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Effect of thermochemical and heat treatments on electroless nickel–boron

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ABSTRACT

Electroless nickel–boron synthesized on mild steel was submitted different post-treatments (heat and thermochemical). The resulting surfaces were examined and characterized by scanning electron microscopy. XRD analysis was performed to investigate structural modifications. The samples were also tested under corrosion conditions and polarization measurements were performed.
For both the as-plated and treated Ni–B coatings, correlations between electrochemical and microstructural characteristics were observed and it was found that post-treatments transform the coating to a crystalline form that increases corrosion resistance.

1. Introduction

Electroless deposition process experienced numerous modifications to meet the challenging needs of a variety of industrial applications since Brenner and Riddell invented the process in 1946 [1]. Nickel–boron (Ni–B) coatings are primarily used in applications that benefit from a coating with relatively high hardness, corrosion and wear resistances. Due to these properties, electroless Ni–B coatings have found many applications, including those in aerospace, nuclear, petroleum, chemicals, plastics, optics, etc. [2].

To improve the Ni–B deposit properties, appropriate treatments (thermochemical and heat treatments) were performed. They modify the deposit structure allowing the precipitation of Ni–B phases. The crystallization and phase transformation behaviour of electroless-plated deposits has been the subject of various investigations. It is shown that different alloy compositions and treatment conditions could affect both the microstructural characteristics and crystallization behaviours of the deposit [3–5].

The present work intends to deposit Ni–B on steel substrates in order to evaluate its structural and corrosion properties. The effects of heat and thermochemical treatments were investigated.

2. Experimental setups

2.1. Electroless nickel–boron plating

Disc steel substrates (disc coupons with a diameter of 100 mm, 1 mm thick) were used for the deposition of Ni–B films. Before coating, the samples were mechanically cleaned. Subsequently, they were manually ground on 1200 and 4000 grade SiC paper successively, degreased with acetone, rinsed in distilled water and air-dried. The sample surfaces were finally activated with 30 vol.% HCl for 1 min, rinsed in distilled water and immersed in the deposition bath.

The bath was based on $NiCl_2 \cdot 6H_2O$, sodium borohydride and sodium hydroxide. It has been described elsewhere [6]. The volume of the bath was 8 dm^3 and it operated under constant agitation.

The coating experiment was conducted without interruption for 90 min with an addition of reactive after the first 30 min (i.e. bath regeneration). The bath regeneration was carried out using statistical data and allowed the realisation of thick deposits. The obtained thickness was over 30 µm. The thickness was calculated from the weight gain.

Some samples were subsequently submitted to heat or thermochemical treatment.

Heat treatments were performed in a furnace, under a controlled atmosphere containing 95% Ar and 5% H_2 at 400 °C during 1 h. This treatment will be referred to as "HT".

Samples were also treated thermochemically. Two kinds of nitrogen diffusion treatments were performed. The first was a low pressure treatment and it was performed in a nitrogen based atmosphere (at 500 °C during 2 h). This thermochemical treatment will be referred to as "TCTN". The second treatment, based on ammonia, was performed using an industrial process by Bodycote (Belgium). This thermochemical treatment will be referred to as "TCTA".

The different kinds of treatment which used were summarized in Table 1.

2.2. Coating investigations

Philips PW 1710 X-ray diffractometer (XRD) apparatus, applying Co Kα, was employed to analyze the crystal structure of the coated film.

Philips XL 20 scanning electron microscopy (SEM) apparatus was used to characterize the structure and morphology of the coatings.

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Table 1
Applied treatments.

	Heat treatment	Thermochemical treatment	
Gas nature	Ar and H_2	N_2-based	Ammonia
Nomenclature	HT	TCTN	TCTA

Corrosion behaviour was investigated using a Parstat 2273 potentiostat. The electrochemical experiments were carried out in 0.1 M NaCl, at room temperature with a conventional three-electrode cell. A platinum grid was used as a counter electrode, an Ag, AgCl/KCl (sat'd) electrode as a reference electrode and the sample was installed as the working electrode. For measurements, the coatings were masked with silicone so that only a 1 cm^2 area was exposed to the electrolyte. The anodic polarization curves were measured by a dynamic potential scanning technique. The electrode potential was raised from −600 to +250 mV at the rate of 10 mV mn^{-1}. The samples were immersed into electrolyte for about 15 min prior to testing to allow the stabilisation of the open-circuit potential.

3. Results and discussions

3.1. Microstructural characteristics

Deposition of the coating is a surface induced phenomenon so all areas are coated with an even thickness including inbound and outside corners and blind holes. The cross section morphologies of the deposit are shown in Fig. 1. The coating is compact; and, as a consequence, good mechanical and anticorrosive properties of the composite coating are expected [7]. Some pores in the coatings at the initial deposition stage may result from hydrogen evolution during the electroless deposition. Bath regeneration is materialized by a white line on the micrograph. SEM shows that Ni–B presents a columnar structure in its as-deposited condition. After "HT" and "TCTN" treatments the structure becomes denser. The "TCTA" treatment produces a structure which is composed by a dense inner layer, a porous outer layer and at the surface a quite denser white layer caused by the nitrogen treatment process.

As-deposited Ni–B films are considered as a mixture of nanocrystalline nickel and amorphous Ni–B phases when analyzed by X-ray diffraction [8–11] and even by TEM [12]. The effects of treatment on the film structure are dependent on the conditions (time, temperature, pressure and treatment medium chemistry and nature), as shown on Fig. 2. Heat treatment induces the apparition of the Ni_3B phase, Fig. 2A. The deposits appear thus to be composed of Ni_3B nickel boride — and likely of partially crystallized boron based phases — instead of Ni_3B, Ni_2B and Ni phases.

TCTA treatment induces a complete crystallization of the deposit but the Ni_3B phases appear to be less predominant in the samples submitted to this treatment as most of its peaks do not appear while more peaks linked to the Ni_2B and Ni_4B_3 are observed, Fig. 2B.

It appears evident that after TCTN treatment, two kinds of crystalline diffraction peaks corresponding to Ni_2B and Ni_3B were observed, Fig. 2D. This indicates that both phases were formed conjointly during the treatment.

3.2. Corrosion properties

Polarization curves are shown in Fig. 3. The corrosion current density (I_{corr}) and the corrosion potential (E_{corr}), determined from the electrochemical test [13] are two parameters that can indicate the resistance of corrosion [14,15]. The loss in protective ability of the coatings is clearly evident from the higher corrosion current densities and the cathodic shift in the corrosion potential.

The result reveals that for the Ni–B coated steel, the value of E_{corr} is less negative and the corrosion rate I_{corr} is lower than the steel sample. These results indicate that Ni–B improves corrosion behaviour of mild steel.

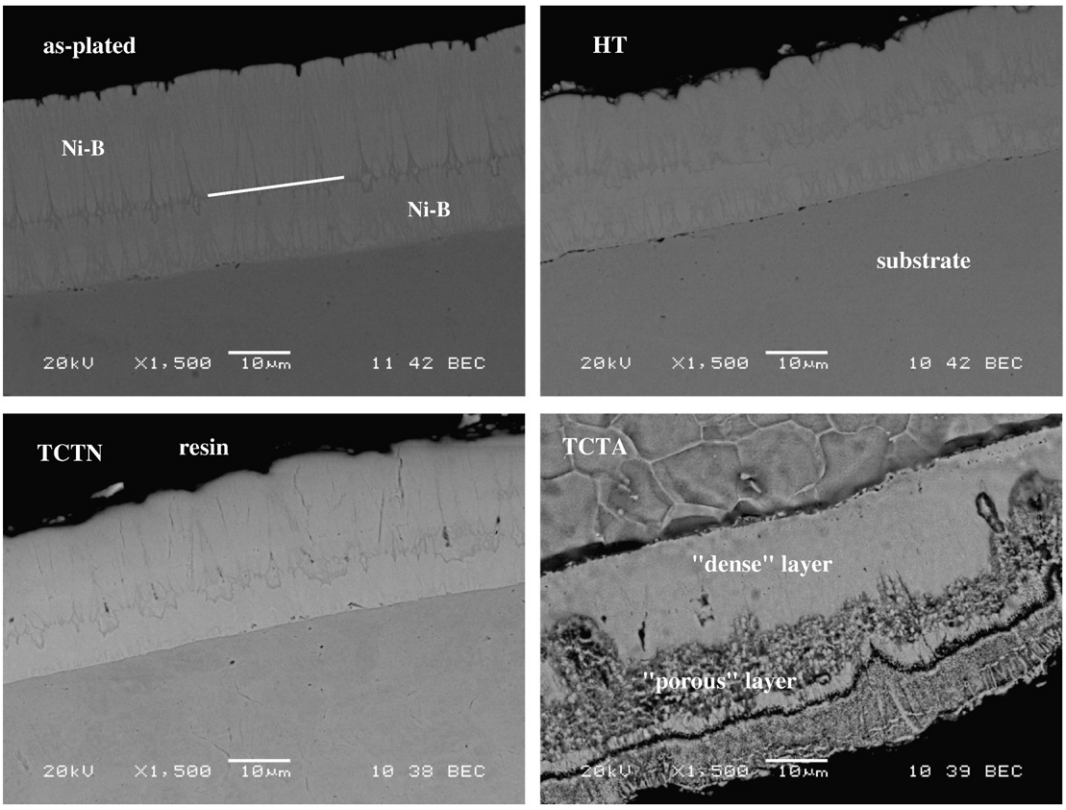

Fig. 1. SEM cross section morphology of Ni–B coating with replenishment.