

A Study of the Chemical Composition and Heat Treatment of Electroless Ni-B-Tl Alloy Coating on AISI 316 Stainless Steel

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Abstract

Despite having some useful properties, stainless steels suffer from the lack of suitable surface hardness. In this research electroless Ni-B-Tl coating was used with the aim to increase their surface hardness. The effects of Nickel chloride, Sodium borohydride, Thallium nitrate and Ethylenediamin on the chemical composition of coating were studied. To achieve an increase in hardness, the effects of heat treatment on the hardness of the deposited layer at various temperatures, were also studied. The results showed that the deposition rate and surface hardness of the deposited layer were affected by the variation in concentration of bath components. The micro structure of the electroless Ni-B-Tl coating consists of nickel and super saturated solid solutions. It was also found that the hardness of the coating was increased due to the formation of Ni₂B and Ni₃B phases during heat treatment.

Keywords: Electroless deposition, Ni-B-Tl coating, Bath composition, Heat treatment.

Introduction

Austenitic stainless steels of types 304, 316, 321, and 347 are the primary materials of choice for a very broad range of applications when one needs corrosion resistance in aqueous solutions at ambient temperatures. While austenitic stainless steels are excellent for their corrosion resistance, they possess low hardness values and cannot be heat-treated to increase their hardness^{1,2}. Several methods such as nickel based electroless, hard chromium electroplating and CVD have been suggested to improve their surface hardness^{3,4}. Among all plating methods, the usage of Ni-B-Tl electroless plating is now spreading because of its higher quality and uniform thickness⁵⁻⁸.

In electroless deposition process, the extent of segregation of metalloid alloys (in this research B and Tl) determines its crystallinity. If the extent of segregation of metalloid alloys is relatively large, the nucleation of nickel phase will be prevented, and this will result in an amorphous structure^{8,9}.

Properties of electroless coating could be affected by variation in concentration of each component of the bath. To achieve a coating with desirable properties, it is very important to determine the optimum concentration of the bath components. The results of previous studies have also shown that a suitable heat treatment improves the tribological and mechanical properties of the electroless Ni-B-Tl coating^{6,7,10}.

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Due to lack of enough investigations on the electroless Ni-B-Tl coatings, the aim of the present work is to study the effects of concentration variations and heat treatment temperature on coating properties.

Experimental procedures

Samples of AISI 316 stainless steel with dimensions 1×10×40 mm were used as substrate material for deposition of electroless Ni-B-Tl coatings. First, the surfaces of samples were mechanically cleaned from corrosion products and then degreased with a detergent solution, acetone and NaOH 2.5 N solution at 60 °C for 15 min. The samples were then rinsed in distilled water and were finally deoxidized and activated by using HCl 30 Vol.% at an ambient temperature for 2 min, and HCl 20Vol.% at 50°C for 30 s. The chemical composition of the electroless Ni-B-Tl coating bath is given in Table 1.

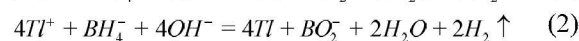
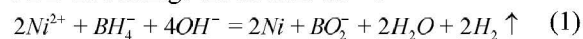
Chemical composition of the coating was evaluated using GBC XM atomic emission inductively coupled with plasma-atomic emission spectroscopy.

Deposition of coating was conducted at 94 °C for 1 hour, maintaining a ratio of solution volume to deposition area of approximately 25 ml/cm². The structures of deposits were determined using a D5000 Siemens X-ray diffraction with the wavelength of CuK_α radiation. Vickers micro hardness measurements of the deposited layer were also carried out using a Bohler apparatus and by employing a load of 100 g for a period of 10 s.

Table 1. Chemical composition of employed Ni-B-Tl bath.

Bath composition		g/l
Metallic ions	Hexahydrated nickel chloride	15-50
	NiCl ₂ × 6H ₂ O	
Alkalinity reserve	Sodium hydroxide	42
	NaOH	
Complexing agent	Ethylene diamine	32-72
	N ₂ C ₂ H ₈	
Stabilizer	Thallium nitrate	0.012-0.042
	TlNO ₃	
Reducing agent	Sodium borohydride	0.5-1.8
	NaBH ₄	

The global deposition reactions in electroless Ni-B-Tl coatings are as follows ¹¹⁾:



Results and discussion

The scanning electron micrograph of electroless Ni-B-Tl coating is shown in Figure 1. It seems that the surface of the as-plated samples has uniformly and continuously been covered by cauliflower-like precipitates. Micrograph from transverse direction revealed that the coating has a fixed thickness all over the surface and is made up of three distinct internal, intermediate and external layers (Figure 2). It seems that the external layer is less compact as compared to internal and intermediate layers.

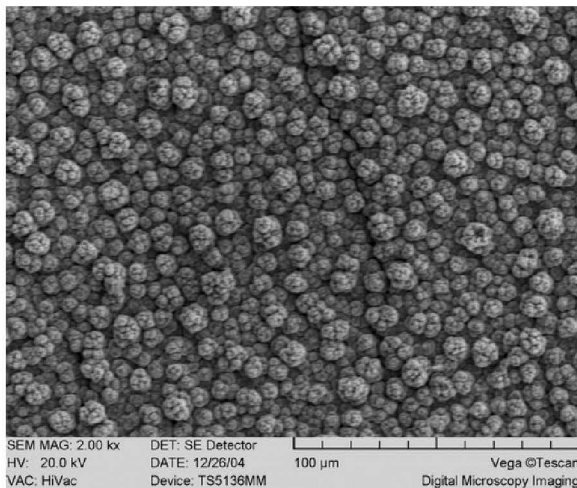


Fig.1. Scanning electron micrograph of electroless Ni-B-Tl coating.

The effect of NiCl₂ concentration on chemical composition of the coating over the concentration range of 15 to 50 g/l is shown in Figure 3.

According to reaction 1, the amount of deposited nickel on surfaces of specimens initially

increases with an increase in NiCl₂ concentration up to 31 g/l, and then decreases. The reason is related to the NiCl₂ content. When its content is more than 31 g/l, ethylene diamine concentration is not enough to form Ni-containing complex due to formation of Ni(OH)₂ precipitation in solution, resulted in a reduction in weight percentage of nickel in the deposited layer.

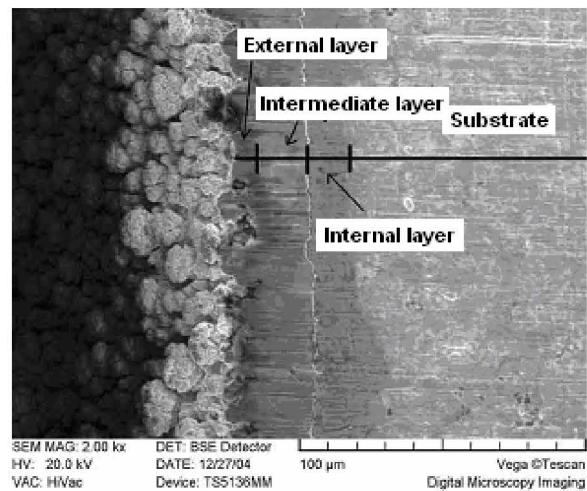


Fig.2. Electroless Ni-B-Tl coating in transverse section.

Figure 4 shows the effect of variation in ethylene diamine concentration (32-72 g/l) on chemical composition of the coating. Similar to the effect of NiCl₂, the nickel content of the coating increased with increasing ethylene diamine concentration up to 52 g/l. Further increase in its concentration reduced the stability and resulted in decomposition of the coating bath. Consequently, the weight percentage of the nickel was reduced. The formation of Ni(OH)₂ particles over the optimum concentration of ethylene diamine facilitated the reduction of nickel ions through the bath, and decomposition of the bath coating occurred because the small particles are suitable sites for nickel nucleation.

NaBH₄ is the most effective reducing agent. Variation in chemical composition of the coating as a

function of NaBH_4 concentration (0.5-1.8 g/l) is shown in Figure 5. Reactions 1-3 are accelerated due to an improvement in reduction ability of the coating bath achieved with increasing NaBH_4 concentration. Although all three reaction rates are accelerated, only the amount of Ni in coating is considerably increased as compared to those of B and Tl due to its higher concentration in the bath. The maximum weight percentage of Nickel was achieved at 1.2 g/l of NaBH_4 . Further addition of NaBH_4 gave rise to more decrease in Ni and an increase in B and Tl amounts of the coating due to gradual decrease in stability of the coating bath.

Figure 6 shows the effect of thallium nitrate on chemical composition of the electroless Ni-B-Tl coating over the concentration range of 12-42 mg/l. Thallium nitrate is the most powerful stabilizer, and

increases the deposition rates. However, further increase in TlNO_3 concentration to levels higher than its optimum amounts reduces the deposit rates due to its effect on lowering the oxidation- reduction reaction rate at the interface between solid and liquid.

According to the above reports, nickel reduction rate decreases with increasing TlNO_3 content beyond 22 mg/l.

The effect of heat treatment over the temperature range of 200-550°C for 1 hour on the micro hardness of the coating is shown in Figure 7.

It seems that heat treatment at temperatures 200°C improves the adhesion of the deposits on substrate only, and does not change their hardness. But heat treatment at a temperature above 350 °C enhanced the microhardness of the coating.

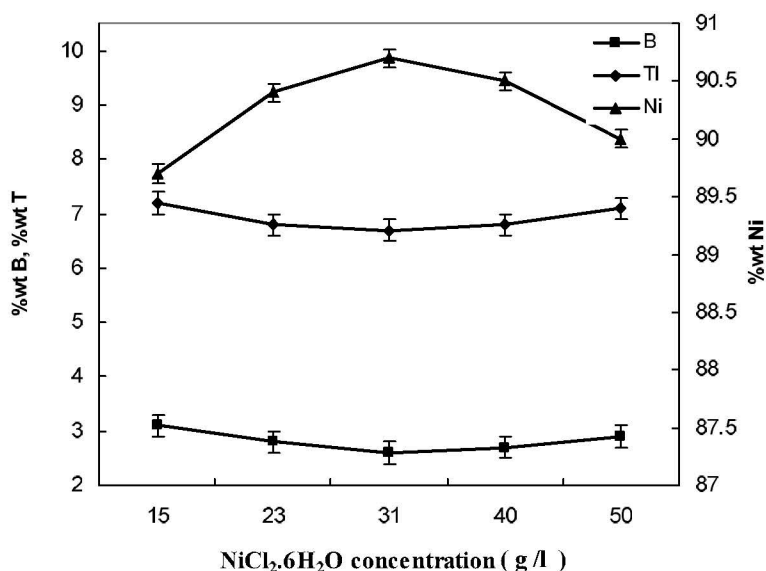


Fig.3. Effect of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ on chemical composition of the coating.

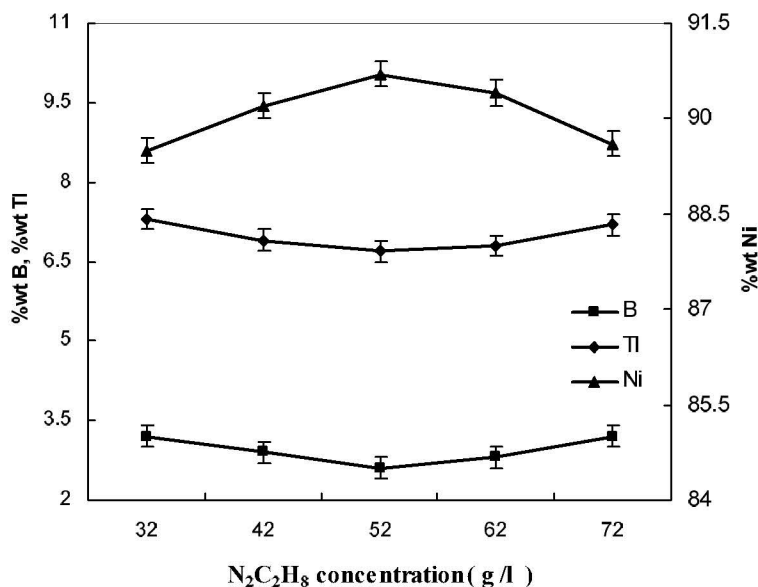


Fig.4. Effect of $\text{N}_2\text{C}_2\text{H}_8$ on chemical composition of the coating.

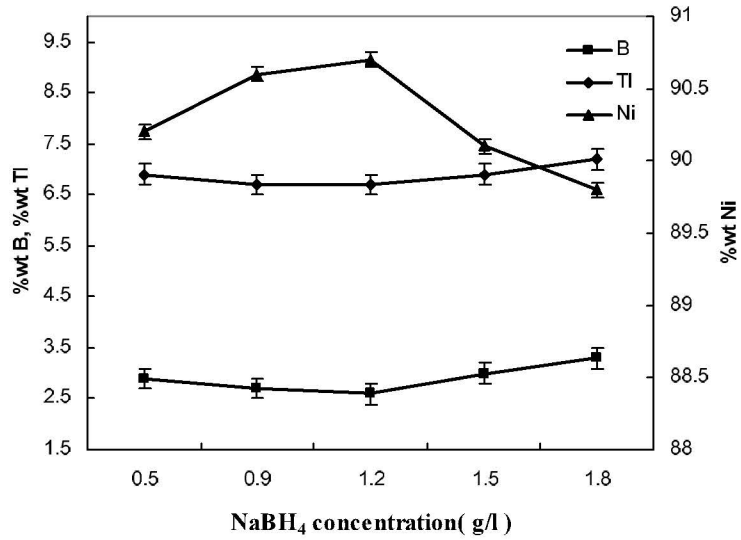


Fig. 5. Effect of Sodium borohydride on chemical composition of the coating.

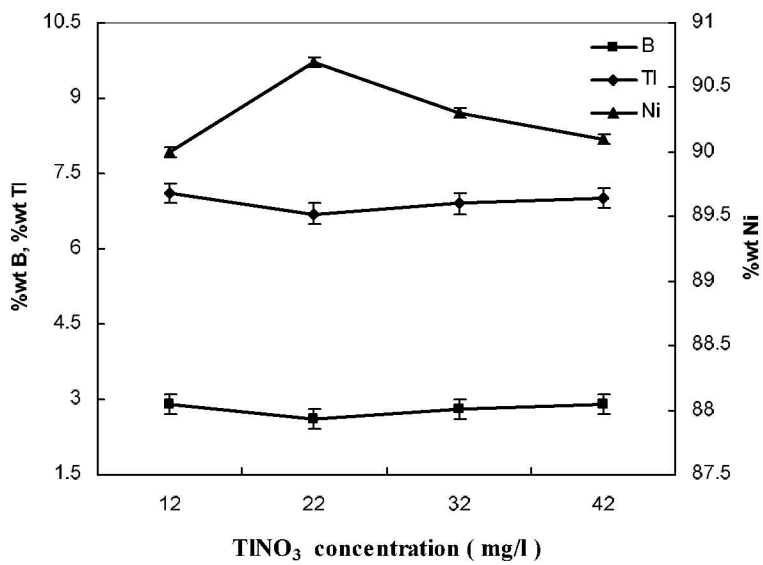


Fig. 6. Effect of Thallium nitrate on chemical composition of the coating.

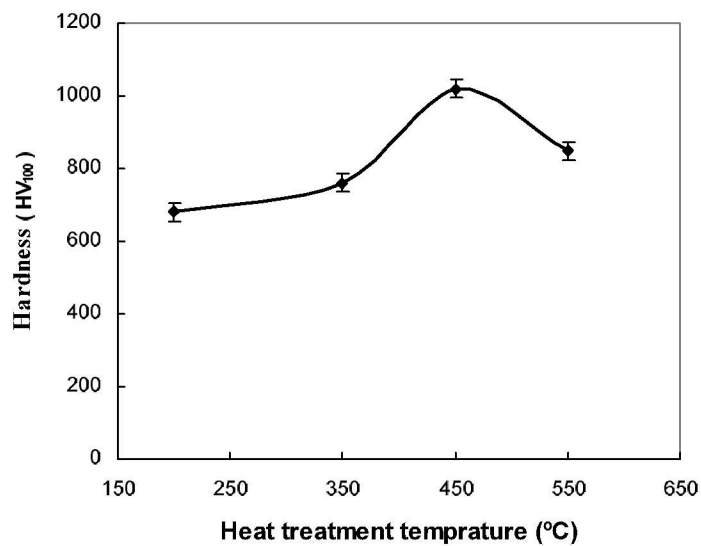


Fig. 7. Change in microhardness of electroless Ni-B-Tl deposit as a function of heat treatment temperature.

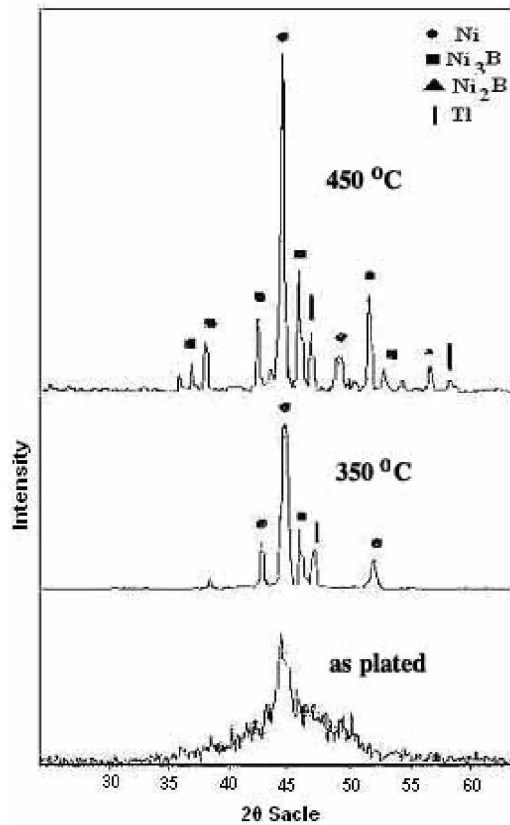


Fig.8. X-ray diffraction pattern of Ni-B-Tl coating after 1 h heat treatment at varies temperatures.

Maximum microhardness number of 1000 was achieved at 450 °C. The results of X-ray diffractometry from coated samples before and after heat treatment is shown in Figure 8. According to this figure Ni_3B and Ni_2B precipitates were gradually formed during heat treatment over the temperature range of 200-450°C.

The precipitation of the crystallized Ni_3B and Ni_2B particles resulted in an increase in hardness of the coating. At temperatures above 450°C, the microhardness of the coating was decreased due to growth of the nickel borides particles.

Conclusions

- 1- Electroless deposition technique resulted in the formation of a hard, uniform and continuous layer of Ni-B-Tl coating on the AISI 316 stainless steel.
- 2- The maximum nickel content of coating was achieved at following concentrations of coating bath: Nickel chloride: 31g/l, ethylene diamine: 52 g/l, sodium borohydride: 1.2 g/l and thallium nitrate: 22 mg/l.
- 3- During heat treatment over the temperature range of 200-550°C for a constant time (1h), maximum hardness was achieved at 450°C.

Acknowledgments

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