Initiation and formation of electroless nickel–boron coatings on mild steel: Effect of substrate roughness

V. Vitry [a,*], A.-F. Kanta [b], F. Delaunois [a]

[a] Université de Mons, Service de Métallurgie, Place du Parc, 20, 7000 Mons, Belgium
[b] Université de Mons, Service de Science des Matériaux, Place du Parc, 20, 7000 Mons, Belgium

ARTICLE INFO

ABSTRACT

The initial deposition and growth of electroless nickel–boron deposits on mild steel were studied: the films were prepared in an electroless plating bath using sodium borohydride as reducing agent. Samples were immersed in the plating solution for times from 5 s to 1 h and the morphological evolution of the deposit was followed by scanning electron microscopy (SEM) observation of the surface and prepared cross sections. Energy dispersive X-ray spectrometry (EDX) and glow discharge optical electro spectroscopy (GDOES) analyses were used to obtain information about the chemistry of the deposits and their results were correlated with the morphology of the coating. The initiation mechanism of electroless deposition on mild steel was identified. The effects of substrate roughness variation on the morphology and growth rate of the coatings were investigated by reproducing the experiment on samples with various surface preparation (grinding) states. We observed that the increase of substrate roughness favors the deposit initiation: the density of nickel nodules increases with increasing roughness of the substrate. Longer immersions in the bath lead to homogenization and densification of the coating and the nodules are clearly distinguishable.

1. Introduction

Electroless coating is a well-established surface engineering process that was developed by Brenner and Riddel in 1946 [1]. It involves deposition of a metal–metalloid alloy coating on various substrates (including dielectric materials) by electrochemical reactions in aqueous solution. Electroless nickel deposits possess a number of interesting properties such as uniform thickness, high hardness, good corrosion resistance, etc. [2–5].

Electroless nickel deposits are usually classified according to the nature of the reducing agent. Nickel–phosphorous deposits (based on reduction by the hypophosphite ion) are the most studied and used but the properties of nickel–boron deposits are of very great interest for several industrial applications like aeronautics, petrochemical industry, food industry, firearms, etc.: their hardness is higher than nickel–phosphorous, and their electrical and tribological properties are very promising [6–14].

Most of the papers focused on electroless nickel and particularly on nickel–boron describe the optimization of plating parameters, the coating properties or the effect of heat treatment. There are very few papers dealing with deposit formation [7,8].

Electroless plating occurs by the reduction of nickel ions at the surface of the active substrate immersed into the plating solution and further growth of the coating is due to a catalytic action of the deposit itself [15,16]. There are 3 known ways of inducing the initiation of electroless nickel deposition. Either the substrate is spontaneously catalytic for the oxidation of the reducing agent, or it is more easily oxidizable than nickel, in which case a thin catalytic layer of nickel is spontaneously deposited, or finally it can be activated by dipping in a solution of catalytically active metal salts (like Pd) or by galvanic coupling [4]. The few studies dedicated to the initiation mechanism of electroless deposition focused on systems in which catalysts, such as Pd are used [17–22]. This means that if no catalyst is used, the actual mechanism that allows initial deposition on a determined substrate is rarely known and is at best proposed by assumptions.

The initiation and the growth of nickel–boron coatings have a non-negligible influence on their properties. In the case of experimental, unreplenished baths, the structure and the composition of the coating are not homogeneous over the coating thickness but change during the deposition, as was shown in the extreme case of a non-agitated bath by Rao et al. [23]. However, the observation of the formation of nickel–boron deposits has not been studied extensively yet, opposite to the growth of nickel–phosphorous coatings that has been studied on various substrates with and without catalytic activation [17–22,24–27].

* Corresponding author. Tel.: +32 65 37 44 38; fax: +32 65 37 44 36.
 E-mail address: veronique.vitry@umons.ac.be (V. Vitry).

Table 1
Deposition time for the observation of the initiation of electroless deposits.

Sample	1	2	3	4	5	6	7	8	9	10
Deposition time	5 s	15 s	30 s	60 s	90 s	4 min (240 s)	7 min (420 s)	10 min (600 s)	30 min (1800 s)	60 min (3600 s)

It is also well known by the electroless platers that the state of the substrate has a great influence not only on the plating process, but also on the coating properties [28,29]: surface roughness can for example affect the coating appearance. Although this may appear to be the most trivial of the problems caused by surface roughness, it is often important in terms of potential lost revenue [30]. It is thus clear that controlling surface roughness is important in terms of quality and functionality.

The substrate roughness is a parameter that is sometimes difficult to control in an industrial process: most parts are supplied by the client without particular surface preparation. They also often have complicated geometries (because the plating of this kind of parts is a major application of electroless plating). For this reason, mechanical preparation (such as grinding) may be difficult to implement. As such, it is of great interest for the final application of the process to gain the most extensive knowledge of the influence of the substrate surface condition on the initiation.

The aims of this work were to observe and describe the initiation and formation of electroless nickel–boron deposits on mild steel, to relate the properties of the coating to this formation and to evaluate the effects of substrate roughness on the formation of the deposit. To study the influence of roughness on the initiation, samples were submitted to different mechanical preparation processes, using varying grades of SiC grinding paper.

2. Experimental details

2.1. Sample preparation

The morphological and chemical evolution of the deposited material during the plating was investigated on the same substrate (St 37 steel). Samples (steel sheets with a thickness of 1 mm) were prepared for deposition by mechanical grinding, acetone degreasing, acid etching (activation) in 30% hydrochloric acid and deionised water rinse. They were then immersed in the electroless nickel–boron bath. The bath was based on nickel chloride and sodium borohydride, with lead tungstate as a stabilising agent. More details on the bath composition have been given by Delaunois et al. [31,32]. The same bath composition was used for the whole process.

The samples were immersed in the plating solution from 5 s to 60 min (Table 1). After immersion in the electroless bath, the samples were rinsed with deionised water and then dried in hot air.

A specific experiment, using a bath without reducing agent, was designed for the identification of the initiation mechanism.

To study the influence of roughness on the initiation, mild steel (St 37) samples were submitted to different mechanical preparation processes (with varying grades of SiC grinding paper) before the chemical step of the surface preparation (Table 2).

Table 2
Mechanical preparation processes for substrate roughness influence on deposit initiation.

	Polishing process description
N_P	Unpolished substrate (as received)
P_1	Polished with grade 220 SiC paper
P_2	Polished with grade 1200 SiC paper
P_3	Polished with grade 4000 SiC paper

2.2. Deposit analysis

To assess the nucleation sites and the initiation mechanism, the progressive spreading of the deposit on the surface, and other parameters linked to the first stages of the deposition process, the surface was investigated by several analytical techniques, such as SEM, EDX analyses and roughness measurement.

The roughness of the samples was measured by the mechanical stylus method, using a Zeiss Surfcom 1400D-3DF apparatus.

A Jeol JSM 5900 LV scanning electron microscopy (SEM) apparatus was used to characterize the structure and superficial morphology of the coatings. Cross sections were ground to mirror polish using a diamond paste (1/4 μm) and then etched using 10% nital before SEM observation.

During the SEM experiment, the average nickel and iron content of the surface was measured by EDX analysis. This allowed us to obtain an approximation of the nickel coverage ratio of the surface and subsurface (EDX analysis is not limited to the surface of the sample but gives an average composition for the upper part of the sample).

EDX analysis was used to determine a 'nickel coverage ratio' of the coating. To obtain consistent results, a surface of 1 mm^2 was analyzed at a magnification of 100 times, during 60 s. The results of this analysis represent the composition measured on the surface of the sample. However, this does not represent the uppermost surface because the penetration depth of the EDX analysis is of the order of 1 μm. Moreover, as boron is not detected by this technique, the nickel/iron ratio cannot be used as a quantitative tool. Nevertheless, this analysis allows detecting the complete absence of nickel on the surface and gives qualitative indications about the formation of a continuous coating.

Profile composition of the coating was determined by GDOES using a Horiba-Jobin-Yvon GD-Profiler 2 apparatus.

3. Results and discussion

3.1. Initiation and formation of the deposit on polished mild steel substrates

The first step of the study was the observation of the formation and morphological evolution of the nickel–boron deposit on substrates submitted to the standard surface preparation method (that was used for most of our studies: mechanical polishing of all surfaces up to the grade 4000 SiC paper [33]). All the samples studied in Sections 3.1 and 3.2 were synthesized in a complete deposition bath containing the reducing agent, as opposed to the bath used in Section 3.3.

3.1.1. Surface observation

Immersion in the bath up to 15 s brought no evidence of nickel deposition detectable by SEM observation. This period can be considered, as far as the microscopic observation is concerned, as an induction period. The first nodules of electroless deposit are observed after an immersion of 30 s and are preferentially concentrated on the scratches and defects of the surface. As can be seen on Fig. 1a, they do not form a continuous layer yet and their size is in the range of 0.1–0.2 μm. After 60 s, the islands have colonized the whole sample surface but they do not form a continuous layer yet (Fig. 1b). At very high magnification, it is possible to see that, on some places of the samples, several layers of nodules are present