Homogeneous electroless Ni–P/SiO₂ nanocomposite coatings with improved wear resistance and modified wear behavior

Yoram de Hazana,*, Denise Zimmermanna,b, Markus Z'graggenc, Sigfried Roos d, Christos Anezirisc, Hans Bolliere, Peter Fehre, Thomas Graulea,b

a Laboratory for High Performance Ceramics, Empa, Swiss Federal Laboratories for Materials Testing and Research, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
b Institute of Ceramic, Glass and Construction Materials, Technische Universität Bergakademie Freiberg, Agricolastraße 17, 09599 Freiberg, Germany
c IWT, Institut für Werkstofftechnologie, Richtistrasse 15, CH-8304 Wallisellen, Switzerland
d Laboratory for Nanoscale Materials Science, Empa, Swiss Federal Laboratories for Materials Testing and Research, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

Abstract

Highly homogeneous Ni–P/SiO₂ nanocomposite coatings were prepared by electroless deposition from composite baths containing well dispersed SiO₂ nanoparticles. The particle concentration in the coatings increases gradually with the SiO₂ concentration in the bath and reaches an observed maximum of 25 vol.% at a bath concentration of 10 g/l. Tribological measurements of the heat treated coatings indicate that while the hardness of the coating is decreased compared to that of the Ni–P coating without particles, an improvement in Pin-on-Disk wear resistance up to a factor of 2 can be achieved. The aspect ratio of the wear track of samples heat treated above 270 °C is found to increase with the concentration of nanoparticles in the coatings. This observation indicates that the nanoparticles also modify the wear behavior of the coatings.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

With the new prospects to improve the properties of composite electro and electroless nickel (EN) coatings by incorporation of submicrometer and nanometer size particles these research fields are receiving increasing attention lately [1–16]. Submicron and nanoparticles are able to improve the tribological properties of the coatings through modification of the crystalline growth of the growing nickel films [1–5] and creation of dispersion hardening effects at low incorporation levels [1,17].

The potential benefits of such reinforcement by nanometer size dispersions can only be understood and quantified if the particles are sufficiently dispersed in the nickel coating. Most ceramic nanoparticle dispersions are unstable in the high ionic strength/high temperature electro and EN plating baths without special surface modification, which is able to prevent particle agglomeration [6–9]. SiO₂ is one exception to this rule due to its low Hamaker constant in aqueous media implying reduced attraction between particles [18,19] and/or the existence of hydration (solvation) layers which prevent particle agglomeration [19–21].

The exploration of nanoparticles to improve the tribological properties of electroless Ni–P nanocomposite coatings dates back to the work of Metzger et al. [22]. In this comprehensive work which involves Ni–P/SiC and Ni–P/Al₂O₃ also Ni–P/SiO₂ nanocomposite coatings were prepared and tested for wear resistance. While SiC and Al₂O₃ have shown improvement of the Taber wear resistance, the incorporation of SiO₂ (in the form of precipitated silica nanopowder) has not yielded an improvement. Fabrication and testing of Ni–P/SiO₂ nanocomposite coatings is also described in recent work [10–15]. Most recently and relevantly, Dong et al. [15] have examined the effect of silane modified SiO₂ on the wear resistance of Ni–P/SiO₂ coatings. While an improvement of wear resistance with particles was claimed, no comparison of wear resistance with Ni–P coatings was made for heat treated coatings. Moreover, no conclusion as for the effect of particle concentration in the coatings can be drawn.

In this paper we present a systematic investigation on the effect of low cost, commercially available pyrogenic SiO₂ nanoparticles on the tribological properties of high phosphorus Ni–P/SiO₂ coatings. This work validates our earlier (unpublished) findings with medium phosphorus Ni–P/SiO₂ coatings [23].

2. Materials and methods

2.1. Materials

Aerosil OX50 (Evonik Degussa, Germany) a spherical, non aggregated pyrogenic powder with a mean particle size of 40–
50 nm and surface area of 50 m²/g was used as the SiO₂ nanoparticle [19]. The SiO₂ nanoparticles were used as received without any surface modification. NiPlate500, a commercial high phosphorus EN plating solution was obtained from Micron s.r.l., Italy. The EN solution is supplied in two makeup parts (A and B) and an additional replenishing part (Part C). Part A contains primarily NiSO₄ and parts B and C contain the reducing agent NaH₂PO₂ along with proprietary complexing agents such as citrate and lactate.

2.2. Preparation of dispersions and composite Ni-P bath

20 wt.% colloidal silica dispersions in DI water were prepared by ball milling (90 rpm) with 0.5 mm ZrO₂ balls for 12 h. Mixing of the composite plating bath was performed in a plating vessel, a 5 l glass beaker, under magnetic stirring in the following order: 1 l DI water, SiO₂ dispersion, 300 ml NiPlate500 part A, 450 ml of part B, balance DI water to 5 l. The initial bath contains 6 g/l nickel and 35 g/l NaH₂PO₂. The pH of the mixed bath is 4.7 ± 0.1. All mixing procedures are done at room temperature (RT). The particle size distribution (PSD) was measured with a Beckman Coulter LS230 equipped with polarization intensity differential scattering (PIDS) for reliable analysis in the submicrometer range. Fig. 1 shows the PSD of the SiO₂ particles in DI water (pH = 4.5) and after addition to the nickel plating solution. The dispersion in DI water is monomodal (main peak around 120 nm) indicating a well dispersed system. The absolute particle size given by the LS230 in the low submicrometer range, however, is not accurate due to an imperfect optical model [8,9]. An additional peak around 300 nm appears in the nickel solution indicating that partial aggregation occurs in the system. The ratio of the two peaks suggests that the aggregates may consist of only several primary particles.

2.3. Electroless Ni-P composite plating

Disks with a diameter of 40 mm (0.25 dm² in area) made of 100Cr6 steel were used as substrates for composite EN plating. One side of the disk, which was later used for tribological measurements had a maximum (Rt) and average surface roughness (Ra) of 0.138 µm and 0.012 µm, respectively. Table 1 lists the steps employed in the pretreatment of the 100Cr6 steel substrates. Substrates were degreased, etched, activated, coated with 0.2 µm nickel strike layer and subsequently coated with Ni-P without particles at 87 °C for 2 min directly before composite plating. This procedure was found necessary to obtain good interface for composite coating. The mixed composite bath was heated to plating temperatures of 86–87 °C. 5 pretreated samples having a total surface of 1.25 dm² hanged on a steel rod were placed in the bath immediately after the pretreatment.

The bath was mixed by a magnetic stirrer (100–200 rpm) and kept at temperature (+1 °C) with a temperature controlled heating jacket. The pH was kept at 4.7 ± 0.1 by frequent additions of 25% ammonia solutions. No special measures to prevent particle agglomeration (such an in situ ultrasound [16]) have been employed or found necessary during codeposition.

2.4. Characterization of nanocomposite coatings

Particle size distribution and concentration in the Ni-P/SiO₂ composite coatings were evaluated by SEM/EDS (LEO 1455/Oxford instruments). For the examinations, cross sections of the disks were embedded in a conductive resin. The metallographic preparation followed a standard procedure. The last polishing step was 1 µm Diamond. The SEM conditions for all measurements were: a working distance of 15–20 mm, an acceleration voltage of 20 kV and a probe current of 350–500 pA. The pictures were taken using a BSE Detector. The EDS signal was calibrated with a cobalt standard before each series of measurements. Each experimental point is the average of a section of thickness of 2 µm and a length of 100 µm. The tribological properties of the coatings were measured after three heat treatment procedures conducted in air: a) 270 °C for 10 h, b) 390 °C for 2 h and c) 480 °C for 1 h. The samples treated at 390 °C or 480 °C in air possess a thin (100–200 nm) oxide layer at their surface. This thin oxide layer has not been removed prior to hardness and POD measurements since its effect on the results was negligible and its removal would have modified the surface roughness.

Vickers hardness (Melit 430SVD, Switzerland) was measured at a force of 3 N (HV₀.3) for 15 s. The hardness was measured for a set of 9 points across the diameter of the disks from which a mean value and standard deviation were calculated.

The wear resistance of Ni-P/SiO₂ composite coated disks was measured against a 10 mm 100Cr6 steel ball by the Pin-on-Disk (POD) method (CSEM Tribometer, Switzerland). Sample rotation speed at a radius of 11 mm was 20 cm/s. A load of 10 N was used. Experiments with total distance of 11.5 km were made (16 h). Such long distance was necessary to obtain statistically valid data (weight loss in the range of 0.5 mg ± 0.1 mg). No lubricant was used. Ambient temperature was kept at 25 °C and humidity at 50% in all experiments. The weight loss of the samples and the ball during the test was measured. The weight change of the ball was very small in all experiments, within the measurement error and therefore not reported here.

The volumetric wear rate of the samples was obtained using the SiO₂ particle concentration measured by EDS, assuming the density of the coating obeys the rule of mixtures: 
\[ \rho = \rho_{NiP} x_{NiP} + \rho_{SiO2} x_{SiO2} \]
where \( x_{SiO2} \) is the weight fraction of SiO₂ in the Ni-P/SiO₂ nanocomposite coating and \( \rho_{SiO2} \) and \( \rho_{NiP} \) are taken as 2.2 and 8.0 g/cm³, respectively.

A universal wear rate factor (WRF) can be calculated by the following equation:

\[ WRF = \frac{V}{F \cdot d_{weartrack}} \cdot \left( \frac{m^3}{N \cdot m} \right) \]
where $V_{\text{removed}}$ is the volume of substrate removed during the POD test, $F$ is the force applied and $l_{\text{weartrack}}$ is the distance traveled.

Tencor P-10 surface profiler (Tencor, USA) was used to analyze the POD wear track (depth, width and shape) of the tested samples. The wear track dimensions were measured at four equally spaced locations from which a mean value and a standard deviation were calculated. The volume of the wear track was also estimated by measuring the race track cross sectional area and multiplying it by the wear track length. The wear track area was measured by printing the profiles on a paper, cutting and weighing the papers. The weights were normalized with a weight of paper with a known area.

3. Results and discussion

3.1. Preparation of homogeneous Ni–P/SiO$_2$ nanocomposite coatings

Fig. 2 shows the SEM cross section of Ni–P/SiO$_2$ nanocomposite coatings plated for 3 h from a high phosphorus bath containing 1–20 g/l SiO$_2$ nanoparticles (the 100Cr6 steel substrate is visible at the bottom of the SEM images). All coatings produced are between 25 and 30 $\mu$m thick and exhibit homogeneous distribution of nanoparticles in their cross section.

The coatings viewed at higher resolution (Fig. 3) show that the nanoparticles are well dispersed in the coatings at all SiO$_2$ bath concentrations studied. Most large agglomerates seen in the coatings are in the range of 100–150 nm, consisting of only several primary particles. This is in qualitative agreement with the particle size distribution shown in Fig. 1. It is interesting to note that coatings deposited from baths with lower SiO$_2$ concentrations (1 and 3 g/l) exhibit somewhat larger aggregates.

Fig. 3 also shows a gradual increase in particle concentration in the Ni–P/SiO$_2$ nanocomposite coatings with particle concentration in the bath. The average SiO$_2$ particle concentration in the coatings, measured by EDS analysis is shown in Fig. 4 as a function of the SiO$_2$ concentration in the plating bath. The cross sectional area used for averaging was 100 $\mu$m × 25 $\mu$m. The concentration of SiO$_2$ particles in the coating increases gradually and predictably to a maximum level of 25 vol.%, observed experimentally at 10 g/l. At 20 g/l a small decrease to 22 vol.% is seen. The experiments at 1 and 10 g/l have been repeated with identical findings, confirming the high incorporation levels of 25 vol.%. At 20 g/l SiO$_2$ concentration in the plating bath macroscopic agglomerates of SiO$_2$, forming presumably at the liquid bath/air interface are observed. At the same time, an interpolation between 3 and 10 g/l SiO$_2$ in Fig. 4 suggests that coatings with 22 vol.% can more conveniently be produced from baths with a SiO$_2$ concentration of ∼7 g/l.

3.2. Wear behavior of Ni–P/SiO$_2$ nanocomposite coatings

The Vickers hardness values (HV$_{0.3}$) of the Ni–P/SiO$_2$ coatings after heat treatment procedures of 270 °C/10 h, 390 °C/2 h and 480 °C/1 h are shown in Fig. 5 as a function of particle concentration in the plating bath. Due to the relatively high standard error only some conclusions can be made. Counter to other findings (e.g. reference [15]), the Ni–P coatings without particles exhibit the highest hardness values after all heat treatments. It is not clear if this discrepancy is related to differences in the plating solution, particle surface modification or perhaps the force used during HV measurements (3 N vs. 0.5 N). A clear dependence of hardness on the particle concentration in the bath is apparent at 480 °C. Interestingly, the

Fig. 2. Cross section of Ni–P/SiO$_2$ composite coatings (100Cr6 steel substrate is at the bottom). a) 1 g/l SiO$_2$, b) 3 g/l SiO$_2$, c) 10 g/l SiO$_2$, and d) 20 g/l SiO$_2$. Scale bar is 20 $\mu$m.
maximum hardness which is normally observed after heat treatment at 400 °C \cite{15}, is not observed here for the Ni–P coating without particles after heat treatment at 390 °C.

Due to poor adhesion to steel, the as deposited coatings on 100Cr6 steel are unstable without heat treatment above ~200 °C. The as deposited coatings are destroyed in a matter of minutes during POD tests. Fig. 6 shows the POD wear resistance of the composite coatings as a function of particle concentration in the bath and heat treatment temperature. The gravimetric wear rate based on sample weight loss during the POD test (Fig. 6a) is converted to volume loss by normalizing to the density of the samples (See Section 2.4) and presented as the volumetric wear (Fig. 6b). Despite this correction, Fig. 6a and b show qualitatively the same picture. The Ni–P/SiO₂ nanocomposite coatings show in general superior wear resistance compared to Ni–P coating without particles at all heat treatment temperatures studied (the only two exceptions in the data are 20 g/l at 270 °C and 1 g/l at 480 °C).

Table 2 lists the best improvement in wear resistance by considering the ratio of the wear rate factors \( WRF_{\text{Ni–P}} / WRF_{\text{composite}} \). An improvement by a factor of 1.5 is found at 270 °C (at 15 vol.% nanoparticles) and 2 at 390 °C (21 vol.% nanoparticles). The best improvement appears to be always at or around 15 vol.% nanoparticles in the coatings (corresponding to SiO₂ concentration of 10 g/l).
to bath concentration of 3 g/l), irrespective of the heat treatment temperature.

After heat treatment at 270 °C, the coating from bath containing 3 g/l SiO2 represents a minimum in the wear rate curve (Fig. 6) whereas at 390 °C it represents the beginning of a plateau. In any case, coatings made from baths with 1 g/l SiO2 or less show consistently inferior wear resistance.

Using the universal wear rate factor, one can compare absolute results from different systems (although not without great caution). In any case, the WRF found here are around $10^{-15}$ for the Ni–P and $5 \times 10^{-16}$ for the nanocomposites over 11.6 km. For comparison, Dong et al. [15] show the best value of WRF of $10^{-14}$, 10–20 times higher than in the present work. The exact measurement distance is not reported but may be as short as 12 m judging from the data presented in Fig. 5 of reference [15].

The friction coefficient (average of last 4 km) as a function of particle concentration in the coating. This trend continues after heat treatment at 270 °C (Fig. 8a). Also here the highest sensitivity of the wear track dimensions to particle concentration is seen after heat treatment at 390 °C (Fig. 8b). The general trend is an increase in depth and a decrease in width of the wear track with increased particle concentration in the coating. This trend continues after heat treatment at 480 °C, but the variation with particle concentration is much diminished (Fig. 8c). Fig. 9 illustrates two extreme examples of wear track profiles, both obtained after heat treatment at 390 °C. While the 1 g/l SiO2 sample exhibits a relatively shallow and broad wear track, the 10 g/l SiO2 shows a deep and narrow track (note the different scales in the x and y axes). It is important to note that the width and depth of the race track at 270 °C do not predict the large reduction in volume loss seen with the nanoparticles (Fig. 6 and

Table 2

<table>
<thead>
<tr>
<th>Thermal treatment</th>
<th>SiO2 in coatings (vol%)</th>
<th>WRF (m$^3$/Nm)</th>
<th>WRF$<em>{NiP}$/WRF$</em>{composite}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>270 °C, 10 h</td>
<td>0</td>
<td>1.1E-15</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>7.3E-16</td>
<td></td>
</tr>
<tr>
<td>390 °C, 2 h</td>
<td>0</td>
<td>1.5E-15</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>7.7E-16</td>
<td></td>
</tr>
<tr>
<td>480 °C, 1 h</td>
<td>0</td>
<td>8.7E-16</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>4.9E-16</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 6](image-url) Effect of SiO2 particle concentration in the plating bath and heat treatment temperature on the wear rate of the Ni–P/SiO2 nanocomposite coatings. a) Gravimetric, and b) volumetric.

![Fig. 7](image-url) Effect of SiO2 particle concentration in the plating bath and heat treatment procedure on the friction coefficient of the Ni–P/SiO2 nanocomposite coatings.
Table 2). A more precise estimation of the volume loss during POD tests involves the estimation of wear track cross sectional area. Fig. 10 shows the volume loss during POD test of samples heat treated at 270 °C, estimated from POD weight loss data (from Fig. 6b) or by estimation of volume from the profiles of the wear track. Reasonable agreement is found in Fig. 10, predicting a somewhat lower improvement of wear resistance by a factor of 1.35 compared to 1.5 shown in Table 2. Good agreement is also found after heat treatment at 390 °C and 480 °C.

The temperature dependency seen in Fig. 8 is in general quite similar to the dependence of friction coefficient on particle concentration (Fig. 7). In other words, the dimensions of the wear track and the friction coefficient may be influenced by material properties. Alternatively, the dimensions of the race track may determine the friction coefficient.

Fig. 9. Comparison of wear track profiles of Ni–P/SiO₂ nanocomposite coatings heat treated at 390 °C. Top — 7.5 vol.% SiO₂ (1 g/l), and bottom — 25 vol.% SiO₂ (10 g/l).

Fig. 10. Volume of wear track after heat treatment at 270 °C estimated from weight loss during POD tests or by integration of wear track cross sectional area.
The information shown in Fig. 8 can also be represented by a single parameter, the aspect ratio of the wear track which is defined as the (depth of wear track)/(width of wear track). The variation of the aspect ratio of the wear track (AR) with the SiO₂ particle concentration in the Ni-P/SiO₂ coating is plotted in Fig. 11. The AR is independent on SiO₂ concentration after heat treatment at 270 °C. However, after heat treatment at higher temperatures (most dramatically at 390 °C) an increase of the AR with particle concentration in the coating is observed above 7.5 vol.% SiO₂. The absolute value of the AR, ranges between 0.01 and 0.14. This systematic change, which to our knowledge is observed here for the first time, indicates a variation of the wear behavior of the Ni-P/SiO₂ nanocomposite coatings with embedded nanoparticles. This perhaps is indicative of a gradual shift to the adhesive wear regime with increase in SiO₂ nanoparticle concentration in the coating and may dictate the specific applications of the coatings. The Ni-P coatings without particles show a steady increase in the aspect ratio with heat treatment temperature. Interestingly, at 7.5 vol.% SiO₂ (1 g/l) the aspect ratio is independent of the heat treatment temperatures studied. The analysis above shows that nanocomposite systems have complex wear behavior and should not be characterized by volumetric wear rate alone. Although the Ni-P/SiO₂ nanocomposite coatings exhibit significantly lower wear rates, due to the difference in their aspect ratios, the depth of the wear track may not be reduced in a similar way. In fact, an increase in the depth of the wear track with the incorporation of SiO₂ nanoparticles is also observed in Fig. 8. It is important to note that while POD analysis provides a good guide for wear behavior, specific tests are necessary for specific applications. For these, the benefit of the Ni-P/SiO₂ nanocomposite coatings would need to be evaluated independently.

4. Conclusions

Homogeneous Ni-P/SiO₂ nanocomposites were prepared from stable composite electroless baths containing SiO₂ nanoparticles. The particle concentration in the coatings increases gradually with the SiO₂ concentration in the bath and reaches a maximum of 25 vol.% at 10 g/l. The hardness of the heat treated coating is decreased compared to Ni-P without particles. At the same time an improvement in Pin-on-Disk wear resistance by factors of 1.5 and 2 is achieved after heat treatment at 270 °C and 390 °C, respectively. The friction coefficient which is independent of particle concentration after heat treatment at 270 °C can also be markedly improved by the nanoparticles after heat treatment at higher temperatures. The increase of the aspect ratio of the wear track with concentration of nanoparticles in the Ni-P/SiO₂ coatings indicates that the nanoparticles also influence the wear behavior of the coatings. The benefit of this different wear behavior needs to be assessed independently for specific applications.

Acknowledgments

This work was supported by the Swiss KTI Project No. 8511.2.

References