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In-situ SEM study of crack initiation, propagation and interfacial debonding of Ni-P coating during tensile tests: Heat treatment effect

H. Bouaziz [a,*], O. Brinza [b], N. Haddar [a], M. Gasperini [b], M. Feki [a]

[a] Laboratoire Génie des Matériaux et Environnement (LGME), Ecole Nationale d'Ingénieurs de Sfax (ENIS), Université de Sfax, B.P.1173, 3038 Sfax, Tunisie
[b] Université Paris 13, Sorbonne Paris Cité, Laboratoire des Sciences des Procédés et des Matériaux (LSPM), CNRS(UPR3407), 99 av. J.B. Clément, F-93430 Villetaneuse, France

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ABSTRACT

This study focuses on the effect of annealing temperature onto the mechanisms of crack initiation, propagation and interfacial debonding of the electroless nickel/phosphorus (Ni-P) coatings deposited on steel. An in-situ tensile test has been carried out in a SEM chamber for coated samples annealed at 400 and 600 °C, and at a strain rate of 0.1 μm/s. It is observed that when an as deposited Ni-P on steel system is subjected to a uniaxial tensile test, a bended crack is formed on the surface of coating and leads to a debonding of coating at a small strain level. Incontrast, in case of an annealed sample, the N-iP coating shows a severe multiple parallel crackings due to the localized plastic deformation of the substrate. The crack density firstly increases with the rising tensile strain, and then reaches saturation. The spacing between the resulting saturated parallel cracks in the coating surface is defined in the shear lag model to quantify the interfacial shear strength. Despite the large plastic deformation of the substrate, there is no spallation observed at the interface between the two materials. The hardness and the young's modulus of the coating before and after heat treatment are determined by nano-indentation tests. The stiffness of the coatings increases owing to the Ni_3P phase precipitation during heat teatment.

1. Introduction

The electroless nickel/phosphorus coatings deposited on steel has been developed for a vast range of applications [1]. These materials have been characterized by interesting mechanical properties such as high adhesion, resistance to abrasive wear, and hardness. Previous studies have revealed that mechanical and tribological properties of the Ni-P layer depend strictly on their structure. Rolf Weil and Konrad Parker [2] considered that the structure of electroless Ni-P coating deposits was amorphous when the Phosphorus content exceeded 7%. The amorphous structure of the deposits was thermally unstable and could undergo a crystalline transition at moderate temperatures (300–400 °C) [3,4,5,6]. In the case of thermal processing for improving deposit hardness, the typical temperature to achieve maximum hardness in electroless Ni-P deposits would be approximately 400 °C for 1 h. Keong et al. [7] attributed this growth of hardness to the crystallization of Nickel and the precipitation of fine particles of Ni_3P. In addition, they reported that Ni_3P, which was stable phase, had a higher strength and a shear modulus, causing a hardening effect on the coating. Other researchers [7] suggested that the hardening was affected by the raise of the number of precipitated fine grains (Ni and Ni_3P). On the other hand, Lacourcelle and others [2,8] revealed that the adhesion between the substrate and the Ni-P coating could be raised by annealing the sample at 600 °C for 1 h. It was already pointed out that annealing above 600 °C to form a diffusion layer could improve the bond between the Ni-P coating and steel. The evaluation of this adhesion was essential to characterize the strength of composite. Several methods were used to quantify the adhesion between the coating and the substrate [9–20], including three [9] or four bend tests [10,11], tape and pull-out tests, indentation [12,13–16] and scratch techniques [9]. Nevertheless, the accuracy of these methods is compromised by the presence of a third body. Contrariwise, the tensile test method, detailed in the present work, is free of third-body interactions. It enables quantifying the cohesive properties (which control cracking) and the adhesive properties of coating on high strain substrates.

Experimentally, a large volume of studies has been carried out on the failure behavior of composite on a broad range of coating/substrate combinations, mainly ceramic/metal [17,21,19,22,23], metal/metal [24,25], and ceramic/polymer [26,27]. The failure of these coatings has been observed by optical or electron microscopy. In addition, the mechanics of crack initiation and propagation in a coating/substrate system have been well understood. Chen [17] and others revealed that four sequentially morphologies of the crack were observed on the surface of coating: multiplication, stabilization, cross-linking and spallation [26,21]. On the contrary, others have reported that the debonding of coating would occur following the saturation of parallel cracks [19,20,22,28–30]. This dissimilarity could be attributed to the adherence between two the materials.

* Corresponding author.
E-mail address: hela_mat@yahoo.fr (H. Bouaziz).

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Table 1
Basic constituents of the electroless nickel/phosphorus bath.

Constituent	Role
$NiSO_4 \cdot 6H_2O$	Ni source
$NaH_2PO_2 \cdot H_2O$	Reducing agent
CH_3COOH/CH_3COONH_4[a]	Complexing and buffering agent
NH_3[a](aq)(50%) or H_2SO_4	pH adjuster

[a] To make better environment compatibility of the bath composition, CH_3COONa and Na_2CO_3 can be used instead of CH_3COONH_4 and NH_3 respectively.

Lu [31] performed tensile testing on the amorphous Ni-P film as deposited on a confinement of nanograined Ni substrate. He demonstrated that the substrate could be further strained without necking because of the competitive movement and intersection of shear bands. To inhibit the propagation of one dominant shear band in the amorphous Ni-P film, it would be required to choose the well bonded interface with a minimum interface roughness, the matched strength and modulus, and the uniform plastic deformability of the substrate.

Interestingly, there have been few studies on the effect of annealing temperature into the cracking behavior and the adhesion of brittle Ni-P coating on a ductile substrate. Joel et al. [5] conducted a series of experiments, using a microscopic tensile test, to explore the annealing temperature effect (420 and 600 °C) into the cracking behavior of an electroless Ni-P layer on a low carbon steel substrate. They demonstrated that the annealing at 420 °C caused an important improvement in the adhesion level of the coating and more precisely of the Ni-P matrix. However, the roughness of the substrate under a tensile test has not taken into consideration to study the failure strain of coating. This remark is intriguing since numerous studies have interpreted that the spallation occurs when the surface of substrate is more rugged and developed than the coating [17,20]. Hamad et al. [32] revealed that the stress transferred from the substrate to the coating segments was dependent on the elastic and elastic/plastic properties of the coating and the substrate. Furthermore, the segmentation of the coating and the delamination depended strongly on the film and substrate properties. An increase in the value of (E_{coat}/E_{subst}) resulted in a reduction in the coating strain generation and vice versa. Depending on the material, Anna and others [33,34] depicted that the crack might stop at the interface, penetrate into the substrate, or bifurcate onto the interface.

Keeping this in mind, we first made an attempt to describe the effect of the annealing treatment on the crack onset strain and fracture damage of the electroless N-iP coating during an in-situ tensile test. After that, we looked at correlating the Ni-P and the substrate failure with further developments. Finally, the interfacial strength, according to a modified Agrawal and Raj method [23], was investigated to examine the influence of the annealing temperature on the mechanical behavior of the Ni-P coating.

2. Experimental Procedure

Ni-P coatings were electrolessly deposited onto a hot rolled medium steel substrate (2 mm of thickness). Before deposition, the substrates were mechanically polished to achieve a surface finish Rz = 0.11 μm, which is then ultrasonically cleaned in ethanol and pickled in an acidic solution at room temperature. The basic constituents of the Ni-P coating bath (high phosphorus 11%) is given in Table 1. The process of deposition was carried out at pH 4.6 and a range of temperature between 84 and 90 °C. The coating bath was stirred at 250 rpm using a magnetic stirrer. Thus, the obtained layer thickness is 8 μm.

The coated samples were annealed under vacuum at 400 and 600 °C for 1 h at a pressure of 10^{-5} bar. The morphology of the electroless nickel/phosphorus layer was studied from the top side of the layer using Scanning Electron Microscopy (SEM).

Nano-indentation tests were performed using an MTM instrument equipped with a Berkovich indenter. The tests were conducted in three steps: (1) applying the load on the indenter at a constant rate of 0.2 N/min, (2) holding the maximum load for 5 s and (3) unloading with the same rate as loading. Prior to the indentation test, coated samples were mechanically polished with a fine grain diamond (0.3 μm). On each pattern, nine indents were performed with maximum loads of 0.1 N.

To study the fracture and adhesion properties of the different heat treated films, tensile testing was employed. The uniaxial tensile tests were carried out on samples with a computer-controlled tensile testing machine at a displacement control, 1 μm/s, and equipped with a 10KN maximum load cell. The tensile unit was mounted in FEG SUPRA 40VP SEM and the sample was loaded stepwise up to predefined nominal strain levels, ε. Owing to test fixture restrictions, a sub-sized standard specimen was used, as shown in Fig. 1.

The fracture morphology and cross section of the samples was observed with SEM and a Leica DM ILM optical microscope respectively in order to reveal the multiple cracking and flaking off behavior of the Ni-P coating.

3. Results and Discussion

3.1. Morphology of Electroless Ni-P Coating

Fig. 2 shows the electroless nickel/phosphorus coating surfaces before and after annealing at 400 and 600 °C. In the as-deposited state, the coatings present a cauliflower-like surface, due to a Ni–P nucleation at the isolated points. After that, there is a growth in the lateral directions, and then an impingement between them. After heat treatments at 400 °C, the nodules grow and coalesce on each other. Annealing at 600 °C exhibits a higher number of nuclei at the nodule with a small size.

3.2. Nano-indentation Hardness Test

The load-displacement curves for the Ni-P deposit and the computed hardness and young modulus of the electroless coating at different annealing temperatures are presented in Fig. 3a. First, an elastic deformation occurs in the specimen. Following the load increase, the specimen enters into the plastic regime. After the maximum load or the optional hold period, the applied load is reduced. The maximum indentation

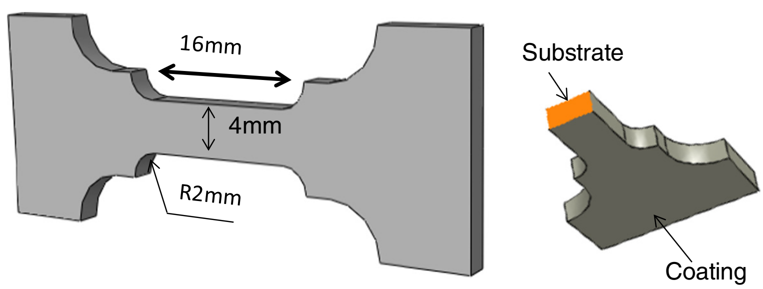

Fig. 1. Schematic diagram of the specimens used for the in situ SEM tensile tests (Specimen thickness = 2 mm).