

A Study of Electroless Nickel-Boron Coating Process

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(Received 4th June 2007, revised 5th April 2008)

Summary: An electroless nickel-boron coating method has been developed that attempts to overcome the problems that are generally associated with the process of applying coatings. The problems include irregular film deposits and brittleness. The method is versatile and is applied for coatings on a number of substrates, including brass, copper, mild steel and stainless steel AISI 316L. Growth rates of 14 to 22 microns per hour are possible. The deposited coating thickness varied with the amount of complexing agent added to the solution, sodium borohydride concentration and to the bath temperature. When the deposits are annealed at 400 °C, transformations of amorphous nickel-boron deposits to crystalline nickel and Ni₃B are obtained. The boron content in coated film varied from 1.26 % to 4.15 %.

Introduction

Electroless nickel deposits have been studied extensively, since Brenner and Ridell [1] discovered the electroless deposition process. The nickel-boron deposits [2-4] have got wider application than the nickel-phosphorus deposits, due to the superior hardness, wear resistance and solder ability. The nickel-boron coating is deposited by an autocatalytic reduction of nickel ions by borohydride compounds, typically sodium borohydride. The requirements for the nickel-boron deposits are; nickel salts in a suitable form, a reducing agent to convert the nickel salt to its metallic form, a stabilizer to control the reaction conditions and a catalyst. The characteristics of a nickel-boron electroless coating solution and its deposits are determined by the composition of the components. The reaction conditions are controlled in such a way that deposition ceases at room temperature and can only commence when energy is supplied in the form of heat. Normal operating temperatures for plating are from 85 to 95 °C.

To start the coating process a very small current is produced by a galvanic action between two dissimilar metals. Once the first layer is formed the reaction is autocatalytic and newly formed nickel acts as the catalyst for the further breakdown of the nickel chloride into nickel boride and nickel. The chemical reaction causing the deposition of metal will continue as long as the conditions are satisfied and reactants remain in contact.

In this study, an attempt has been made to deposit electroless nickel-boron. A number of

parameters such as solution temperature, concentration of complexing agent and sodium borohydride concentration have been varied to see their effect on the deposition rate. Micro hardness, structural features and phase transformation of the nickel-boron films before and after the heat treatment are also investigated.

Results and Discussion

Dependence of deposition rate on temperature, complexing agent and sodium borohydride concentration was studied. These parameters were found to be the main factors determining the deposition rate. Complexing agent is added to avoid spontaneous decomposition of the solution and to control the reaction so that deposit only forms on the substrate. Ethylene diamine was used as complexing agent here, which also prevents precipitation of nickel hydroxide. However, such strong complexing agent decreases the rate of deposition as shown in Fig. 1. It was observed that the rate of deposition decreases with the increase of ethylene diamine. Optimum concentration of 60 ml/L was chosen, as below this concentration the solution was unstable and precipitation as nickel hydroxide occurred.

Temperature has a strong effect upon the deposition of nickel-boron alloy from borohydride reduced solutions. It was observed that the deposition was very low at 60 °C but, increased rapidly with the increase of temperature as shown in Fig. 2. The deposition was found maximum at 95 °C. However,

above this temperature solution became unstable and decomposed at a much quicker rate than when working at 85 to 95 °C.

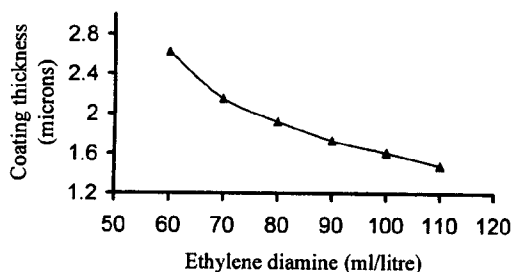


Fig. 1: Influence of ethylene diamine concentration on the nickel-boron deposition.

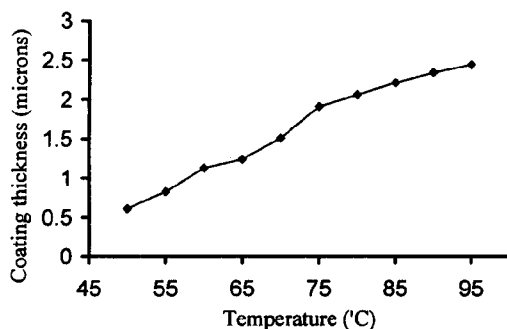


Fig. 2: Influence of solution temperature on nickel-boron deposition.

Fig. 3 showed the variation of deposition at different concentrations of sodium borohydride. It was observed that the deposition rate decreased with the increase of sodium borohydride concentration. It was noticed that at higher concentrations beyond 0.75 g/L the solution became unstable and decomposed rapidly with the formation of metallic nickel on the walls of the container (glass).

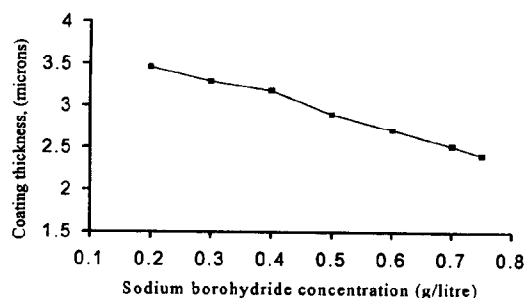


Fig. 3: Influence of sodium borohydride concentration on nickel-boron deposition.

The thickness of the coating was measured with an optical microscope. An optical micrograph of nickel-boron film deposited on a copper substrate at 400X magnification was shown in Fig. 4. It was found that the deposit was uniform over the entire surface of the substrate. The coating thickness would be controlled up to a limit of 21 micron by simply controlling the deposition time. The plating specimens were examined microscopically and the examination revealed negligible porosity and excellent adherence of the deposit on the substrate.

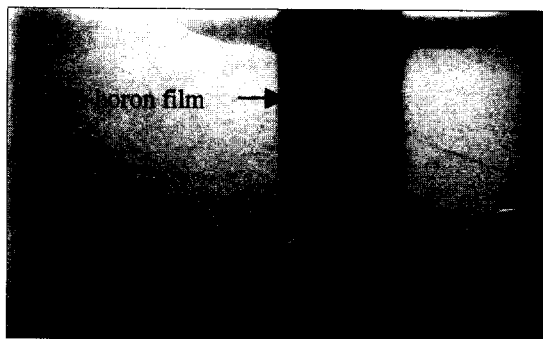


Fig. 4: Optical micrograph of as deposited nickel-boron film at 400X magnification.

To study structural transformations in as deposited coatings on annealing, XRD spectra were taken. The X-ray diffraction spectrum of the as deposited coating showed no peak of crystalline nickel or nickel boride in the 2θ region of 40° and 50° showing that the as deposited films are amorphous (Fig. 5(a)). The 2θ peaks at 43.2 , 50.3 , 74.2 and 89.9 are of the $\text{Cu}\alpha_1$ due to the copper substrate. A typical X-Ray diffraction spectrum obtained after annealing at 400°C was shown in Fig. 5(b). The diffraction spectrum clearly showed that crystallization has taken place. The reflections from the film surface were identified as those from crystalline nickel and Ni_3B phase. Sharp reflection peak corresponding to Ni (III) (which has a FCC structure) and less intense peaks of Ni_3B (which has orthorhombic structure) were observed. This proved that the phase of crystalline nickel predominates over the Ni_3B phase.

Fig. 6 showed the influence of annealing temperature on the hardness of the film. It was observed that as the temperature of annealing increased from 250°C to 400°C the film hardness increased due to the formation of crystalline nickel

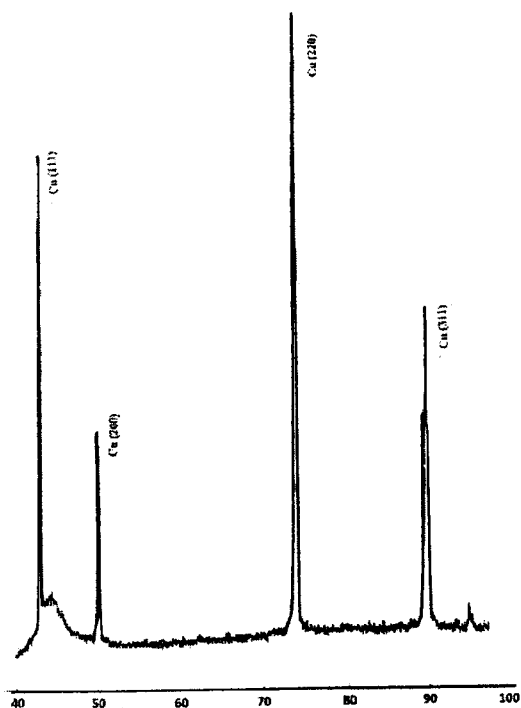


Fig. 5(a): X-ray diffraction spectrum of as deposited nickel-boron coating on copper substrate.

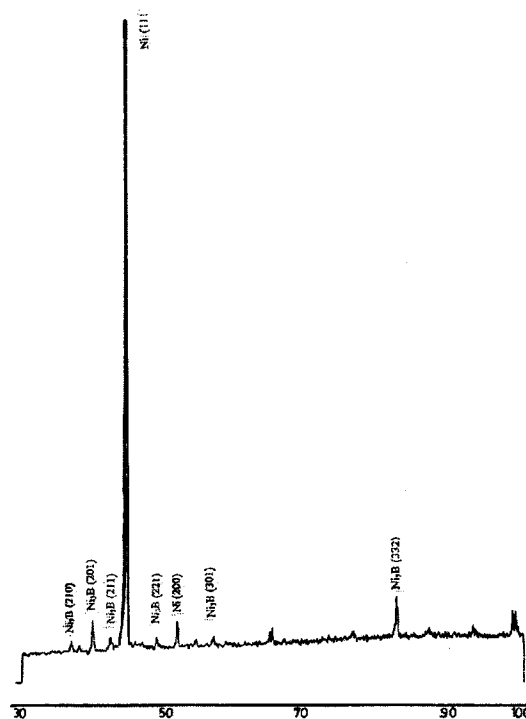


Fig. 5(b): X-ray diffraction spectrum of nickel-boron deposit annealed at 400 °C for 2 hours duration.

and Ni_3B . Above this temperature up to 600 °C a decrease in film hardness was noticed, which might be due to the re-crystallization of the precipitates and growth of the precipitates as explained by Kumar and Nair [5] and Gaevskaya *et al.* [6].

The results of this study demonstrated the possibility of obtaining electroless nickel-boron deposits on brass, copper, mild steel and stainless steel 316L. On annealing at 400 °C, it is seen that the nickel-boron film transforms to crystalline nickel and

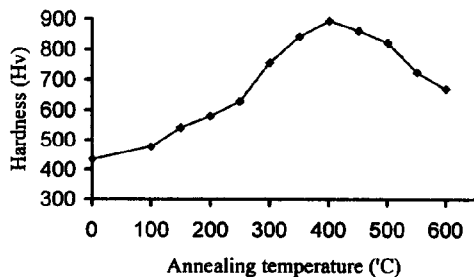


Fig. 6: Variation in hardness of nickel-boron deposit at different annealing temperatures.

Ni_3B phase. The micro hardness of the as deposited film was about 500 Hv and after annealing at 400 °C it increased to about 1100 Hv.

Experimental

Chemicals

All chemicals, nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) E. Merck, sodium borohydride (NaBH_4) Sigma, sodium hydroxide (NaOH) E. Merck, ethylene diamine ($\text{C}_2\text{H}_8\text{N}_2$), orthophosphoric acid (H_3PO_4) E. Merck, and hydrochloric acid (HCl) E. Merck, were of analytical reagent grade. Distilled water was used to dissolve the chemicals and to make up the solutions up to the mark, as required.

Rectangular specimens of stainless steel 316L, mild steel, copper and brass measuring $10 \times 20 \times 2$ mm size were cut from their respective sheets. Pretreatment of the specimens was carried out to prepare them for electroless nickel-boron coating. Oxide (scale) was removed by rough polishing. All the specimens except stainless steel were polished

down to 1 micron. Stainless steel specimens were polished electrolytically. The chemical composition of the polishing solution is given in Table-1.

The stainless steel specimens were treated as anodes in the polishing solution at current densities of 8 to 10 A/dm² for 10 minutes duration at 50 °C temperature. Stainless steel is passive and needs surface activation in a strike solution to permit application of nickel-boron deposit. The chemical composition of the strike solution is given in Table-2.

Table-1: Composition of polishing solution.

| | |
|----------------------|--------|
| Chromium trioxide | 120 g |
| Orthophosphoric acid | 840 ml |
| Distilled water | 140 ml |

Table-2: Composition of nickel strike solution.

| | |
|-------------------|--------|
| Nickel chloride | 45 g |
| Hydrochloric acid | 100 ml |
| Distilled water | 850 ml |

Stainless steel specimens were cathodically treated in the strike solution at current densities of 5A/dm² for 1 minute duration at room temperature prior to nickel-boron deposition. Fig. 7 'a' and 'b' showed the flow sheet of the pre-plate and post-plate treatments adopted for plating the specimens.

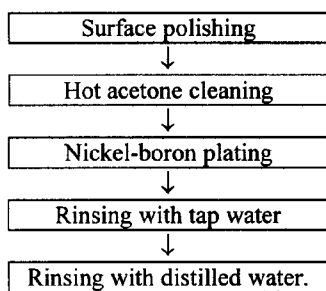


Fig. 7(a): Flow sheet (pre- and post-plate treatment) for copper, brass and mild steel specimens.

Several compositions were investigated. The most suitable composition found is given below:

| | |
|--------------------|---------|
| Nickel chloride | 25 g/L |
| Sodium borohydride | 1.5 g/L |
| Ethylene diamine | 60 ml/L |
| Sodium hydroxide | 70 g/L |
| Sodium citrate | 50 g/L |

The pH of the solution was maintained from 12 to 14 with the addition of sodium hydroxide. The

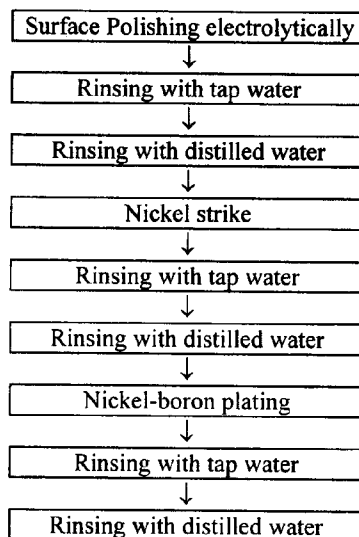


Fig. 7(b): Flow sheet (pre- and post-plate treatment) for stainless steel AISI 316.

solution was some what unstable and needed careful control to prevent decomposition.

Boron contents in the deposits were determined using Varian (Model 1475) atomic absorption spectrophotometer. Thickness of the films was determined metallographically at a magnification of 400 X. To observe the effect of heat treatment on film hardness the deposits were annealed at 250 °C for 90 hours and air cooled. Oxidation of the deposits did not occur after annealing at 250 °C. The deposits were also annealed at 250, 300, 350, 400, 450, 500, and 600 °C at a heating rate of 35 °C per minute for two hours in an argon atmosphere and air cooled. Micro hardness testing was performed with DM-400T, LECO micro hardness tester. Loads between 25g and 100g were employed. Measurement of indentation size was carried out using the optics of the instrument. Micro hardness of the deposits was estimated by using the equation as follows [7]:

$$H_f = H_s + \frac{(H_c - H_s)}{2C_{1,2} t/D - C_{1,2}^2 (t/D)^2} \quad (1)$$

where H_f , H_s and H_c were the hardnesses of the film, substrate and composite, respectively. The subscript 1 is for model 1, where the film is assumed to be plastically strained to match the shape of the indenter tip, and the subscript 2 is for model 2, which is used for a hard and brittle film on a soft substrate (model 2

has been used in our present case). In the equation, $C_1 = 0.1403$, $C_2 = 0.0728$, t is the film thickness and D is the indent penetration depth.

X-ray diffraction data were collected from a microprocessor controlled JEOL X-Ray diffractometer system (Model JDX-9C) with vertical goniometer using filtered copper $K\alpha$ radiation operated at 40kv and 30mA as the tube voltage and current, respectively.

References

1. A. Brenner and G. Riddell, *Proc. Amm. Electroplaters Soc.*, **33**, 23 (1946).
2. M. Takahashi, Y. Tatento, M. Koshimura and T. Suzuki, *Japan T. Appl. Phys.*, **19**, 2335 (1980).
3. K. Masui and M. Masuda, *J. Metal Finishing Soc. Japan*, **36** (2), (1985).
4. G.O. Mallory and V. A. Lloyd, *Plating and Surface Finishing*, **72**, 64 (1985).
5. P. S. Kumar and P. K.Nair, *Metals, Materials and Processes*, **7**, 131 (1995).
6. T. V. Gaevskaya, Novotortseva and L. S. Tsybulskaya, *Metal Finishing*, **6**, (1996).
7. B. Jonsson and S. Hogmark, *Thin Solid Films*, **114**, 257 (1984).