8	450.1	911.2	1442.8
	190° C; t=24 μm	H_V	537	536	537	501.5	445.5	389.5
		d^2	51.8	86.5	172.7	369.8	832.5	1428.3
	420° C; t=24 μm	H_V	1136	1132.5	1072	1053	951.5	856
		d^2	24.5	40.9	86.5	176.1	389.8	649.9
P20S40	None; t=24μm	H_V	449	437	429	418	404	400
		d^2	62	106.1	216.1	443.6	918	1390.8
	190° C; t=27 μm	H_V	599	545	549	513	453	397
		d^2	46.4	85.1	168.9	361.5	818.7	1401.3
	420° C; t=27 μm	H_V	1159	1114	1107	1002	927	763
		d^2	24	41.6	83.8	185.1	400	729.1

The data in Table 1 were further processed by a regression statistical treatment according to the Hays-Kendall model expressed by eq.(4); a straight line dependence F versus d^2 was obtained for each sample. The resulting W and K values as well as the confidence factor r^2 for each coating are given in Table 2 together with the true hardness calculated by means of eq.(5). Also indicated in Table 2 is the deviation ΔH in percent from the true hardness of the measured hardness $H_{V\ (15)}$ $H_{V\ (50)}$ $H_{V\ (100)}$ and $H_{V\ (300)}$,, each obtained at a selected value for the load (F=15; 50;100;300 g).

Table 2

True hardness H_V [kgf/mm^2] for the investigated Ni-P/SiC composite coatings obtained by the Hays-Kendall theoretical model applied to the experimental hardness data

Sample	Heat treatment	r^2	W	K	H_V	ΔH_{15} %	ΔH_{50} %	ΔH_{100} %	ΔH_{300} %
P0S40	None	0.999972	1.2258	0.1067	198	0.6	2.5	1.5	0.10
P0S40	190° C	0.998434	4.3291	0.1206	224	13.4	8.2	7.6	-0.45
P0 S40	420° C	0.999827	6.7021	0.1363	253	37.2	19.8	8.3	2.00
P5 S40	None	0.994155	7.7874	0.2179	404	16.1	16.3	15.8	-0.50
P5 S40	190° C	0.997813	8.5885	0.2577	478	35.9	19.5	16.5	0.94
P5 S40	420° C	0.997104	9.2536	0.3403	631	33.4	27.3	20.9	1.90
P10 S40	None	0.998880	4.0437	0.2082	386	12.7	8.3	6.7	1.30
P10 S40	190° C	0.992047	13.0296	0.2080	386	39.1	39.1	29.9	0.91
P10 S40	420° C	0.994873	10.5598	0.4582	850	33.6	26.1	23.9	0.71
P20 S40	None	0.999882	3.0712	0.2141	397	13.1	8.1	5.3	0.75
P20 S40	190° C	0.992370	13.3584	0.2116	392	52.8	40.0	30.9	1.27
P20 S40	420° C	0.986495	15.9282	0.4086	758	52.9	46.0	32.2	0.66

DISCUSSION

The true hardness values in Table 2 derived by the Hays-Kendall model allow each coating to be characterized by a unique hardness value that may be used to recommend the hard coating for a tribological application. These true hardness values also allow the influence of the chemistry and structure of the Ni-P/SiC coatings to be discussed in a quantitative manner. For instance it is interesting to compare the lowest true hardness value in Table 2 with the highest one. The lowest value H_V = 198 kg/mm^2 belongs to the as plated composite coating containing no phosphorus in its Ni metallic matrix. Its hardness is twice the value reported in[8] for pure Ni that is 110 kg/mm^2 and this increase in hardness has to be ascribed to the reinforcing effect of the SiC particles dispersed in the Ni matrix of the coating. Taking this lowest value H_V =198 as a reference the true hardness values in Table 2 point to the possibility of an increase of the coating hardness as large as 4 times by introducing P in its Ni metallic matrix during the electroplating process and further on by an efficient handling of this phosphorus through a precipitation hardening heat treatment that takes P out of the Ni based supersaturated solid solution and redistributes it as finely dispersed Ni_3 P particles.

Our results in Table 2 have a more general meaning. Indeed in comparison with the true hardness the values measured at a single small load F show large deviations up to 53%. The deviation ΔH is not the same for different materials being the largest for harder materials. So our results demonstrate on a quantitative basis that the common practice is unsatisfactory even for comparison purposes. Our results show that by increasing the load F the ISE effect is diminished and ΔH becomes smaller and smaller. At high enough loads (as for instance 300g in Table 2) ΔH becomes insignificant. Unfortunately such high loads cannot be used for thinner coatings than the ones used in this paper (micronic or submicronis films) without the misleading influence from the underneath support material. Hence a theoretical model for processing the experimental data is the safest method to obtain reliable hardness values for thin coatings.

CONCLUSIONS

The true hardness of Ni-P/SiC electroplated composite coatings calculated by processing the experimental microhardness data (measured at various loads applied on the indenter in the range 15 up to 300 g) by making recourse to a theoretical model show that one may commit important errors if one characterizes a thin coating by the usual procedure consisting in indicating the hardness value measured at a single low load. Our investigation has shown that errors as large as 53% in comparison with the true hardness are manifest if the heat treated Ni-P/SiC coatings are characterized by the hardness value measured at a low load equal to 15g.

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