Effect of Thallium Content on the Physicochemical Properties of Electroless Ni-B Alloys

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The Ni-B-Tl alloys having 86.5–90% Ni were prepared from electroless nickel-acetate baths containing dimethylamine borane as a reducing agent. The co-deposition of Tl significantly decreased the B content of the alloys. Effect of Tl content on the structure of the alloys was investigated by X-ray diffraction and differential scanning calorimetry. Physicochemical properties of alloys having different Tl contents were discussed on the basis of the chemical composition and metallurgical structure of the Ni-B-Tl alloys.

1. Introduction

In general, electroless plating systems are unstable in a thermodynamic sense because of the presence of oxidizing and reducing agents in the same solution. It is possible, however, to improve the stability of the electroless bath by careful selection of stabilizers and operating conditions. For example, organic and inorganic thio-compounds as well as some heavy metal cations are commonly used as a bath stabilizer. In particular, thallous nitrate has the effective stabilizing action in electroless Ni-B plating system (1). However the effects of thallium co-deposited in Ni-B coatings are not fully understood.

In this study, Ni-B-Tl alloys prepared from the nickel-acetate bath by using dimethylamine borane (DMAB) as a reducing agent in the presence of thallous nitrate were tested. DMAB is oxidized on a catalytic surface and leaves electrons on the substrate. In the presence of nickel and thallous ions, Ni-B-Tl alloys are deposited on the catalytic surface. Physicochemical properties of the alloys, such as corrosion resistance, electrical resistivity and hardness, were examined in some detail as a function of the concentration of thallous nitrate in the bath.

2. Experimental Procedure

The Ni-B-Tl alloys with different thallium content were prepared from the electroless nickel-acetate bath shown in Table 1. The buffering action of the bath was so excellent that pH of the bath remained substantially constant during plating. Copper substrates (2×2.5 cm^2) subjected to the pretreatment described in the previous paper were employed (2). The deposition rate of the alloys was determined by measuring the weight gain due to plating.

The corrosion resistance of the alloys was evaluated by the weight loss during immersion in deaerated 0.5 M H_2SO_4 solution at 30°C. The potential sweep method (12.5 mV/s) was also employed to measure the polarization curves of Ni-B-Tl alloys

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Table 1 Composition and operating conditions of chemical nickel plating bath

$NiCl_2 \cdot 6H_2O$	0.08 M
$CH_3COONa \cdot 3H_2O$	0.40 M
$TlNO_3$	0 - 0.5 g/l
$(CH_3)_2NHBH_3$	4.0 g/l
pH	6.5
Temp.	60 °C

for the evaluation of corrosion resistance. The thickness of the coatings examined was about 10 μm.

The microhardness of the deposits plated on a copper substrate (15 μm) was examined with a Shimazu hardness tester at a load of 50 g. The electrical resistivity of the coatings (1 μm) plated onto a cylindrical ceramic (Mullite) was determined with a portable double bridge device (Model 2769, Yokogawa Electric Works). The hardness and electrical resistivity of the alloys were measured at room temperature before and after heat treatment. The heating was made at 400 °C for 1 h in vacuum (5×10^{-4} Torr).

An X-ray diffraction analysis of Ni-B-Tl alloys was carried out using Cu Kα (45 kV, 50 mA) to find out structural changes with thallium content of the alloys and the effect of heat treatment. Differential scanning calorimetry (DSC) was also performed at a heating rate of 10 °C/min under nitrogen atomosphere.

The thallium and boron contents of the alloys were determined by the method described elsewhere, and nickel content was calculated from the balance (2).

3. Results and Discussion

3.1 Deposition rate and composition of Ni-B-Tl alloys

The deposition rate of Ni-B-Tl alloys and thier composition are shown in Fig. 1.

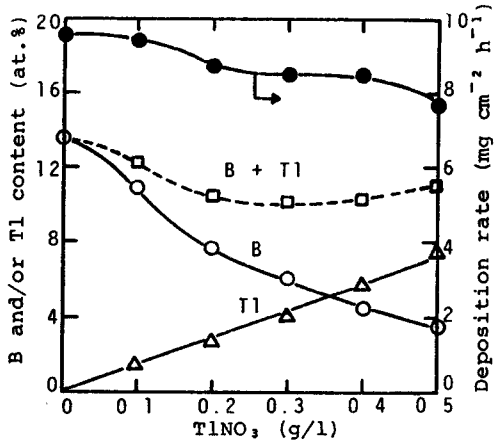

Fig. 1 Effects of $TlNO_3$ concentration on the deposition rate of alloy and its composition

The deposition rate of the alloys decreased from 9.5 to 7.6 mg cm^{-2} h^{-1} upon addition of 0.5 g/l $TlNO_3$. However, the effect of thallous nitrate on the deposition rate of the alloys was not critical under these conditions. The Ni-B-Tl alloys from the bath containing 0–0.2 g/l of thallous nitrate gave a granular surface with many micro-cracks. In contrast, smooth and sound deposit of Ni-B-Tl alloy was obtained by further addition of thallous nitrate. Thallium content of the alloys increased linearly up to 7.8 at.% with an increase in the concentration of thallous nitrate. This fact can be explained by assuming that the co-deposition of thallium may occur under diffusion control. On the other hand, boron content of the alloys decreased from 13.5 to 3.5 at.% with an increase in thallium content of the deposits; i.e., the co-deposition of boron was strongly inhibited by the presence of thallium. The sum of the thallium and boron contents, as indicated by dashed line in Fig. 1, had a minimum value in the range between 0.2 and 0.3 g/l, which corresponded to the maximum nickel content of about 90 at.%.

3.2 Corrosion resistance of Ni-B-Tl alloys

Corrosion resistance of the electroless nickel coating has been investigated by many authors in the past (3–4), however, little is known about the electrochemical aspects of co-deposited thallium and its effect on corrosion resistance. Corrosion rate of the Ni-B-Tl alloys was evaluated by the weight loss as well as the polarization technique. In the latter case, corrosion rate was calculated from the corrosion current obtained from the intercept of the Tafel lines in anodic and cathodic regions. The corrosion rates evaluated by the two methods were in good agreement. These data indicate that coatings having superior corrosion resistance can be obtained from the bath containing thallous nitrate of 0.2–0.3 g/l. Polarization curves of the Ni-B-Tl alloys were measured in deaerated 0.5 M H_2SO_4 solution to find the reason why the corrosion resistance varied with the concentration of thallous nitrate in the bath. In the cathodic region of the polarization curves as shown in Fig. 3, hydrogen evo-

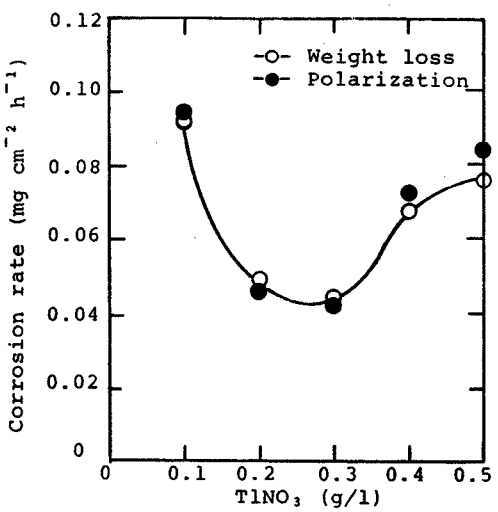

Fig. 2 Effects of $TlNO_3$ concentration on the corrosion rate of alloys

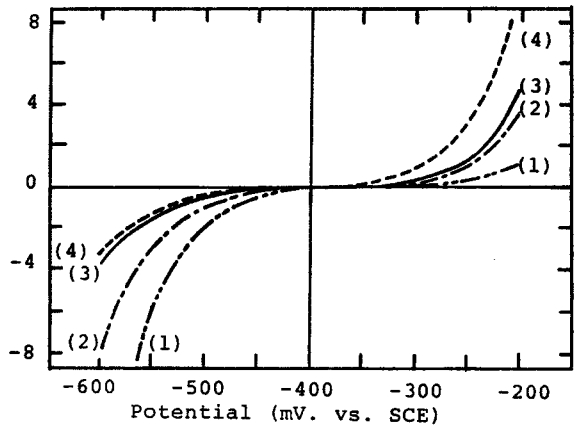

Fig. 3 Changes in polarization curves of alloys with $TlNO_3$ concentrations
$TlNO_3$ (g/l); (1) 0.1, (2) 0.2, (3) 0.3, (4) 0.4

lution reaction was strongly inhibited by the presence of thallium, which decreased the dissolution rate of Ni-B-Tl alloys. On the other hand, anodic reaction was accelerated by the presence of thallium, which gave rise to the increase in the dissolution rates of the Ni-B-Tl alloys. As a result of the superposition of the two opposite factors described above, the maximum corrosion resistance of Ni-B-Tl alloys can be obtained in the presence of 0.2 to 0.3 g/l $TlNO_3$.

3.3 Resistivity and hardness of Ni-B-Tl alloys

The electrical resistivity of electroless nickel coatings is an important physical property which can be modified by its composition and structure of the deposits. The resistivity of electroless Ni-B coating was found to be in the range of 13–136 $\mu\Omega$ cm (5–6), depending on the composition of the bath and operating conditions. In this study, the electrical resistivity of Ni-B-Tl alloys was investigated as a function of thallous nitrate concentration in the bath. The specific resistance of as-plated Ni-B-Tl alloys was in the range of 80–200 $\mu\Omega$ cm as shown in Fig. 4. These values are considerably higher than that of pure Ni (6.8 $\mu\Omega$ cm). This may be due to the highly disordered state of as-plated coatings as will be shown later by X-ray diffraction analylsis. On the other hand, resistivity of the alloys decreases significantly by heating at 400 °C for 1 h, which is in the range of 20–100 $\mu\Omega$ cm. Such a decrease in resistivity of the Ni-B-Tl alloys corresponded to the recrystallization of nickel and the formation of Ni_3B.

Hardness of electroless Ni-B deposits was found to increase from 600–700 Hv to 1100–1500 Hv upon heat treatment at 400 °C (1, 7). Such an increase in hardness was explained as a result of the precipitation of Ni_3B. Another factor affecting the hardness of the alloys, i.e., thallium content, was investigated in this study. The microhardness of the Ni-B-Tl coatings from the bath containing 0–0.5 g/l $TlNO_3$ is shown in Fig. 5. The hardness of the as-plated alloy coatings increased with the co-deposition of thallium until a limiting value of 850 Hv. In contrast, the hardness of the heat-treated samples decreased significantly with an increase in the thallium content of the alloys. According to the conventional precipitation hardening

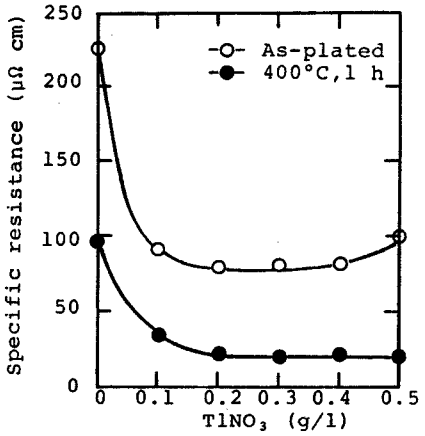

Fig. 4 The specific resistance of Ni-B-Tl alloys as a function of $TlNO_3$ concentration

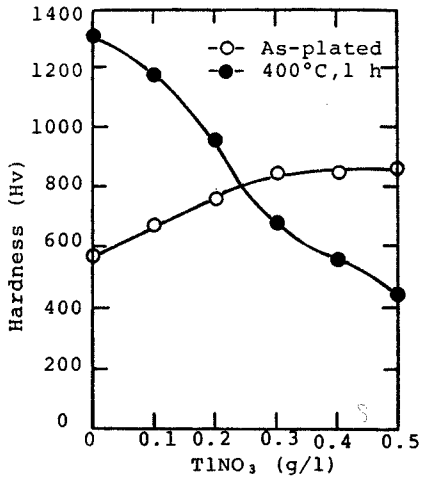

Fig. 5 The hardness of Ni-B-Tl alloys as a function of $TlNO_3$ concentration

mechanism, the higher boron content gives the harder deposits. This is true in this situation, as the harder deposits can be obtained for the higher boron content of the deposits (cf. Fig. 1). Heat-treated samples containing 3 at.% Tl or above became softer than as-plated samples. Under these conditions, the effect of the precipitation of Ni_3B becomes negligible, and that of the recrylstallization of nickel and relaxation of internal stress will be predominant.

3.4 X-ray and thermal analysis

The evidence of formation of Ni_3B was confirmed by the X-ray diffraction and thermographic analysis (1, 7). In the present study, the effect of thallium content on the phase transformation during heating of the Ni-B-Tl alloys are shown in Fig. 6.

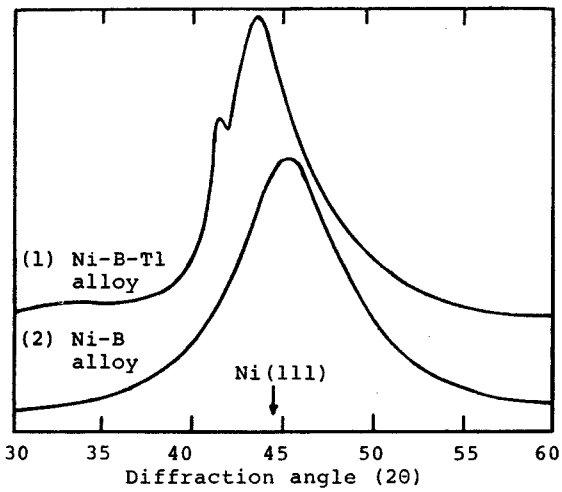

Fig. 6 Typical X-ray diffraction patterns of as-plated Ni-B and Ni-B-Tl alloys

As-plated Ni-B coatings had only one diffuse line corresponding to Ni (111); d=2.023Å. In contrast, Ni-B-Tl coatings containing 4.0 at.% Tl gave the double peaks corresponding to d=2.067Å and d=2.181Å. This fact implies that the lattice spacing between the planes of Ni (111) was increased by the co-deposition of thallium. The broadness of the diffraction lines indicates the characteristics of micro-fine structrues having essentially no long-range order. However, an apparent crystallite size calculated from Scherrer's equation was found to increase from 13 to 16 Å by the co-deposition of thallium. After heating in vaccum, the recrystallization of nickel and thallium as well as the formation of Ni_3B was confirmed in Fig. 7. When

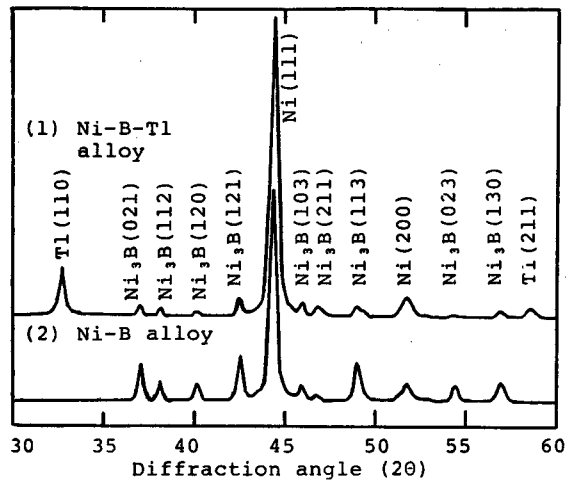

Fig. 7 Typical X-ray diffraction patterns of Ni-B and Ni-B-Tl alloys after heating at 400°C for 1 h

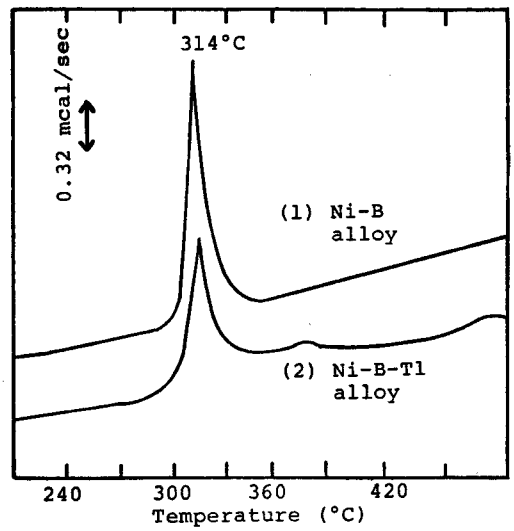

Fig. 8 Typical data for differential scanning calorimetry of Ni-B- and Ni-B-Tl alloys

heating was carried out in air, new peaks of Tl_2O_3 (222) and Tl_2O_3 (400) were observed while the intensity of the Tl (100) decreased. The intensities of the diffraction lines corresponding to Ni_3B or Tl were found to be proportional to the content of each component in the Ni-B-Tl alloys.

The typical data of the thermal analysis (DSC) of the alloy deposits are shown in Fig. 8. As can be seen from curve (1), the formation of Ni_3B occurs at ca. 314 °C, and this value agrees fairly well with the values reported by other authors (1, 7). As the boron content was highly depressed by the co-deposition of thallium, the heat of Ni_3B formation was confirmed to decrease with the co-deposition of 4 at.% Tl as shown by curve (2) in Fig. 8.

4. Conclusions

Effects of the variation in thallium content (0–7.8 at.%) on the structure, corrosion resistance, electrical resistivity and hardness of the Ni-B-Tl alloys were studied. It was found that an increase in thallium significantly depressed the boron content in electroless nickel coatings. X-ray diffraction and thermographic analyses of the alloy deposits showed that such a variation in composition of the alloys was accompanied by structural changes in the deposits. The electroless Ni-B-Tl alloys having 2.6–4.0 at.% Tl gave the superior corrosion resistance in sulfuric acid solution. The specific resistance of the alloys was found to change as a function of the thallium content. However, resistivity of the as-plated coatings was substantially constant (80 $\mu\Omega$ cm) under suitable conditions (0.2–0.4 g/l $TlNO_3$). After heating at 400 °C for 1 h, resistivity decreased to about 20 $\mu\Omega$ cm due to the recrystallization of nickel and thallium as well as the formation of Ni_3B. The hardness of the Ni-B-Tl alloys varied also as a function of the thallium content. The hardness of the as-plated samples increased with an increment of thallium content up to 800 Hv. On the contrary, the hardness of the heat-treated samples decreased monotonously from 1300 to 400 Hv with an increase in thallium content, which can be explained in terms of the decrease in boron content in the alloy deposits.

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