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Electroless deposition of nickel-boron coatings using low frequency ultrasonic agitation: Effect of ultrasonic frequency on the coatings

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ABSTRACT

The effect of ultrasound on the properties of Nickel-Boron (NiB) coatings was investigated. NiB coatings were fabricated by electroless deposition using either ultrasonic or mechanical agitation. The deposition of Ni occurred in an aqueous bath containing a reducible metal salt (nickel chloride), reducing agent (sodium borohydride), complexing agent (ethylenediamine) and stabilizer (lead tungstate). Due to the instability of the borohydride in acidic, neutral and slightly alkaline media, pH was controlled at pH 12 ± 1 in order to avoid destabilizing the bath. Deposition was performed in three different configurations: one with a classical mechanical agitation at 300 rpm and the other two employing ultrasound at a frequency of either 20 or 35 kHz. The microstructures of the electroless coatings were characterized by a combination of optical Microscopy and Scanning Electron Microscope (SEM). The chemistry of the coatings was determined by ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometry) after dissolution in aqua regia. The mechanical properties of the coatings were established by a combination of roughness measurements, Vickers microhardness and pin-on-disk tribology tests. Lastly, the corrosion properties were analysed by potentiodynamic polarization. The results showed that low frequency ultrasonic agitation could be used to produce coatings from an alkaline NiB bath and that the thickness of coatings obtained could be increased by over 50% compared to those produced using mechanical agitation. Although ultrasonic agitation produced a smoother coating and some alteration of the deposit morphology was observed, the mechanical and corrosion properties were very similar to those found when using mechanical agitation.

1. Introduction

Seventy years after the discovery of electroless Ni by Brenner and Riddell in 1946 [1], the electroless deposition process underwent several modifications to meet the challenging needs of a variety of industrial applications. Electroless deposited Ni coatings have been widely used in different industries such as electronics, automotive, aerospace, medical, petrochemical, food and military etc. This wide field of application can be explained by a well-known combination of properties, including high corrosion resistance, excellent wear resistance, uniformity of coating thickness and magnetic properties [2–9].

Nickel alloys obtained by electroless deposition are categorized according to their alloying elements. The most widely used and studied alloy is nickel–phosphorous (NiP), which is obtained using sodium hypophosphite as the reducing agent. Electroless NiB alloys (that have borohydride ion or amine–borane compounds as the reducing agent) are the second most used electroless Ni alloy, possessing very interesting properties that support industrial requirements. When compared with NiP coatings, electroless NiB deposits present a much higher hardness (up to 900 hv_{100} against 500–700 hv_{100}) [10], have better wear and scratch resistances and promising electrical behaviour [11–21].

Compared with electrodeposited Ni coatings, electroless NiB is far superior regarding uniform plating thickness distribution. This is an important factor when plating components with complex shapes and miniaturised features. In addition, electroless NiB composite deposits might present higher corrosion resistance, superior mechanical properties and the ability to be deposited on a much wider range of materials, such as dielectric substrates (important for electronic applications).

Sonochemistry has attracted much interest in the research community because of its broad application in materials engineering.

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Ultrasonically assisted Ni plating can alter the chemical and physical properties of electrolytic Ni and electroless Ni deposits. The addition of an acoustic field has been shown to promote beneficial effects on electrochemical processes in general [22–28,24,29] and electroless deposition in particular [30–39,30,31]. The use of ultrasound in electrochemical processes has been reported to improve the electrodeposition process itself as well as the characteristics of Ni deposits. Previous studies have indicated that ultrasonic agitation can increase the deposition rate [24,32,34,40,41] and increase the deposit hardness [24,25,28,34]. Other studies have shown that the acoustic field tends to decrease the residual stress [25,28] and enhance the wear resistance [28] and adhesion of the deposit to the samples [24,33]. In addition, a reduction of porosity has been observed [41,42].

While there are a number of studies concerning ultrasonically assisted methods for electrolytic Ni deposition [28,32,43,44] and others that have investigated the use of ultrasound in electroless NiP plating [45–49], there are only a few studies about the addition of ultrasound in electroless NiB coatings [43,50]. In addition, the previous studies concerning the creation of ultrasonically assisted NiB coatings were developed mainly for baths using amineborane compounds rather than sodium borohydride. The aim of this preliminary study is to develop ultrasound assisted NiB coatings reduced by borohydride to improve the properties of alkaline NiB plating. Electroless NiB is described in the literature as a high performance coating, however price of the chemicals used in the process are relatively expensive and this makes it less popular than other coatings in the industry. This work aims to increase the plating rate with the addition of ultrasound in the bath, in order to decrease production time and cost.

Ultrasound (20 kHz and 35 kHz frequency) was employed to agitate NiB electroless solutions to produce NiB coatings on mild steel. The microstructures, hardness, wear and corrosion resistances of the deposits were compared with mechanically agitated electroless NiB coatings.

2. Experimental procedure

2.1. Preparation of substrate

Mild steel (St-37) samples with dimensions of 25 mm × 25 mm × 1 mm were used as substrates. A hole of 2 mm in diameter was drilled in the border of one edge of each specimen for convenient hanging in the solution during plating. The substrates were prepared by mechanical grinding with SiC paper of 180, 500, and 1200 grit. After this process, the samples were cleaned and degreased with acetone. Just before plating, the samples were activated by etching in 32 vol.% hydrochloric acid for 3 min, directly followed by rinsing in flowing distilled water and immersion in the electroless Ni-B solution.

2.2. Electroless nickel baths

Electroless plating baths (500 ml) were prepared on a regulated hot plate (95 ± 1 °C) with magnetic stirring. The NiB bath was composed of sodium borohydride ($NaBH_4$) as reducing agent, nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) as nickel source, ethylenediamine ($NH_2–CH_2–CH_2–NH_2$) as complexing agent and lead tungstate ($PbWO_4$) as stabilizer. The bath pH was 12 ± 1. The precise bath composition is presented in Table 1.

Table 1
Bath composition of sodium borohydride reduced electroless Ni bath.

Nickel chloride	24 g/l
Sodium hydroxide	39 g/l
Ethylenediamine $NH_2CH_2CH_2NH_2$	60 ml/l
Lead tungstate	0.021 g/l
Sodium borohydride	0.602 g/l

2.3. Bath agitation

Three different methods of bath agitation were used during the plating process. The first (= classical) was a mechanical agitation generated by magnetic stirring while the temperature was maintained at 95 °C by a temperature regulated hot plate. For the second one, the agitation was generated by an ultrasonic probe with a frequency of 20 kHz and a power of 0.058 W/cm^3, estimated by the calorimetric method [26], with the temperature maintained once again at 95 °C by a temperature regulated hot plate. The third procedure consisted of a bath agitated by ultrasound at 35 kHz and 0.065 W/cm^3 of power while the temperature was kept at 95 °C by a thermostated water bath. Therefore for both the ultrasonically agitated solutions the power density used was approximately the same meaning that the main effect was ultrasonic frequency. In all three cases, the preparation of bath was carried out on a hot plate with mechanical agitation generated by magnetic stirring. Fig. 1 clarifies the methods employed for bath preparation and plating process.

2.4. Coating characterization

A Scanning Electron Microscope (Hitachi's SU8200) was used to study the cross morphology through a section of the coating, while the surface morphology was analysed by a HIROX KH-8700 Digital Optical Microscope.

In order to obtain the overall composition of the deposits, the samples were dissolved in aqua regia (1/3 nitric acid - 2/3 hydrochloric acid) and the resulting solutions were analysed by ICP-AES (inductively coupled plasma - atomic emission spectrometry).

Roughness measurements were carried out using a Zeiss 119SURFCOM 1400D-3DF. A Microhardness tester (Mitutoyo HM-200) equipped with Koop indenter was employed for hardness measuring. Hardness measurements were carried out on the specimens' cross sections under a load of 100 gf and load exertion time of 20 s.

The tribological behaviour of the samples was investigated using a pin-on-disk CSM microtribometer (without the use of lubricants) where the coated samples served as the disks and the counterparts were 6 mm diameter alumina balls with hardness of 1400 HV. The sliding speed and sliding distance were, respectively, 12 cm/s and 200 m. Wear tests were carried out under normal loads of 10 N, at 20 °C and with 45% humidity.

Bio-logic SP-50 equipment was used in this study to obtain potentiodynamic polarization curves in 0.1 M NaCl solution. The tests were performed in a standard three-electrode cell. Platinum plate and Ag/AgCl (KCl saturated) electrode were used as counter and reference electrodes, respectively. Before the polarization analysis a 20 min OCP was applied. A potential range of ±0.6 V Vs OCP, at 1 mV/s scan rate, was employed.

3. Experimental results and discussion

3.1. Structural and morphological characterization

Surface observation of the coatings by optical microscope (Fig. 2) shows the typical cauliflower-like texture for mechanically agitated electroless NiB coatings (a). The surface texture of NiB coatings produced using 20 kHz ultrasonic agitation has a similar structure but visually appears smoother. However when 35 kHz