

## Effect of Annealing Temperature on the Corrosion Resistance of Electroless Produced Ni-B-W Coatings

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**Abstract.** The present work deals with the formation of Ni-B-W coating on steel by electroless plating process and evaluation of their corrosion resistance after applying heat treatments at different temperatures for 1 h. The Ni-B-W coating was prepared using alkaline borohydride-reduced electroless nickel bath. Scanning electron microscopy of the surface cross-sectional view of the electroless Ni-B-W coating was analyzed and layer characteristics was investigated. Coating structure was investigated using XRD. The study reveals that the Ni-B-W coating is amorphous in their as-plated condition and upon heat treatment at 400 °C for 1 h, Ni-B-W coating crystallize and produce nickel and nickel borides in the coatings. Annealing temperature dependence of the corrosion resistance of the coating was investigated by potentiodynamic polarisation measurements. These results show that the Ni-B-W coating annealed at 650 °C exhibit better corrosion resistance than those of coatings with other annealing temperature. The corrosion resistance increased after the crystallisation of the coating, due to factors like; decrease of porosity and internal stress and the formation of tungsten oxide on the surface acting as a protective layer.

### Introduction

Among various surface techniques, electroless deposition is a chemical deposition technology, involving the deposition of metals from solution onto surfaces without applying an external electric voltage. Electroless nickel coatings, which exhibit characteristics of high hardness, uniform thickness, corrosion and wear resistance, have been considered as a promising hard coating and widely used for a variety of industrial applications [1-3]. In recent years attention has shifted towards borohydride reduced electroless nickel deposits because Ni-B coatings have higher hardness and wear resistance. The major limitation of Ni-B coating is its relatively poor corrosion resistance compared to electroless Ni-P deposits [4]. Some ternary nickel based alloys are developed to further improve the properties of binary systems by adding a second to meet some special demands. Codeposition of W element has been of considerable interest because of its unique properties, such as excellent corrosion-, wear-, electrical- and high temperature resistant [4]. By applying heat treatment, structure of the coating changes from amorphous structure to crystalline. This change causes an increase in hardness and wear resistance due to the formation of grains and hard precipitations [5,6]. But unfortunately up to date, only limited investigations have been conducted on the effects of heat treatment and nanocrystalline structure on corrosion properties of Ni-B-W coatings. The present work aims to analyze the effect of heat treatment on Ni-B-W coating characterized for their morphology and to evaluate its corrosion resistance.

### Experimental Procedures

10x10x60 mm plain carbon steel (AISI 1020) samples were used as the substrate material. The plain carbon steel substrates were grinded (up to 1200 paper) and polished and then soaked in the trichloroethylene, cleaned with detergent in an ultrasonic bath at 70 °C. Lastly, samples were placed in a 30% HCl solution for 2 minutes followed by a rinse using distilled water. Immediately after the

treatment, electroless deposition was carried out, according to the specification given in Table 1. A new formulation was formed for electroless Ni-B bath. Any water-soluble borohydride can be used; however sodium borohydride was preferred because of having high degree of water solubility and stability in aqueous solutions [7]. The stabilizer used was lead tungstate. It does not have environmental problems like thallium nitrate [8]. Potassium hydroxide was preferred to establish. Any water soluble salts can be added to provide nickel ions into the bath. Nickel chloride was used because its anions are inert with respect to the other ingredients in the alkaline coating bath. To prevent precipitation of nickel hydroxide, complexing agents such as ethylenediamine is required in the bath because of the high alkalinity of the coating bath [9]. The bath composition and operating conditions used for preparing Ni-B-W coating was given in Table 1. During preparation of the bath, a magnetic stirrer was used. 2.6 ml reducing solution and 2.6 ml stabilizing solution were added into the heated bath every 30 minutes during the coating procedure and then cleaned substrates were placed in the bath.

**Table 1:** Composition of the bath and experimental parameters used for electroless Ni-B-W coating

Operation	Plating bath composition		Condition
Electroless Ni-B-W	NiCl <sub>2</sub>	24 g/l	pH 13.5 ±0.2 Temp. 88±2 °C Time 2 h
	EDA	60 ml/l	
	KOH	26.5 g/l	
	NaBH <sub>4</sub>	120 g/l	
	NaOH	263 g/l	
	PbWO <sub>4</sub>	2.6 g/l	
	EDTA	13 g/l	
	Na <sub>2</sub> WO <sub>4</sub> 2H <sub>2</sub> O	40 g/l	

The boron content of the deposits was analyzed by atomic absorption spectrophotometer. The nickel content was analyzed gravimetrically after precipitating nickel as Ni-DMG complex. The structure of the Ni-B-W deposit, in as-plated and heat-treated (at different temperatures for 1 h) conditions was assessed by X-ray diffraction (XRD), with a Cu-K  $\alpha$  radiation ( $\alpha = 0.154178$  nm) and a monochromator at 50 kV and 300mA. Scanning electron microscope was used to obtain the cross-sectional micrographs and surface morphology of Ni-B-W layer. Corrosion resistance and possible passivation behavior of the samples, electrochemical measurements were performed on an Electrochemical Analyzer. Linear sweep voltammetry experiments were carried out in a 3,5 wt.% NaCl aqueous solution using a classic three-electrode cell with a platinum plate (Pt) as counter electrode and a Ag/AgCl electrode as reference electrode at room temperature. The working electrode was cleaned in acetone agitated ultrasonically, rinsed in deionized water before the test. The coated samples were masked with lacquer so that only 1 cm<sup>2</sup> area was exposed to the electrolyte. During the potentiodynamic sweep experiments, the samples were first immersed into electrolyte for about 10 min to stabilize the open-circuit potential (OCP)  $E_0$ . Tafel plot was transformed from the recorded data and the corrosion current density ( $i_{CORR}$ ) was determined by extrapolating the straight-line section of the anodic and cathodic Tafel lines.

## Results and Discussions

**Composition and morphology of the coatings.** The chemical composition of the coating was analysed by using EDS. Results can be seen in table 2.

Table 2: Chemical composition of Ni-B-W coating (wt. %)

Ni	B	W
93,8	5,1	1,1

Figure 1 shows the XRD pattern of Ni-B-W coatings on the steel substrate in as plated and heat treated conditions. The diffraction patterns of as deposited Ni-B-W and Ni-B-W coating annealed at 250° C had only a single broad peak at  $2\Phi=44.8^\circ$  corresponding to the (111) plane of FCC structure of nickel phase and it is clear from the patterns that the Ni-B-W depositions were amorphous. Heat

treated Ni-B-W coatings at 350° C were decomposed to produce nanocrystalline Ni and Ni<sub>3</sub>B phases as shown in figure 1. However crystallization of Ni<sub>2</sub>B phase has not started before 400° C heat treatment of the coatings. Peak intensities of nanocrystalline nickel phase increased sharply and the broadness of the peaks has been decreased due to grain size growth of nickel phase upon heat treatment.

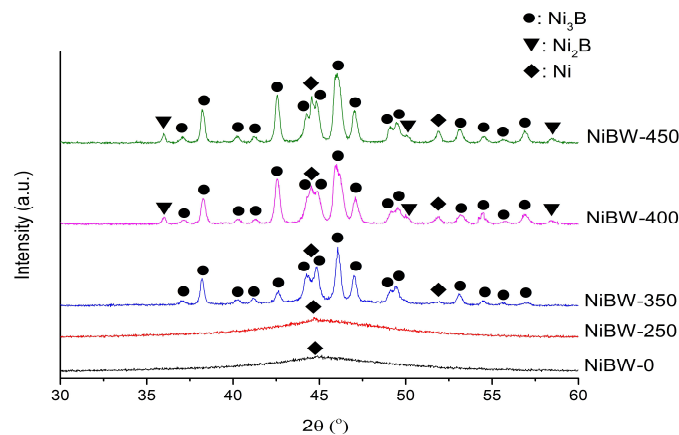


Figure 1: XRD pattern of the Ni-B-W coating at different annealing temperatures

The as-plated Ni-B-W coating (fig. 2-a) shows typical spherical nodular morphology with good uniformity. The surface morphology of the Ni-B-W coating after heat-treatments above 300 °C (figures 2 c-e) indicates the formation of well developed crystallites. The regions, which appear spherical nodules, are due to the precipitation of crystalline nickel and nickel borides (Ni<sub>2</sub>B and Ni<sub>3</sub>B) in the coatings. It is evident that the coating is uniform. The cross-section morphology of the as-plated Ni-B-W coating detected by SEM was shown in figure. 2-f. It can be seen that the coating is also connected closely to the substrate and hence should exhibit good adhesion to the substrate.

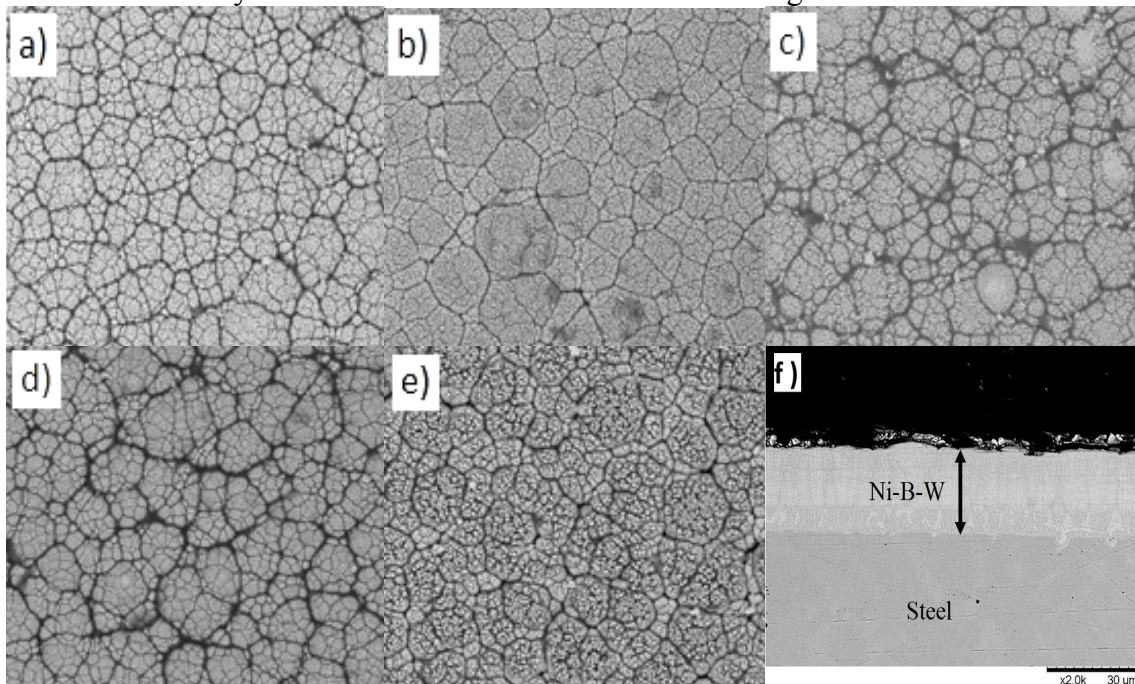


Figure 2: The surface morphology of as-plated (a), heat treated at 250 0C (b), 350 0C, (c) 400 0C, (d) 450 0C Ni-B-W coating and the cross-section (f) detected by SEM

**Potentiodynamic polarisation.** At the beginning of the analysis of the corrosion resistance, the effect of the addition of tungsten in the coating is investigated by polarization curves (table 3). Ni-B and Ni-B-W coatings show great positive shifts in corrosion potential and evident decreases in corrosion current density in comparison with their steel substrate. From table 3 can be seen that addition of W lead to an increase in corrosion resistance. Similar finding has been reported byXiao-ming and co-workers [10].

Table 3: Corrosion resistance of as plated electroless Ni-B and Ni-B-W coatings in 3.5% sodium chloride solution evaluated by potentiodynamic polarization

System studied	E <sub>corr</sub> (mV)	i <sub>corr</sub> (μA/cm <sup>2</sup> )
Substrate (St)	-611	23,08
Ni-B	-476	16,43
Ni-B-W	-468	9,25

The corrosion resistance of the as-deposited and heat treated Ni-B-W coatings is investigated by polarization curves. The results can be seen in table 4. Figure 3 shows the electrochemical polarization curves of Ni-B-W coatings in as-plated (a) and heat treated for 1h at 250 °C (b), 350 °C (c), 400 °C (d), 450 °C (e), 550 °C (f) and 650 °C (g) conditions in a 3,5 wt% NaCl aqueous solution at room temperature. No defects were assumed to be present in the tested samples according to the polarization curve. As seen from figure 3, the cathode reaction in the polarization curves corresponded to the evolution of the hydrogen and the anodic polarization curve was the most important features related to the corrosion resistance. As shown in Table 4 and figure 3, the Ni-B-W coating heat treated at 650 °C has the most positive corrosion potential E<sub>corr</sub> and the lowest corrosion current density i<sub>corr</sub> among the studied coatings.

Table 4: Corrosion resistance of as plated and annealed electroless Ni-B-W coatings at different temperatures in 3.5% sodium chloride solution evaluated by potentiodynamic polarization

Ni-B-W coating	i <sub>CORR</sub> [mA/cm <sup>2</sup> ]	E <sub>CORR</sub> [mV]
As-plated	5,13	-502
250 °C	7,39	-504
350 °C	4,44	-502
400 °C	7,07	-517
450 °C	3,2	-470
550 °C	3,17	-394
650 °C	3,4	-298

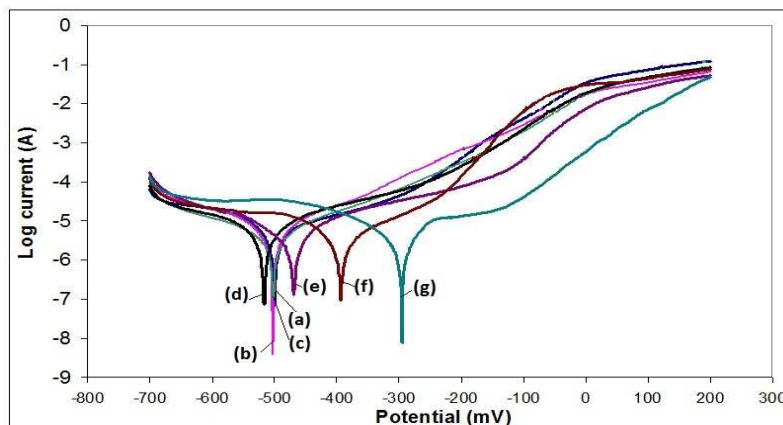


Figure 3: Anodic polarization curves of as-plated (a) and annealed Ni-B-W coatings for 1 h at b) 250 °C, c) 350 °C, d) 400 °C, e) 450 °C, f) 550 °C, g) 650 °C in a 3,5 wt% NaCl aqueous solution

The corrosion potential E<sub>corr</sub> of was -298 mV and the corrosion current density i<sub>corr</sub> was 3,4 μA/cm<sup>2</sup>. The most corrosion resistance had the 400 °C heat treated coating with corrosion potential E<sub>corr</sub> of 517 mV and corrosion current density i<sub>corr</sub> of 7.07 μA/cm<sup>2</sup>. It also can be seen that corrosion resistance increased after heat treatment at 400 °C.

In figure 4 the surface morphology of as-plated (a), heat treated at 350 °C (b), 400 °C (c), 450 °C (d) Ni-B-W coatings, detected by SEM after polarization test in 3.5% sodium chloride solution, can be seen. Pin holes, formed due to corrosion on the coating surfaces which are heat treated at 400 °C, can clearly be seen.

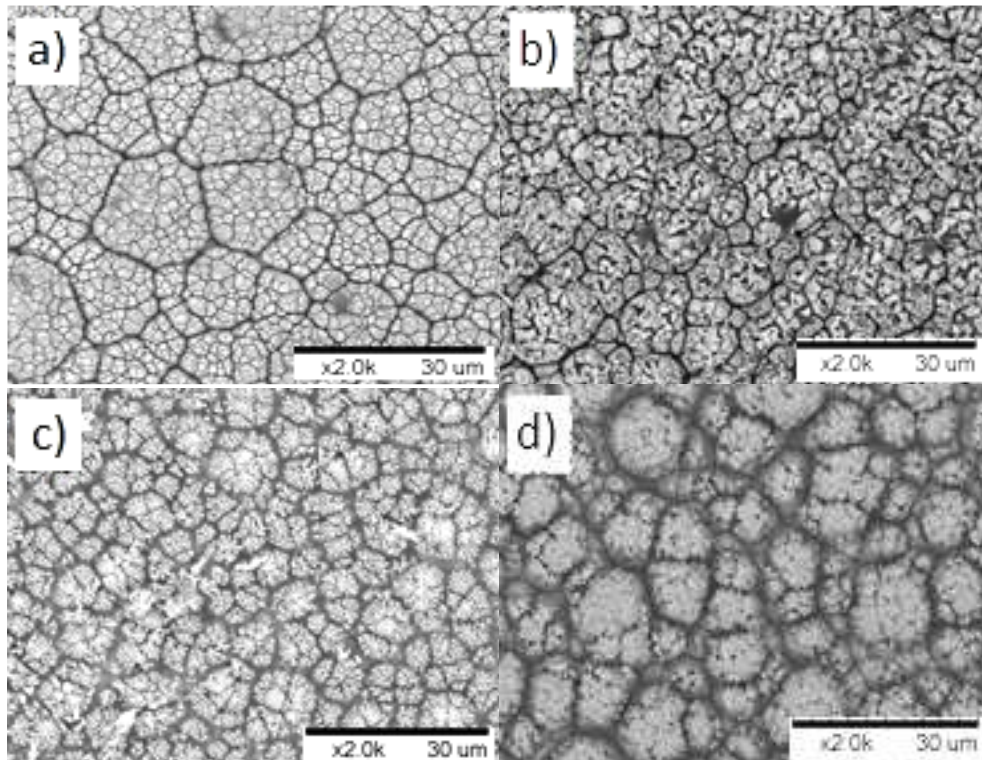


Figure 4: Surface morphology of as-plated (a), heat treated at 350 °C (b), 400 °C (c), 450 °C (d) Ni-B-W coatings detected by SEM after polarization test in 3.5% sodium chloride solution

In order to explain the variation of corrosion resistance with annealing temperature, factors which might be involved in corrosion mechanism, are analyzed. These factors are; degree of crystallisation, grain size, relative amount of various phases, internal stress, the addition of a third metal and amount of porosity [11]. According to the early work by Song [12] and Xie et al [13], the internal stress produced in the process of electroless deposition is tensile. Corrosion resistance of coatings is affected by the stress state of the coating; and larger tensile stress causes greater tendency for corrosion to occur. During electroless plating, the whole deposition reaction process is accompanied by hydrogen evolution. The hydrogen atoms are occluded in as-plated deposits, generating internal tensile stress within the coatings. Therefore, when the coating is subjected to a heating process, relief of the tensile stress is expected, which may enhance corrosion resistance of the coatings. Combined effects from several factors result in the lowest corrosion resistance for the coating annealed at 400 °C. At this temperature, the phase transformation from amorphous to a crystalline structure is detected. These formed nanocrystals and grain boundaries are adequate to corrosion attack. Also the precipitation of  $\text{Ni}_2\text{B}$  and  $\text{Ni}_3\text{B}$  phases are enhancing the formation of micro-galvanic cells between these phases and Nickel. Another factor, which increased the corrosion resistance after heat treatment at 400 °C for 1 h, is the existence of tungsten. By addition of a third passivation element, tungsten, corrosion resistance of the coating improved due to the huge amount of grain boundaries acting as diffusion paths provided by the nanostructure. The diffusion of tungsten through the grain boundaries to the coating surface resulted in the formation of the dense tungsten oxide film on the surface, which act as a protective layer. By increase of annealing temperature, amount of porosity inside the coating is decreased, which could be another reason for increase of corrosion resistance.

## Conclusion

Ni-B-W coatings was prepared on steel by electroless deposition using suitable baths. The Ni-B-W coating is amorphous in their as-plated condition. After heat-treatment at 400 °C for 1 h, Ni-B-W coatings crystallize and produce nickel and nickel borides. SEM of the surface morphology and cross-section view of the coatings reveals that the coatings are uniform and the compatibility is good. Corrosion resistance of the Ni-B-W coating strongly depends on the annealing temperature.

Corrosion resistance of the coating annealed at 400 °C, at which crystallization formation was detected, was the worst among all coatings. By further increase of annealing temperature, corrosion resistance increased. Corrosion resistance of the coating annealed at 650 °C was the highest among the coatings annealed. This was because of factors like; the decrease of internal stress and amount of porosity, the formation of Ni<sub>2</sub>B and Ni<sub>3</sub>B phases which generated micro-galvanic cells and the existence of tungsten. Tungsten diffused through the grain boundaries and formed a dense tungsten oxide film on the surface. This work reveals that by applying heat treatment on Ni-B-W coating over 400 °C, not only hardness and wear resistance increases, as mentioned in the literature, but also corrosion resistance increases. This property could not be detected by Ni-P coatings. This study will be developed by analyzing the effect of annealing temperature on corrosion resistance of different Ni-B-X coatings, where X refers to a third element, such as molybden, cobalt or copper.

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