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Electrodeposition of Ni-Ti Alloys from an Aqueous (NH₄)₂TiF₆ Bath

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The electrodeposition of Ni-Ti alloys from various aqueous and non-aqueous baths has been examined. Ni-Ti alloy coatings containing up to 20 wt% Ti can be produced by the electrolysis of an aqueous solution of (NH₄)₂TiF₆ (0.1 – 0.2 M), NiSO₄ (0.1 M) and glycine (0.2 M) with pH 3.5 – 4.5 at 20°C. The alloy deposits seemed to consist of metallic Ni and Ti oxide with a small portion of the metallic Ti.

Introduction

The properties of titanium as a light metal of extremely good corrosion resistance and also heat resistance have attracted much attention in recent years in an attempt to develop a new and less expensive coating method on the steel substrate.

Even though a great number of studies have been made for the electrodeposition of Ti from molten salt and non-aqueous solvents as well as from aqueous solutions^{1)–6)}, there seemed no feasible plating bath to be applied for the commercial process.

The standard electrode potential of Ti is -1.75 V vs. NHE (25°C); therefore, when the electrolysis was carried out in an aqueous solution, hydrogen evolution can not be excluded before the deposition of Ti.

Another difficulty in depositing the pure Ti metal coating from an aqueous solution is the characteristic properties of Ti metal itself. Very stable passive films (oxide or nitride) can be easily formed when the pure Ti metal surface is exposed to air. These types of oxide films on Ti metal can be formed in an aqueous solution. Therefore, even if the pure Ti metal coating was obtained on the electrode, Ti surface will be covered with a thin oxide layer which might interfere the further deposition of Ti.

In alloy plating processes, there is possibility to codeposit an inactive metal with some more active metals. Ti-Co alloy deposition has been studied by Kochergin⁷⁾ from an aqueous HF-H₃BO₃ bath. Recently, the electrodeposition of Ni-Ti alloys has been studied by Koura et al.⁸⁾; however, Ni-Ti alloy deposits obtained by these authors seemed to consist of metallic oxide rather than pure metals.

Based on the preliminary study on the electrodeposition of Ti from the aqueous solutions, an attempt was made for the electrodeposition of Ni-Ti alloys from an aqueous solution containing (NH₄)₂TiF₆, NiSO₄ and glycine.

Experimentals

The compositions of the baths studied are shown in Tables 1 and 2.

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Table 1 Electrodeposition of Ti and Ni-Ti from non-aqueous solution

(1) Ti electrolyte

Bath composition and electrolysis condition				Deposits and Ti content	
TiCl ₄	0.1M				
LiCl	0.1M in EtOH	20°C	2Adm ⁻²	Black	35wt%
TiCl ₄	0.05M				
LiCl	0.1M in DMSO	20°C	1Adm ⁻²	Black powder	
Ti ₄	0.04M				
LiI	0.1M in DMSO	20°C	1Adm ⁻²	Gray powder	22wt%
Ti(CF ₃ COO) ₄	0.3M in EtOH	20°C	1~3Adm ⁻²	Ti(IV) → Ti(III)	
Ti(CF ₃ COO) ₄	0.3M in MeOH	20°C	1~3Adm ⁻²	Ti(IV) → Ti(III)	
Ti(CF ₃ COO) ₄	0.1M in HCONH ₂	20°C	1~3Adm ⁻²	Colloidal ppt.	
Ti(SO ₄) ₂	0.1M in MeOH or EtOH	20°C	1~3Adm ⁻²	Ti(IV) → Ti(III)	

(2) Ni-Ti electrolyte

TiCl ₄	0.1~0.2M in			Black-brown	
NiCl ₂	0.01~0.1M EtOH:MeOH	20°C	2~8Adm ⁻²	peeling	7.4wt%
LiCl	0.1M (1:1)				
TiCl ₄	0.1M				
Ni(CF ₃ COO) ₂	0.1M in EtOH	20°C	1~2Adm ⁻²	Black powder	6.0wt%
LiCl	0.1M				
TiCl ₄	0.05M				
NiBr ₂	0.01~0.02M in DMSO	20°C	1~1.75Adm ⁻²	Black powder	27.1wt%
LiBr	0.1M				
TiCl ₄	0.05M				
Ni(CF ₃ COO) ₂	0.05M in DMSO	20°C	1Adm ⁻²	Black powder	0.4wt%
LiCl	0.1M				
Ti(CF ₃ COO) ₄	0.3M in EtOH				
Ni(CF ₃ COO) ₂	0.2M or MeOH or HCONH ₂	20°C	3~4Adm ⁻²	Black powder	30wt%

The cathodic polarization curves for the electrodeposition of Ti and Ni-Ti alloys were measured by the potential sweep method (50 mV/min). The potentials measured were referred to a saturated calomel electrode.

For the analysis of the deposits, Ti and Ni-Ti coatings deposited on Pt electrode were dissolved in 6N HCl + H₂O₂ solution and the composition of Ti and Ni-Ti deposits was analyzed by the atomic absorption spectroscopy and also by the colorimetric method. The amount of hydrogen evolved during the electrolysis was measured by the gas measuring device attached to the electrolytic cell.

Surface appearance of the Ti and Ni-Ti alloy deposits was examined by an optical microscope.

An x-ray diffraction analysis was also carried out to determine the structure of the deposits.

Table 2 Electrodeposition of Ti and Ni-Ti from aqueous solution

(1) Ti electrolyte					Deposit and Ti content	
Bath composition and electrolysis condition						
$\text{Ti}(\text{SO}_4)_2$	0.125M	pH 1.5		$0.5\sim 2\text{Adm}^{-2}$	—	
Na_2SO_4	1.0M	20°C				
$(\text{NH}_4)_2\text{TiF}_6$	0.1~0.4M	pH 3.5	20°C	$1\sim 2\text{Adm}^{-2}$	Gray powder	
(2) Ni-Ti electrolyte						
$\text{Ti}(\text{SO}_4)_2$	0.0625M					
NiCl_2	0.125M	pH 5~9		$2\sim 7\text{Adm}^{-2}$	Dull smooth 0.5wt%	
H_3BO_3	0.4M	20°C				
Citric acid	0.5M					
Glycine	0.5M					
$\text{Ti}(\text{SO}_4)_2$	0.0625M					
NiCl_2	0.125M	pH 5~7		$2\sim 7\text{Adm}^{-2}$	Dull smooth 2wt%	
H_3BO_3	0.4M	20°C				
Lactic acid	0.5M					
Glycine	0.5M					
$(\text{NH}_4)_2\text{TiF}_6$	0.1~0.2M	pH 3.5~5.5		$1\sim 2\text{Adm}^{-2}$	Black smooth 10~20wt%.	
NiSO_4	0.1M	20°C			or	
Glycine	0.2M				gray powder 25wt%	

Surface state of Ti and also Ni on the deposits was analyzed by the ESCA.

Results and Discussion

Preliminary experiments

Screening of the electrolyte suitable for the electrodeposition of Ti has been made with the special reference to the Ti compounds.

Tables 1 and 2 show the experimental results obtained from various non-aqueous and aqueous solutions containing different Ti compounds.

In the study of non-aqueous Ti plating system (Table 1), organic solvents tested were MeOH and EtOH as a prototype solvent, and dimethyl sulfoxide as a non-protonic solvent. In the electrolysis of these organic Ti baths, the reduction of $\text{Ti}^{\text{iv}} \rightarrow \text{Ti}^{\text{iii}}$ or $\text{Ti}^{\text{iii}} \rightarrow \text{Ti}^{\text{ii}}$ was observed; however, no deposition of metallic Ti was detected.

In the non-aqueous Ni-Ti alloy plating baths listed in Table 1, the deposits obtained were found to be black powdery or black brown, and sometimes, non-adherent coating was obtained. Therefore, non-aqueous Ti plating bath does not seem to give the sound Ti and Ti alloy deposits.

Ti containing coatings were obtained from the aqueous electrolyte containing $\text{Ti}(\text{SO}_4)_2$ and lactic acid or citric acid. The Ti content in the alloy deposits increased with an increase of pH of the bath and current density. Under these conditions, evolution of hydrogen occurred strongly and the surface of the deposits tended to become powdery. In general, the Ti content of the deposits from these baths was found to be less than 2 wt.%.

Among the electrolytes tested for the electrodeposition of Ti, an aqueous solution containing $(\text{NH}_4)_2\text{TiF}_6$ was found to be most promising for the electrodeposition of Ti and its alloys. Therefore, the detailed studies on the evaluation of the $(\text{NH}_4)_2\text{TiF}_6$ bath have been made for the electrodeposition of Ni-Ti alloy coatings.

Electrolysis of $(\text{NH}_4)_2\text{TiF}_6$ solution

The cathodic polarization curves obtained from 0.1 – 0.4 M $(\text{NH}_4)_2\text{TiF}_6$ bath with a Ti electrode by means of the potential sweep method (50mV/min) are shown in Fig. 1.

Effects of the concentration of Ti compound on the cathodic polarization can be found in this figure. An abrupt increase in the current density was observed at the potential of -0.8 V and the current was found to be almost constant beyond the potential of -1.2 V. The current increased again at -1.3 V with the evolution of hydrogen. Under these conditions, the enormous amounts of hydrogen evolved, and the deposits became grayish brown.

The linear relationships between the current density at -1.2 and -1.4 V and the concentration of Ti salt in the bath were observed as shown in Fig. 2.

When the electrolysis was carried out at -1.2 V, dark violet precipitate was formed in the vicinity of the electrode. The electrolysis of the 0.1 M $(\text{NH}_4)_2\text{SO}_4$ solution, however, does not seem to give the reduction current under the same conditions as in the case of $(\text{NH}_4)_2\text{TiF}_6$ bath. Therefore, the current observed at -0.8 V seemed to correspond to the reduction of $\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{III}}$ (3,4).

The cathodic polarization curves obtained in the same $(\text{NH}_4)_2\text{TiF}_6$ bath with a Ni electrode are also shown in Fig. 3. Contrary to the case of Ti electrode, the hydrogen evolution occurred at -0.8 V and no current plateau was observed in the polarization curves.

The potential of the metal deposition at the Ni electrode in the $(\text{NH}_4)_2\text{TiF}_6$ bath was also found to be different from the one in which Ti was used as a cathode.

Differences in the deposition potentials of Ti and H_2 at each electrode may be at-

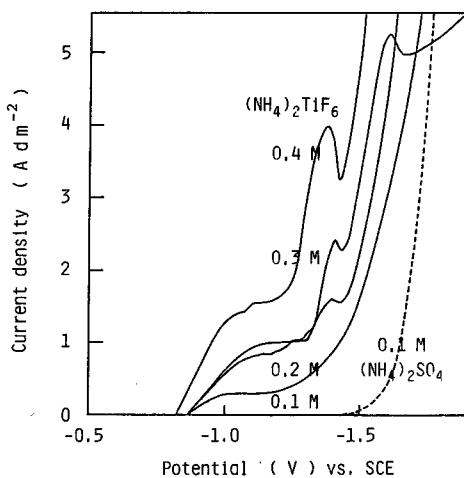


Fig. 1 Cathodic polarization curves on Ti electrode in $(\text{NH}_4)_2\text{TiF}_6$ solution (pH 3.5, 20°C)

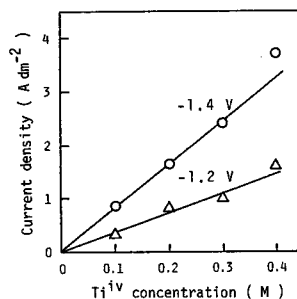


Fig. 2 Relationship between i_{lim} and $C_{(\text{NH}_4)_2\text{TiF}_6}$

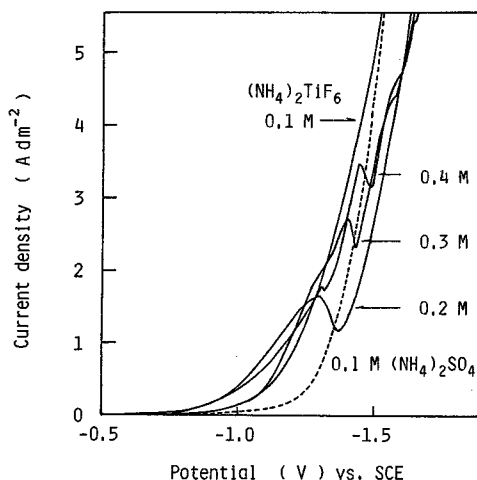


Fig. 3 Cathodic polarization curves on Ni electrode in $(\text{NH}_4)_2\text{TiF}_6$ solution (pH 3.5, 20°C)

tributable to the hydrogen overpotentials of Ti and Ni. Therefore, the cathodic current observed in the potential range between -1.3 and -1.4 V could not be defined whether it may correspond to the deposition of Ti or the evolution of hydrogen.

Deposit obtained from the pure $(\text{NH}_4)_2\text{TiF}_6$ bath was found to be dark gray in the initial stage of the electrolysis; however, the prolonged electrolysis gave rise to the grayish white deposits which, sometimes, tend to peel off from the electrode. Upon drying the deposits, the Ti coatings turned to the non-adherent white powder.

Electrodeposition of Ni-Ti alloys from $(\text{NH}_4)_2\text{TiF}_6$ - NiSO_4 -glycine bath

Based on the preliminary studies on the electrodeposition of Ti from a $(\text{NH}_4)_2\text{TiF}_6$ bath, an attempt was made to deposit the Ni-Ti alloy coatings from the $(\text{NH}_4)_2\text{TiF}_6$ - NiSO_4 -Glycine bath shown in Table 2.

The effect of the current density on the composition of Ni-Ti alloy deposits is shown in Fig. 4 as a function of the concentration of $(\text{NH}_4)_2\text{TiF}_6$ in the bath. The Ti content in the Ni-Ti alloy deposits increased with an increase of the current density to give 20 – 30 wt.% at a current density of 2 – 6 A/dm^2 , and the further increase in the current density does not seem to give the higher Ti content.

The Ti content in the Ni-Ti alloy deposits was found to be high when the concentration of the $(\text{NH}_4)_2\text{TiF}_6$ in the bath is rather low. These results are quite unusual in the deposition of metal or alloys from an aqueous solution.

The total amount of Ni and Ti in the alloy deposits decreased with an increase of current density and it gave only 50% when the 0.1 M solution of each Ti and Ni compound was employed.

These results can be explained by the inclusion of metal hydroxide as well as oxide in the alloy deposits during the electrodeposition of Ni-Ti alloys due to the strong evolution of hydrogen.

The partial current efficiencies for the deposition of Ni, Ti and also hydrogen are

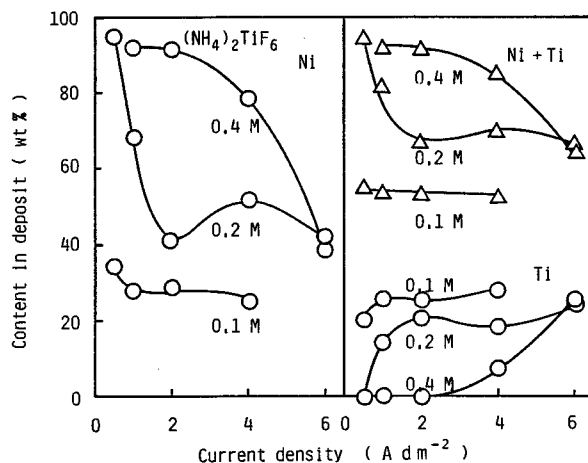


Fig. 4 Effect of current density on the composition of Ni-Ti alloy deposits as a function of $C_{(\text{NH}_4)_2\text{TiF}_6}$
 Bath; 0.1–0.4 M $(\text{NH}_4)_2\text{TiF}_6$ + 0.1 M NiSO_4
 + 0.2 M Glycine

given in Fig. 5. The current efficiency of the Ni deposition seemed to be independent on the current density and also on the concentration of Ti compound in the alloy plating bath to give 15–30%.

On the other hand, the evolution of hydrogen increased with an increase of current density. If the reactions of Ni, Ti and also hydrogen proceed through the electrochemical processes, the total current efficiency for the deposition of Ni, Ti and H₂ can be estimated to be 130% at a current density of 4 A/dm² in the Ni-Ti alloy plating bath containing 0.1 M $(\text{NH}_4)_2\text{TiF}_6$. It seemed, therefore, that the deposition of Ti in this alloy system might be controlled by the chemical process rather than the electrochemical one.

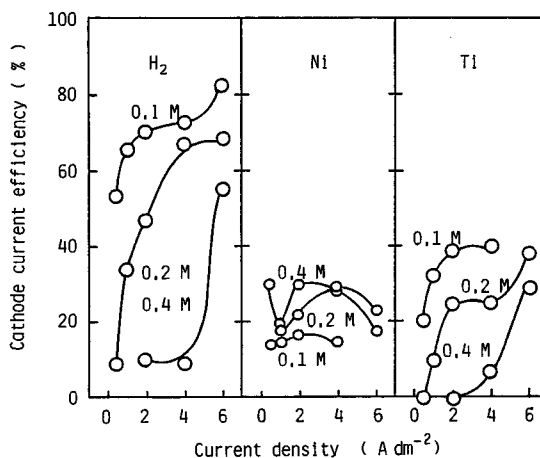


Fig. 5 Effect of current density on the current efficiency in the Ni-Ti alloy deposition as a function of $C_{(\text{NH}_4)_2\text{TiF}_6}$
 Bath; 0.1–0.4 M $(\text{NH}_4)_2\text{TiF}_6$ + 0.1 M NiSO_4
 + 0.2 M Glycine

The current efficiency for the H_2 evolution decreased remarkably with an increase of the Ti concentration in the alloy plating bath. Under these conditions, the current efficiency for the Ni deposition does not seem to increase and the current efficiency for the Ti deposition also decreased.

These results imply that the another reaction might be taking place at the cathode during the electrolysis of the Ni-Ti alloy plating bath; that is, the electrolytic reduction of $\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{III}}$.

From the theoretical point of view, the reduction of $\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{III}}$ will occur in the Ni-Ti alloy plating bath; however, the reduction of $\text{Ti}^{\text{III}} \rightarrow \text{Ti}^0$ does not seem to occur even when the concentration of Ti^{III} is getting higher in the vicinity of the electrode.

Ni-Ti alloy obtained from the $(\text{NH}_4)_2\text{TiF}_6$ bath in the initial stages of the deposition gave rise to silver white deposits. However, no metallic Ti or Ti compound was detected in the deposits.

Deposition of Ti was confirmed to occur when the hydrogen evolution was prevailing during the electrolysis, and the deposits were always black.

The effect of current density on the composition of Ni-Ti alloy deposits is given in Fig. 6 as a function of pH of the alloy plating bath. The Ti content of the alloy deposits increased with an increase of pH of the bath.

The current efficiencies for the Ni and Ti deposition in the Ni-Ti alloy plating bath under the same conditions mentioned above are shown in Fig. 7. The current efficiency for the Ni deposition decreased with an increase of the current density in the pH range 3.5 – 4.5. Moreover, the efficiency for the Ni deposition seemed to be poor in the lower current density region with an increase of pH of the plating bath. In the low pH range, the hydrogen evolution increased with an increase of the current density, and the deposition of Ni was inhibited by the formation of the stable Ni-glycine complexes in the alloy plating bath.

The reduction of Ti was found to occur with the evolution of hydrogen, and the

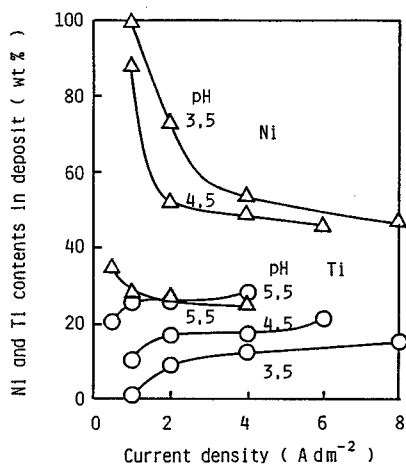


Fig. 6 Effect of current density on the composition of Ni-Ti alloy deposits as a function of bath pH

Bath; $(\text{NH}_4)_2\text{TiF}_6$ 0.1 M
 NiSO_4 0.1 M (20°C)
 Glycine 0.2 M

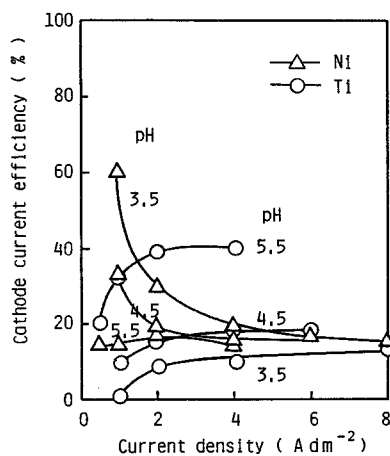


Fig. 7 Effect of current density on the current efficiency in the Ni-Ti alloy deposition as a function of bath pH

Bath; $(\text{NH}_4)_2\text{TiF}_6$ 0.1 M
 NiSO_4 0.1 M
 Glycine 0.2 M

higher the pH of the bath, the easier the deposition of Ti. The deposition of Ti, however, seemed to occur not solely by the electrochemical reaction.

The reaction of Ti on the electrode seemed to consist of the following steps; the hydroxide may be formed in the vicinity of the electrode by the hydrogen evolution, and this compound tends to incorporate into the Ni matrix during the electrodeposition of Ni.

In order to confirm these reaction schemes in the Ni-Ti alloy plating systems, the cathodic polarization curves of the Ni-Ti alloy deposition, as well as the partial current-potential curves for the hydrogen, Ni and Ti were determined as shown in Fig. 8.

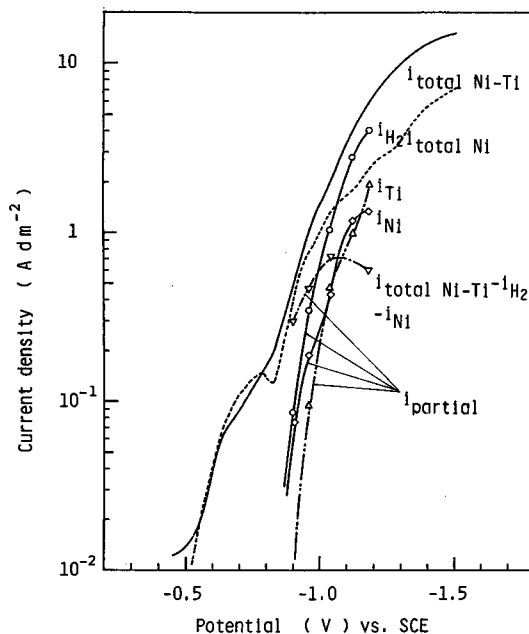


Fig. 8 Cathodic polarization curves on Pt electrode in 0.2 M $(\text{NH}_4)_2\text{TiF}_6$ (or $(\text{NH}_4)_2\text{SO}_4$) - 0.1 M NiSO_4 - 0.2 M Glycine (pH 5.5, 20°C)

The depositions of Ni and also hydrogen were found to be the main reactions occurring at the potential of -0.9 V, and the deposition of Ti does not seem to take part in these electrochemical reactions. However, the total currents at the potential of -0.9 V were found to be larger than those of the hydrogen and Ni depositions.

These results imply that the another reaction might be taking place at the working electrode; that is, the reduction of $\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{III}}$ or $\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{II}}$. The partial current for the reaction of Ti calculated by the subtraction of partial currents of the H_2 and Ni from the total currents has a plateau in the current density range, $0.6 - 0.7$ A/dm² (ca. -1.0 V). However, the partial current for the deposition of Ti estimated from the amount of Ti deposited in the alloy coatings increased sharply at the potential of -0.9 V, and continued to increase with an increase of the electrode potential.

As will be seen in Fig. 8, these two partial current-potential curves for the reduction of Ti are clearly different from each other. The partial current-potential curve obtained by subtraction method should correspond to the reaction of $\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{III}}$ or $\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{II}}$.

→ Ti^{ii} . Deposition of Ti was confirmed to occur at above -1.05 V with an increase of the hydrogen evolution, and the deposition of Ti increased sharply above the limiting current density of the Ti reduction.

Characteristics of the Ni-Ti alloy deposits

i) Surface appearance

Ni-Ti alloy deposits obtained from the $(\text{NH}_4)_2\text{TiF}_6$ - NiSO_4 -glycine bath generally have the cracks as shown in Fig. 9. The cracks on the Ni-Ti alloy deposits became finer with an increase of the current density and also pH of the bath. These phenomena seemed to be attributable to the evolution of hydrogen in the alloy plating bath. Changes in the crack patterns in the Ni-Ti alloy deposits are well accord with the phase structure of the alloy deposits. Therefore, the formation of the cracks in the Ni-Ti alloy deposits might be due to the incorporation of the Ti hydroxide in the alloy deposits.

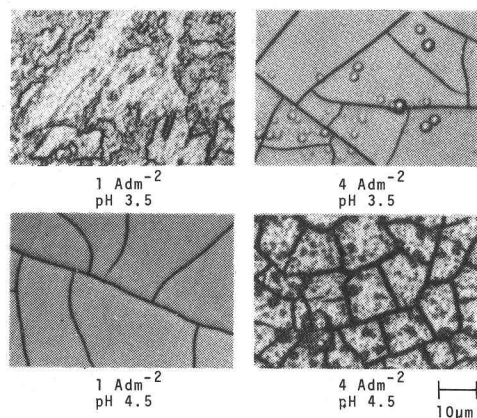


Fig. 9 Surface appearance of Ni-Ti alloy deposited from $0.1 \text{ M } (\text{NH}_4)_2\text{TiF}_6$ – $0.1 \text{ M } \text{NiSO}_4$ – $0.2 \text{ M } \text{Glycine}$ at 20°C (18°C)

ii) X-ray diffraction data

The x-ray diffraction lines corresponding to the Ni(110) and Ni(200) were observed in the Ni-Ti alloy deposits; however, no diffraction lines referred to the metallic Ti were detected. On the other hand, diffraction lines corresponding to the Ti oxide were found in all the Ni-Ti alloy deposits obtained from the $(\text{NH}_4)_2\text{TiF}_6$ bath. The intensity of the corresponding diffraction lines, however, seemed to be rather weak compared to the Ti content in the Ni-Ti alloy deposits. These results imply that the Ti oxide in the Ni-Ti alloy deposits might be composed of the very fine crystallite.

iii) ESCA data

Analysis of the Ni-Ti alloy deposits was also carried out by the ESCA. The Ni-Ti alloy deposits obtained at a current density of 1.0 A/dm^2 and 4.0 A/dm^2 gave rise to the same chemical shift in the ESCA patterns for the Ti and Ni.

However, the Ni-Ti alloy deposits obtained at rather high current density (4.0 A/dm^2) seemed to have a stronger metallic Ti line, which was confirmed by the argon

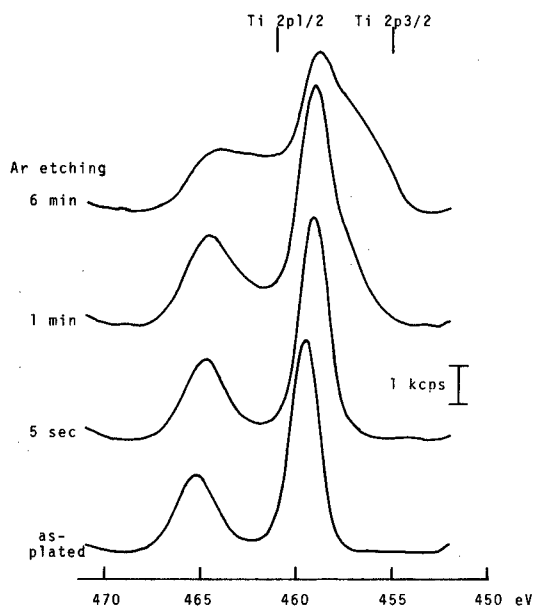


Fig. 10 ESCA patterns for the Ti of Ni-Ti alloy deposit

etching of the Ni-Ti alloy deposits as shown in Fig. 10.

Conclusion

Ni-Ti alloy coatings containing ca. 2 wt.% Ti have been electrodeposited from a $\text{NiSO}_4\text{-Ti}(\text{SO}_4)_2$ bath containing citric acid or lactic acid as a complexing agent.

Organic solvent baths containing TiCl_4 and NiCl_2 or $\text{Ni}(\text{CF}_3\text{COO})_2$ gave rise to the black powdery deposits containing 6–30 wt.% Ti, and these types of the Ni-Ti alloy deposits seemed to have poor adherence to the substrate.

Under the optimum conditions, Ni-Ti alloy coatings containing ca. 20 wt.% Ti can be produced in the electrolysis of an aqueous solution containing $(\text{NH}_4)_2\text{TiF}_6$ (0.1–0.2 M), NiSO_4 (0.1 M) and glycine (0.2 M) with pH 3.5–4.5, 1–2 A/dm^2 and 20°C.

The reaction of Ti on the electrode seemed to consist of the following steps; the Ti hydroxide may be formed in the vicinity of the electrode by the strong evolution of hydrogen and this compound tends to incorporate into the nickel matrix as like as in the case of the dispersion coatings.

Deposition of Ti was confirmed to occur above -1.05 V with an increase of the hydrogen evolution and the deposition of Ti increased sharply above the limiting current density of the Ti reduction.

The Ni-Ti alloy deposits obtained from the $(\text{NH}_4)_2\text{TiF}_6\text{-NiSO}_4\text{-glycine}$ bath seemed to consist of metallic Ni and Ti oxide with a small portion of the metallic Ti.

References

- 1) F.A. Lowenheim Ed., "Modern Electroplating", 3rd. Ed. p. 465 (1974), John Wiley & Sons, Inc. New York.

- 2) K. Aotani, KINZOKU HYOMEN GIJYUTSU, 9, 469 (1959).
- 3) W. Machu, V. Kamel, Werkstoff und Korrosion, 1, 14 (1959).
- 4) M. Morioka, T. Shibata, A. Umezono, NIHON KINZOKU GAKKAI SHI, 21, 32 (1957); M. Morioka, A. Umezono, *ibid.*, 23, 71 (1959).
- 5) A. Kitani, K. Sasaki, DENKI KAGAKU, 52, 302 (1984).
- 6) W.E. Reid, J.M. Bish, A. Brenner, J. Electrochem. Soc., 104, 21 (1957).
- 7) S.M. Kochergin, G.R. Pobedimskii, Zhur. Priklad. Khim., 33, 238 (1960).
- 8) N. Koura, M. Kato, Abstracts of the papers presented at Electrochemical Soc. Japan (1983).