

ELECTRODEPOSITION AND CHARACTERIZATION OF NICKEL-TITANIUM – ZINC TERNARY ALLOY FROM A SULFATE BATH

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ABSTRACT : *Zn-Ni-Ti alloys were electrodeposited from a sulphate baths containing nickel sulphate 50 g/L, zinc sulphate 30g L, potassium titanium oxalate 2.0 g/L, ammonium sulphate 30g/L, concentrated hydrochloric acid 5ml/L. and one of the following addition agents ascorbic acid, glucose, glycerol, citric acid or thiourea. The alloy film containing 10.76- 35.96% Nickel , 0.06-0.75% Titanium and 63.29- 89.18% Zinc were formed. Smooth, grey, fine- grained and compact deposits were generally obtained at comparatively low current densities, pH and at high temperature. Microphotographs of the alloy plates obtained under various plating conditions were taken to examine their morphological behaviour. Microhardness of the films deposited at a given electrolytic condition was measured by Vicker's micro-hardness tester. A maximum value of 405 HV, 0.05 Kg was obtained in the presence of ascorbic acid as additive. Weight loss method was used to determine the corrosion rate of the various alloy films.*

I. INTRODUCTION

The fascinating field of electro deposition covers a wide spectrum of scientific and industrial activity related to rocketry, computers, space technology etc. A host of new innovations and developments have taken place in this field, in recent years. Modern technology has at its disposal a wide range of constructional materials like metals, alloys, plastics, rubbers, ceramics, woods etc. For a number of applications metals and their alloys are preferred to other materials because of their visual tensile-strength, hardness, abrasion resistance, thermal or electrical conductivity and anti-corrosion property etc. Electrolytic production of thin coherent and adherent coatings of substances has become one of the most important techniques in recent years to ensure in them the various properties required for their industrial applications. It is well known that an active metal such as titanium can exhibit a high degree of resistivity against destructive environment influences. Titanium may reduce maintenance cost, save power, avoid product contamination and fight against corrosion.

Furthermore, it is used most widely in aircraft and rocket engineering and other branches of industry, where high unit strength is essential. On the other hand, nickel and its alloys are highly anti corrosive against atmosphere, sea-water, dry gases and a few organic acids. Thus, electrodeposited ternary alloys containing titanium with nickel is potentially more important to achieve the desired properties which cannot be met by the use of these metals alone.

The possibility of using electrolysis with alloy deposition to satisfy practical demands was first indicated in 1835-1845. It

was developed energetically in the beginning of the twentieth century. Kremann(1) first made a systematic study of the electro-deposition of alloys and related processes. Brenner's monumental work (2) further documented this budding field up to 1960 with a theoretical footing.

The electrochemical deposition of binary alloys has of been extensively studied. however, considerable effort has also been directed in recent years to obtain three component alloys as is evident from the appearance of various review articles by Sarojamma and Ramachar (3), Sivakumar and Ramachar (4), Krohn and Bohn (5,6) and Srivastava (7) etc. Several workers (8-11) have attempted to investigate the theoretical aspects and methodology of electroplating of ternary alloys. A review of selected developments related to corrosion and compatibility of steels and other alloys of aluminum, nickel, cobalt and titanium has been presented by Barry (12). A few other properties related to hardness (13), micro-hardness (14) have also been studied.

Electrolytic production of ternary thin films containing nickel has attracted considerable attention in recent years for meeting the practical requirements of industries especially where tensile strength, hardness, corrosion resistance etc and better thermal or electrical conductance are required, as is evident from the available literature. Further, titanium is known to exhibit a high degree of resistivity against destructive environment influences and can fight against corrosion. Several binary alloys involving these metals have been prepared which are found to be highly corrosion an heat resistant.

A brief survey of the relevant literature discussed above (12-14) shows that very few three component alloys containing titanium are electrodeposited mainly from chloride baths and have been found to be highly corrosion resistant with excellent smoothness, workability, weldability and phosphating performances. This has led the Nisshin Steel Co. Ltd., Japan (15) to alloy titanium with nickel and zinc for providing a protective coating on steels. An attempt has been made in this work to deposit a ternary Zn-Ni-Ti alloy from sulphate bath and to study the effects of selected addition agents on the morphology, deposit composition, cathode efficiency, cathode polarization and throwing power of the bath. The details of the electro-deposition of this alloy has been described elsewhere.(16) Purpose of the present work is to study the morphology, micro-hardness and corrosion resistance characteristics of Zn – Ni - Ti ternary alloys electrodeposited under various plating conditions .

II. EXPERIMENTAL PROCEDURE

The electrolytic cell used for electrolysis was similar to that used by Mandelcorn et al. (17) and Schaus (194). It was assembled from a 0.3 thick Perspex sheet (15.5 cm x 3.5 cm x 10 cm) joined by chloroform. Bright stainless steel panel (5 cm x 2cm), sealed on a rectangular Perspex sheet or glass slide of similar size with Araldite, was used as cathode. Its edges were also covered with Araldite to avoid uncertainties of their surface area. Its effective surface area, thus, came out to be 10 cm² and in this way a uniform current density was maintained. It was etched properly, washed, dried dipped in carbon tetrachloride and again washed and dried before each deposition. Platinum wire sealed in a narrow glass tube was used as an anode. Double distilled water was used throughout the work for preparing the various Solutions. Analar or Guaranteed reagent grade chemicals were used in the preparation of the solutions. Other chemicals were purified in the laboratory before use.

The electrodes and the electrolytic cell were thoroughly cleaned before use. The electrodes were placed in position after filling the cell with the electrolytic solution. It was then placed in water thermostat to provide temperature control. A fresh electrolytic solution (225 cm³) containing sulphates of nickel and zinc, potassium titanium oxalate with 30 g/L ammonium sulphate and 5ml hydrochloric acid was electrolysed for 20 minutes under different plating conditions at current densities ranging from 2.0 to 7.0 Adm⁻². Current for this purpose was taken from a D.C. stabilized power supply. Zn-Ni-Ti alloys were electrodeposited from a sulphate baths containing nickel sulphate 50 g/L, zinc sulphate 30g L, potassium titanium oxalate 2.0 g/L, ammonium sulphate 30g/L, concentrated hydrochloric acid 5ml/L. and one of the following addition agents ascorbic acid, glucose, glycerol, citric acid or thiourea. Smooth, grey, fine-grained and compact deposits were generally obtained and their compositions and cathode efficiencies were determined as described elsewhere(16). The alloy film containing 10.76-35.96% Nickel, 0.06-0.75% Titanium and 63.29- 89.18% Zinc were formed at current density 2.0 – 7.0 A/dm²; pH 1.8 – 2.4; temperature 20 – 35 °C. Morphological changes produced by these addition agents were studied(18) by means of photomicrographs. Microphotographs of the alloy plates obtained under various plating conditions were taken to examine their morphological behaviour. Micro-hardness of the films deposited at a given electrolytic condition was measured by Vicker's micro-hardness tester(HV,0.05Kg). Weight loss method was used to determine the corrosion rate of the various alloy films.

III. CORROSION RESISTANCE

It is well known that when a metal surface is not protected it starts decaying and loses useful mechanical properties, develop cracks and breaks upon strain with catastrophic suddenness. Extensive work has been done over the past few years to study the corrosion behaviour which has led numerous technical advances made in the way of new corrosion resistant metals, alloys and preventive corrosion measures. Uniform corrosion is considered to be the most common type of corrosion and is characterized by a chemical

or electrochemical reaction which takes place uniformly over the exposed surface. In this type of corrosion, the metal gradually becomes thin and eventually gets destroyed. For example, a metal or steel sheet immersed in a mineral acid normally dissolves at a uniform rate over the entire surface. This uniform attack can be reduced or prevented by (i) proper methods including coatings (ii) using inhibitors or (iii) cathodic protection.

Corrosion behaviour of alloys is very much different from that of individual metals comprising the alloy. The alloys containing titanium are likely to possess a high degree of corrosion resistance to sea water and humidity and good mechanical properties. Keeping this in view, it was thought to study the corrosion rate of the electrodeposited Ni –Ti - Zn alloy by weight loss method acidic and saline environments in which this alloy may also find its potential use.

The Ni –Ti - Zn alloy film were electrodeposited on stainless steel cathode at 35°C, a pH of 2.0 and a current density of 3.0 Adm⁻² from a sulphate bath as described earlier with alloy composition in percentages is Nickel 15.84, titanium 0.19 and zinc 83.97 respectively. The deposited rectangular specimens were suspended in sulphuric acid and sodium chloride solutions of various concentrations, All the experiments were carried out at room temperature (30 ± 5 °C) with varying duration of immersion. It appears from the results (See Tables 1 & 2) that the weight loss is almost negligible in saline atmosphere even after 30 days and only marginal in sulphuric acid except at its higher concentration. The alloy is thus found to be fairly corrosion resistant in these environments.

Table 1: Corrosion data in sodium chloride solution (saline environment) of various concentrations from weight loss measurements

Duration of immersion (days)	Weight loss(gdm ⁻²) in sodium chloride solution at concentration of		
	0.02 N	0.01 N	0.001 N
5	0.000	0.000	0.000
10	0.001	0.000	0.000
15	0.002	0.000	0.000
20	0.003	0.001	0.000
25	0.004	0.002	0.001
30	0.006	0.004	0.001

Table 2: Corrosion data in sulphuric acid solution (acidic environment) of various concentrations from weight loss measurements

Duration of immersion (minutes)	Weight loss(gdm ⁻²) in sulphuric acid solution at concentration of			
	0.02 N	0.01 N	0.002 N	0.001 N
60	0.182	0.038	0.002	0.001
120	0.270	0.148	0.004	0.002
180	0.402	0.310	0.006	0.004

240	0.462	0.334	0.008	0.006
300	0.512	0.388	0.012	0.008
480	0.662	0.468	0.020	0.012
600	-	-	0.026	0.016

IV. MORPHOLOGICAL FEATURES

The morphological features of the alloy deposits obtained under various plating conditions are summarised in Table 3. It appears from their photomicrographs (Figs. 21, 22 & 34-42) that light Grey, semibright, fine-grained stressed films are generally formed at comparatively low current densities, pH and a high temperature. However, they become dark grey and uneven with increasing nickel, zinc or titanium concentration in the bath and duration of electrolysis. Their smoothness has been found to increase when the current density or pH decreased.

Table 3: Morphology summary of the electro deposited Ni - Ti - Zn alloys under various plating conditions.

Figure No	Bath Composition (gL ⁻¹)	Current Density (Adm ⁻²)	Temperature (°C)	pH	Morphology of Deposit
1	Nickel sulphate 50.0; Potassium titanium oxalate 2.0; Zinc sulphate 30.0; Ammonium sulphate 30.0 and ~ 5ml HCl	3.0	30	2.0	Uneven, semi-bright, light grey, crystalline deposit
2	As in Sl. No 1	5.0	30	2.0	semi-bright, grey, uniform crystalline deposit
3	As in Sl. No 1	3.0	20	2.0	Uneven, semi-bright, light grey, uniform crystalline deposit
4	As in Sl. No 1	3.0	25	2.0	Uneven, semi-bright, light grey, crystalline deposit
5	As in Sl. No 1	3.0	35	2.0	Bright, light grey, fine grained smooth and compact deposit
6	As in Sl. No 1	3.0	30	1.8	Semi-bright, light grey, crystalline and compact deposit
7	As in Sl. No 1	3.0	30	2.2	Uneven, semi-bright, grey, crystalline deposit
8	As in Sl. No 1 Except Nickel Sulphate (52.0)	3.0	30	2.0	Semi-bright, grey, stressed, uneven deposit
9	As in Sl. No 1 Except potassium titanium oxalate (2.5)	3.0	30	2.0	Semi-bright, grey, stressed, uneven deposit
10	As in Sl. No 1 Except zinc sulphate (32.0)	3.0	30	2.0	Semi-bright, grey, stressed, uneven deposit
11	As in Sl. No 1 Except time of deposition (40 min)	3.0	30	2.0	Semi-bright, grey, uniform crystalline deposit



Figure 2



Figure 3



Figure 4

Microphotographs of the alloy deposits under various conditions (magnification x 500)

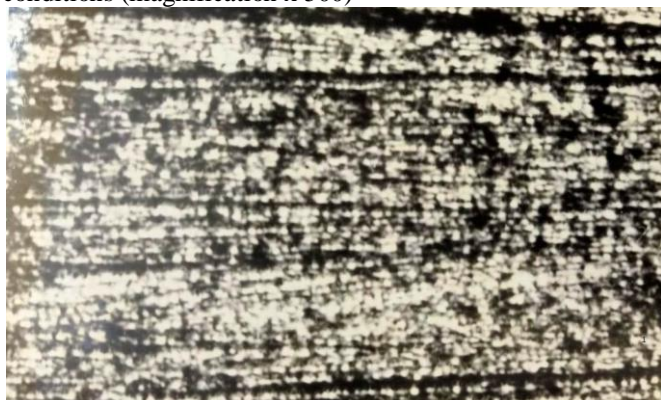


Figure-1



Figure 5



Figure 6

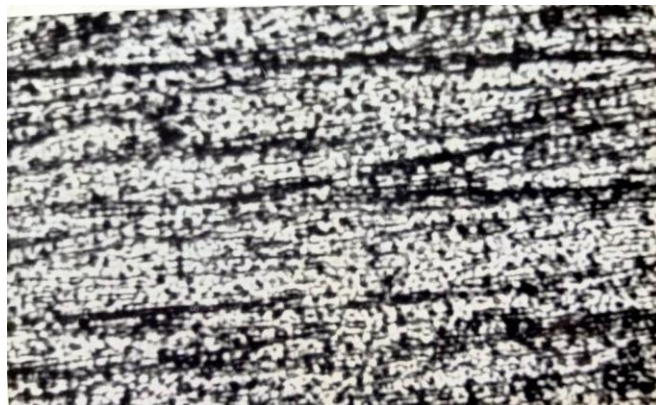


Figure 10



Figure 7



Figure 11



Figure 8

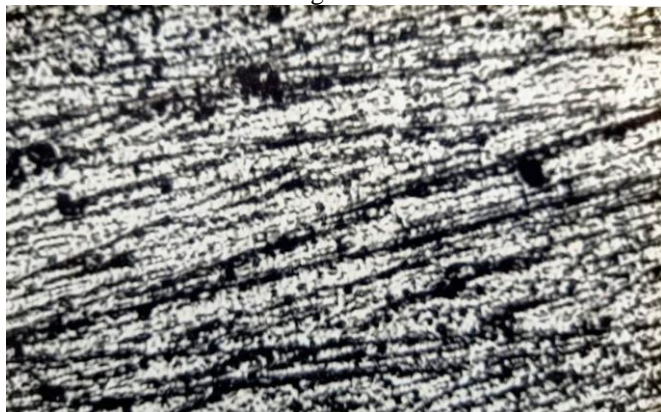


Figure 9

V. MICROHARDNESS

Hardness is a common and widely understood concept, it is not a measure of a single property of metals, rather, it is something which often can be easily and cheaply measured and can be related to significant and useful properties such as tensile strength and ductility. It was therefore proposed to determine the micro hardness of the deposited alloy films under various plating conditions as described earlier. It is significant to mention increases micro-hardness (Vickers) increases with decreasing pH or increasing temperature, current density and the concentration of metals in the bath, as given in Table 4. It has been found in the range of 174 to 405 HV(0.05Kg). It also increases in presence of either of the addition agent in used and is maximum(405 HV,0.05Kg) when the alloy is deposited in presence of ascorbic acid (1.0 g/L) or when 2.5g/L titanium concentration is used in the bath at a pH of 2.0, current density 3.0 A/dm² and 30 oC.

Table 4: Micro Hardness data of the electro deposited Ni - Ti - Zn alloys under various plating conditions.

Fig No	Bath Composition (g/L ⁻¹)	Current Density (A/dm ²)	Temperature (°C)	pH	Micro Hardness (HV, 0.05Kg)
1	Nickel sulphate 50.0; Potassium titanium oxalate 2.0; Zinc sulphate 30.0; Ammonium sulphate 30.0 and ~ 5ml HCl	3.0	30	2.0	175
2	As in Sl. No 1	3.0	30	1.8	181
3	As in Sl. No 1	3.0	30	2.2	174
4	As in Sl. No 1	3.0	35	2.0	297
5	As in Sl. No 1	5.0	30	2.0	351
6	As in Sl. No 1	3.0	25	2.0	222
7	As in Sl. No 1	3.0	20	2.0	363
8	As in Sl. No 1, except Nickel sulphate 52.0	3.0	30	2.0	351
9	As in Sl. No 1, except zinc sulphate 32.0	3.0	30	2.0	351
10	As in Sl. No 1 except potassium titanium oxalate 2.5	3.0	30	2.0	405
11	As in Sl. No 1 With glucose 1.0	3.0	30	2.0	322
12	As in Sl. No 1 With glucose 1.0	5.0	30	2.0	181
13	As in Sl. No 1 With citric acid 1.0	3.0	30	2.0	363
14	As in Sl. No 1 With citric acid 1.0	3.0	30	2.0	297
15	As in Sl. No 1 With ascorbic acid 1.0	3.0	30	2.0	405
16	As in Sl. No 1 With ascorbic acid 1.0	3.0	30	2.0	376
17	As in Sl. No 1 With glycerol 1.0	3.0	30	2.0	306
18	As in Sl. No 1 With glycerol 1.0	3.0	30	2.0	333
19	As in Sl. No 1 With thiourea 1.0	3.0	30	2.0	297
20	As in Sl. No 1 With thiourea 1.0	3.0	30	2.0	351
21	As in Sl. No 1 (With duration of deposition 40 min)	3.0	30	2.0	327

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