Effect of Addition Agents on the Electrodeposition of INVAR Alloys

R. Karthik, R. J. Raja, M. Ramasamy, G. Sheela, S. Madhu, S. Kennedy, Ch. Ramakishan Rao and Malathy Pushpavanam.*

Central Electrochemical Research Institute, Karaikudi- 630 006, T.N., India.

SUMMARY – Iron-nickel alloy of 'INVAR' composition has been prepared from a sulphate- chloride bath. The effect of operating variables on the composition and current efficiency of alloy deposition was evaluated. The effect was studied of seven different additives belonging to the aromatic sulphonic acid group and thiourea derivatives on the characteristics of alloy deposition. Their effect on deposit nature, composition, cathode efficiency and microstructure, hardness etc., is reported.

Keywords: Invar alloy, addition agents, current efficiency, composition and thickness distribution, cracked structure.

INTRODUCTION

Invar is a binary alloy of iron and nickel (64% Fe and 36% Ni) known for its low coefficient of thermal expansion, as low as 0.2 x 10^{-6} to 2.0 x 10^{-6} °C^{-1}.[1] A ternary alloy containing 5% cobalt in this alloy is said to exhibit thermal expansion still lower than Invar.[2] As ternary alloys, codeposited 9% chromium in the alloy combines good corrosion resistance and 5% copper combines good thermal conductivity with low coefficient of thermal expansion respectively.[3,4] More recently, due to their high dimensional stability, these alloys have found applications as microwave guides, laser housings, geodetic tapes and optical assemblies for imaging instruments in Viking and Voyager spacecraft. Invar alloys have also been evaluated as possible materials for optical mirrors in space applications, liquid natural gas container (LNG) tanks and printed circuit cores.[5,6]. Most applications of Invar deal with bulk materials produced by traditional methods of fabrication such as casting and machining which involve a lot of material wastage. Electrodeposition and electroforming have the potential for producing otherwise difficult-to-make articles with high precision.[6] Potential applications for electroforming include the production of thin walled parts with very accurate dimension and complex shape.[5,6]

Depositions of Invar type alloys have not been investigated as extensively as nickel rich permalloy coatings. Iron-rich alloys generally possess high internal stress and brittleness making them difficult to form. The presence of suitable additives can bring down the stress levels and make the alloy workable. The present work was undertaken with the aim of producing binary and ternary Invar alloys, and that relating to the binary system is reported in this paper.

EXPERIMENTAL

Invar alloy deposition was tried in seven different baths as given in Table I. The solutions were prepared using laboratory grade reagents after due purification treatment. Plating was carried out in a 250 cm^3 capacity both under quiescent and stirred condition, at 55 ± 2 °C, using dual anodes. Stirring was provided by a mechanical stirrer. Deposition was carried out on 6 cm^2 area on stainless steel panels. The deposits were stripped from the substrate by chemical dissolution in 50% nitric acid and then analysed for iron, using conventional volumetric procedures. The composition of the alloy, its thickness, and uniformity were later confirmed on panels plated on copper of the same area, using X-

Table I. Bath compositions and operating conditions tested

	Baths						
Constituents	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Nickel sulphamate	404	404	–	–	–	–	–
Nickel sulphate	–		100	260	201	37.5–180	37.5
Nickel chloride	–	–	91	47	–	75	75
Ferrous ammonium sulphate.	–	98	63.2	–	–	–	28
Ferrous chloride	65.6	–	–	–	–	–	–
Ferrous sulphate	–	–	–	150	45	75	–
Boric acid	30	45	45	35	45	45	45
Ascorbic acid	1	1	–	3	1	1	1
Curr. Density A dm^{-2}	3	3	3–5	10	3	3–5	3
pH	3	1.5–4.0	1–4	2–5	3	3–5	3

Bath constituent concentrations in g dm^{-3}

* Author for correspondence

R. Karthik, R. J. Raja, M. Ramasamy, G. Sheela, S. Madhu, S. Kennedy, Ch. Ramakishan Rao and M. Pushpavanam, *Trans Inst Met Fin*, 2003, **81**(2), 68

by fluorescence spectroscopy. Depositions were carried out changing the bath composition, plating variables, additives *etc.*, for known durations on weighed panels. The mass of the deposit was obtained from the weight gained after deposition. Knowing the composition of the alloy, the cathode current efficiency was estimated using the conventional method.

Seven different addition agents, namely Saccharin (SAC), Naphthalene Tri Sulphonic Acid (NTS), Vinyl Benzene Sulphonic Acid (VBSA), Thiourea (TU), Methyl Thiourea (MTU), Acetyl Thiourea (ATU), and Phenyl Thiourea (PTU), were added into separate baths in small increments and their effects on alloy composition, cathode efficiency and nature of deposits examined. Composition and thickness distribution in the alloy deposits at various points across the deposit were determined using an X-ray fluorescence Spectrophotometer. The structure of the deposits was examined using a Scanning Electron Microscope (SEM). The hardness of the deposits was measured using a Vickers Hardness tester at a load of 50 kg. The deposits were heat treated up to 680 °C in vacuum at 10^{-6} Torr for 4 hours, which is normally adopted to improve the properties of Invar alloys, to assess whether there was any change in their ductility or structure.

RESULTS & DISCUSSION

The composition of the alloys obtained, the current efficiency and nature of deposits obtained under various operating conditions are shown in Table II. Based on the results, bath 4 was selected for further studies with additives.

It was deduced from the results that the iron-nickel alloy system follows the anomalous type of codeposition in which the less noble metal, iron, deposits in preference to nickel. It was also noted that the iron content of the alloy and cathode current efficiency increased with increasing current density for the baths having a high metal content or iron content, whereas those having a low metal content or low iron content exhibited the opposite trend. The iron content rose up to pH 3 along with an increase in the current efficiency. Still higher pH lowered the efficiency as well as inducing high stress in the deposits, probably due to the inclusion of trivalent iron or the metal hydroxides. Stirring of the bath enabled higher iron codeposition, especially in baths containing high nickel to iron ratio indicating that it is mass transfer controlled. Saccharin was found to reduce the internal stress and iron content in the deposit. With this background knowledge, Invar alloy of the desired composition was prepared from bath 4, for further studies.

Seven different additives, as mentioned above, were tried at various concentration levels and the nature of the deposits obtained is shown in Table III. The additives could be classified into two groups, those containing the sulphonic acid group and the other as thiourea or its derivatives containing the N-C-S group.

Aromatic sulphonic acids belonging to the Class-I brighteners in nickel plating,[7,8] reduce the internal stress of nickel deposits.[9,10] The sulphur group of these compounds is reduced electrochemically during nickel plating to sulphide ion, S^{2-}, which is incorporated into the deposit.[11,12] It is also known that saccharin molecules are adsorbed on nickel only physically, and hence reversibly; they do not undergo irreversible chemisorption. The sulphur content of the nickel deposit with these additives is around 0.04 wt %. According to Osaka *et al*,[13,14] the sulphur inclusion in Co-Ni-Fe film is 4 to 5 times greater than that of the nickel film in the same concentration level. The large difference in the sulphur inclusion between Co-Ni-Fe and Ni may be due to the difference in the catalytic activity of the two different materials towards breaking the C-S bond.

Table II. Effect of operating variables on the alloy deposition

Bath	Condition		Fe %	CCE%	Remarks
1&2	all	all			Greenish non-metallic, non-adherent deposits
3	pH 1.4	3 A dm^{-2}	56.3	43.9	White adherent deposits
		4 A dm^{-2}	58.4	52.9	Slight cracks
		5	65.8	58.8	Cracked and brown
	pH 1.8	3	56.5	55.5	
	pH 2.1	3	53.5	64.8	Brown
					Slight cracks
	SAC 2 g dm^{-3},	pH 1.4	33.8	58.0	Highly cracked
	3 A dm^{-2}	pH 1.8	41.7	61.2	Brown, cracked
	-do-	pH 2.1	52.0	68.9	
		pH 1.8,stirred	67.7	34.5	
4	pH 3.5, 55°C	2 A dm^{-2}	34.7		Details given in the Figs
		3 A dm^{-2}	40.8		
		5 A dm^{-2}	52.24		
		10 A dm^{-2}	57.89		
	SAC 2 g dm^{-3}, pH 3.5				
	55°C	3 A dm^{-2}	36.14		
		10 A dm^{-2}	47.91		
	-do- pH 2.0	5 A dm^{-2}	58.59		
		10 A dm^{-2}	59.90		
	-do-, stirred	-do-	62.3		
	-do- pH 1.5	-do-	46.97		
	-do-, stirring	-do-	59.21		
5	pH 2	2 A dm^{-2}	55.0	30.96	Brown
		3 A dm^{-2}	54.8	41.9	Stressed edge
	pH 2.8	3 A dm^{-2}	59.2	62.3	Micro cracks
	SAC 2 g dm^{-3}, Stirred	3 A dm^{-2}	57.6	40.4	Dull bright, cracked edge
6	pH 1.4,	3 A dm^{-2}	82.0	62.9	Fully cracked
	Ni/Fe:2	4 A dm^{-2}	79.0	65.5	Less cracks
		5 A dm^{-2}	70.1	52.7	White bright
	Ni/Fe:3	3 A dm^{-2}	71.0	65.0	Good deposit
	Ni/Fe:4	-do-	62.0	75.2	-do-
7	pH 1.4	5 A dm^{-2}	38.4	74.1	Slight cracks
	Ni/Fe:7	3 A dm^{-2}	57.6	41.2	Good
	Ni/Fe:5.5	3 A dm^{-2}	52.6	65.3	Good
	Ni/Fe:5	-do-	57.6	69.2	-do-

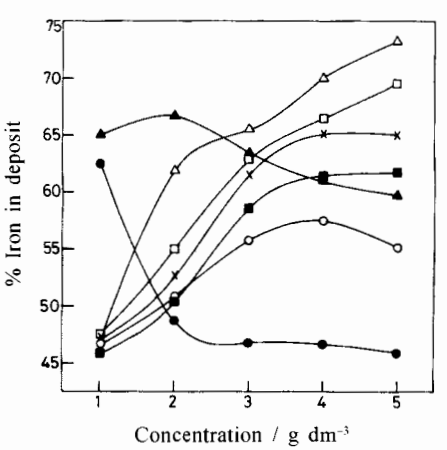


Figure 1. Effect of additive concentration on the percentage iron content of the alloy pH, 2.5; 10 A dm^{-2} ; 55 °C; with stirring: -□- SAC, -■- TU , -Δ- NTS, -▲- VBSA, -○- ATU, -●- PTU, -x- MTU.

Table III. Effect of additive concentration on the nature of deposit

Additive	Conc. /g dm^{-3}	Nature of Deposit
SAC	1	Matte, cracked at edges
	2	–do–
	3	Smooth, turns brown on drying
	4	–do–
	5	Smooth, bright, turns brown on drying
TU	1	Turns dark brown, blisters
	2	Smooth, turns brown, slight blistering
	3	–do–
	4	–do–, patchy
	5	–do–, more patchy
NTS	1	Smooth, cracked at edges
	2	–do–
	3	Smooth deposit
	4	Very smooth, turns yellow on drying
	5	Smooth, turns brown to black on drying
VBSA	1	Bright, greyish, smooth
	2	–do–
	3	Very smooth, bright, turns brown
	4	Bright, cracks at the edges
	5	Smooth grey deposit
ATU	1	Smooth, yellowish slightly cracked
	2	Grey, more cracked
	3	Greenish and yellow at edges
PTU	1	Uniformly stressed
	2	Uniformly cracked
	3	Highly stressed, turns yellow on drying
	4	–do–
MTU	1	Cracked at edges
	2	Slight cracks
	3	Smooth, but cracked
	4	–do–, bright ,cracked

Thiourea, known as a Class II brightener in nickel-plating baths, serves as a levelling agent. Nickel films plated from the bath containing thiourea are known to contain both carbon and sulphur. The atomic ratio of C to S in the nickel film has been shown to range from 0.3 to 0.7, and, according to a study made by Bodnevas,[9] it can be as low as 0.1. These values are consistent with the established fact that thiourea molecules decompose upon contact with the surface of nickel metal, causing sulphidation of the latter to form NiS, and that all the sulphide atoms are trapped in the nickel deposit being formed, whereas the remnant diffuses at least partly into the solution[14,15]. Other reports claim (a) formation of complexes between TU molecules and nickel ions[11,12], (b) formation of nickel sulphide in the colloidal form in the cathode layer[11], (c) electrolytic reduction of TU at the cathode surface, yielding sulphide ion[16], (d) polarising tendency of TU molecules due to strong adsorption on the electrode surface[16].

Results given in Figure 1 indicate that there is a general increase in iron content of the alloy with increasing NTS and SAC concentrations whereas, with VBSA, it decreases above 2 g dm^{-3}. This can be attributed to an inhibitive effect on the iron deposition by VBSA. TU and its derivatives give relatively low iron content *i.e.*, they make the system less anomalous especially at higher concentrations. Iron contents increase only up to 3 g dm^{-3} and then attain a steady value. It has been reported that TU[13] yields deposits with lower cross sectional composition gradient, and the film can be deposited from solution containing a higher Fe^{2+} concentration (comparable with the Ni concentration). This means that in the presence of TU, deposits of lower iron contents are obtained which is in agreement with our results. From the partial polarisation curves it has also been shown that TU acts as a depolariser in the cathodic nickel reduction process and this effect is even more pronounced for Ni-Fe alloy deposition[17]. Figure 2 showing the effect of additive concentration on the current efficiency of alloy deposition indicates that higher efficiencies are obtained in the presence of TU derivatives except for PTU. This has been attributed to the adsorption of these molecules on the electrode surface suppressing hydrogen evolution. It has been shown that TU indirectly affects H_2 evolution rates on Ni or Ni-Fe cathodes[17], particularly at low concentrations. High TU concentration increases the consumption of adsorbed H_2, increases its evolution rate and strongly decreases current efficiency. It has been established that codeposition of nickel and iron is governed by the change in pH at the cathode solution interface[18,19]. Due to suppression of the hydrogen evolution reaction[20,21,22], in the presence of TU derivatives, the iron content is relatively low and for the same reason the current efficiency is high. SAC and other sulphonic acids, except VBSA, support the hydrogen evolution reaction, yield deposits of higher iron content and show a lower current efficiency which decreases on increasing their concentration in the electrolyte. In contrast to SAC, the presence of TU causes least change in composition with change in solution pH and flow conditions. The behaviour of VBSA can be attributed to its influence on hydrogen evolution and on the polarisation effect on iron deposition which will be dealt with separately.

It can be seen from Figure 3, that an increase in cathode current density from 8 to 12 mA cm^{-2} increases the iron content in the deposit significantly using MTU, TU and SAC; VBSA, PTU and NTS showed lower variation in iron content of the alloy with increasing current density. In alloy deposition

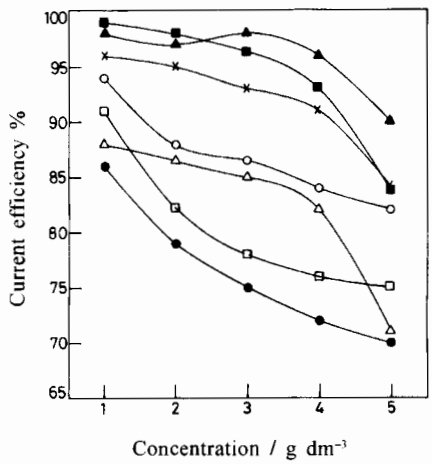


Figure 2. Effect of additive concentration on the cathode current efficiency of alloy deposition. Conditions as above; -□- SAC, -■- TU , -Δ- NTS, -▲- VBSA, -○- ATU, -●- PTU, -x- MTU.

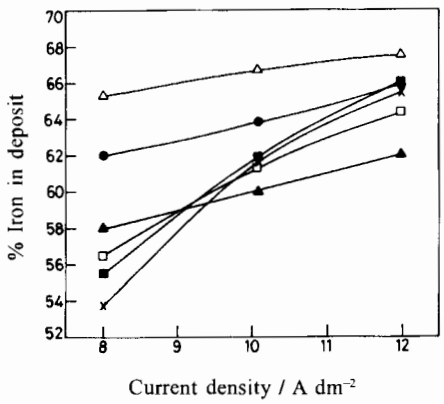


Figure 3. Effect of current density on the percentage iron content of the alloy Conditions as above; Conc. in g dm^{-3} : -□- SAC 2 g dm^{-3}, -■- TU 5 g dm^{-3}, -Δ- NTS 3 g dm^{-3}, -▲- VBSA 4 g dm^{-3}, -●- PTU 1 g dm^{-3},-x-MTU 3 g dm^{-3}.

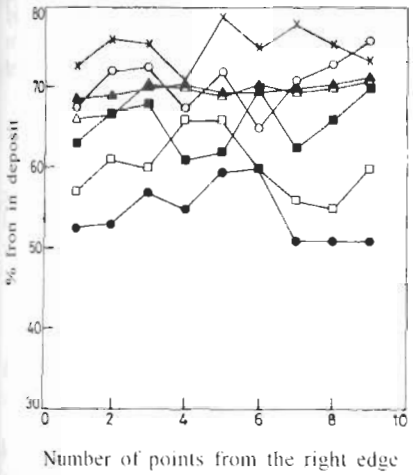


Figure 4. Effect of additives on the composition distribution on INVAR alloy plated panels: -□- SAC, -■- TU, -△- NTS, -▲- VBSA, -◇- ATU, -●- PTU, -x- MTU.

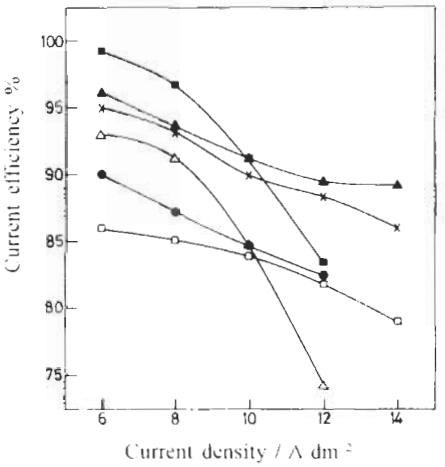


Figure 6. Effect of current density on the cathode current efficiency of alloy deposition Conditions as above; Conc. in g dm⁻³: -□- SAC 2 g dm⁻³, -■- TU 5 g dm⁻³, -△- NTS 3 g dm⁻³, -▲- VBSA 5 g dm⁻³, -●- PTU 1 g dm⁻³, -x- MTU 3 g dm⁻³.

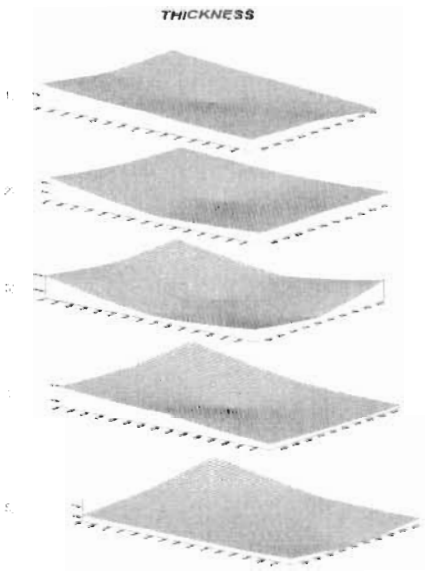


Figure 7. Three dimensional mapping of the thickness distribution of the alloy, on a panel, obtained in the presence of the additives (1) NTS (2) VBSA (3) SAC (4) TU (5) PTU

this latter is the most desired property, known as the "composition dispersion"[1] which should be minimised to get alloys of uniform composition on an intricately shaped component where the current density varies from point to point. XRF examination of the alloy composition at various points, as given in Figure 4 and the three dimensional image of the same, given in Figure 5, confirm that the deposits plated from baths containing VBSA has the least composition dispersion compared to the others.

Figure 6 shows the variation of cathode current efficiency with current density. It is observed that in the presence of TU and NTS, the decrease in current efficiency with increasing current density is steeper than for the other additives. The trend shown by VBSA and PTU indicates that they are the most suitable ones to produce deposits at 10 A dm⁻², which has been fixed as the optimum current density from the previous experiments. The three dimensional mapping of the thickness distribution at various points, given in Figure 7, supports the above view. However, considering the limited solubility of PTU and the highly stressed nature of deposits produced in its presence, VBSA is considered to be the best additive to produce compact bright deposits with uniform composition and thickness distribution.

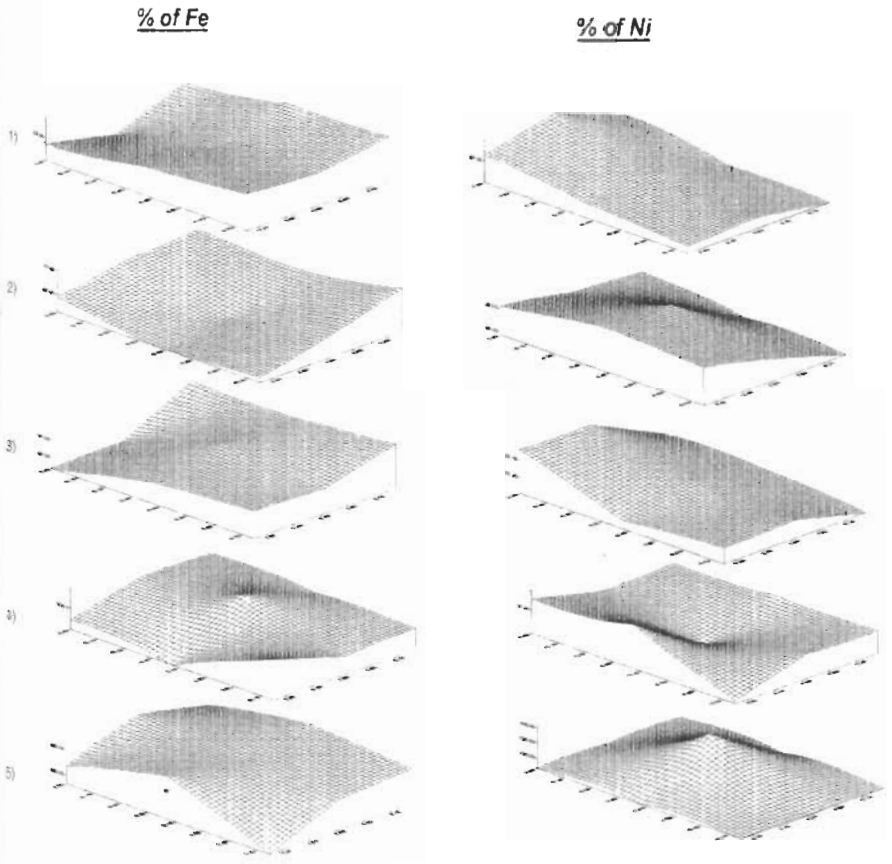


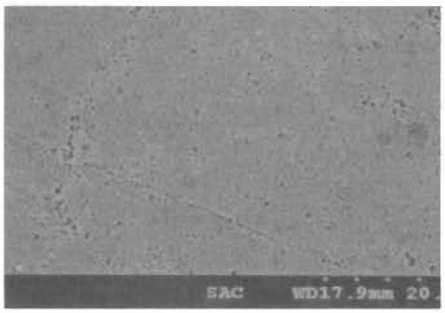
Figure 5. Three dimensional mapping of the composition distribution of the alloy on a panel, obtained in the presence of the additives (1) VBSA (2) NTS (3) TU (4) SAC (5) ATU

Micro hardness of alloy deposits produced in the form of electroformed foils, ranged from 500 to 700 VHN at a load of 20 kg. On heat treatment there was a slight reduction in hardness due to stress relief. However, the readings obtained on highly cracked deposits and after heat treatment were somewhat irreproducible due to improper indentation. On heat treatment the deposits became bent making the measurements difficult. Measurements should be repeated on thick electroformed alloy.

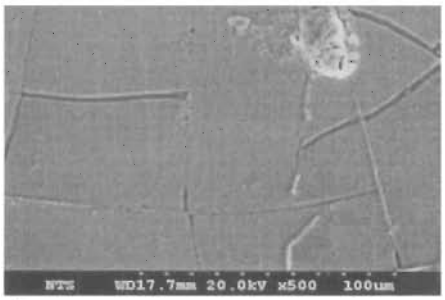
SEM micrographs of the Invar alloy deposits produced in the presence of the additives are given in Figures 8 and 9. SAC, NTS and VBSA yield deposits with a fine-grained structures, which are not resolved even under high magnification. The deposits show fine cracks, which is characteristic of all iron-rich deposits. On heat treatment, the deposits soften and the cracks are reduced. In the case of the deposit plated with NTS, the grains appear, probably indicating the softness of the deposit. Deposits plated with TU and PTU do not show any cracks, but, developed a mud-cracked structure on heating; that plated in the presence of ATU is highly cracked and developed a leafy structure on heating. Deposits plated with TU and its derivatives became very brittle on heating.

CONCLUSION

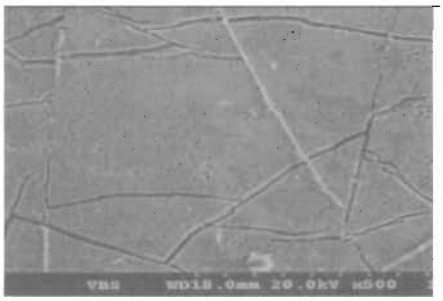
Iron nickel alloy deposits were produced in presence of various additives. The presence of



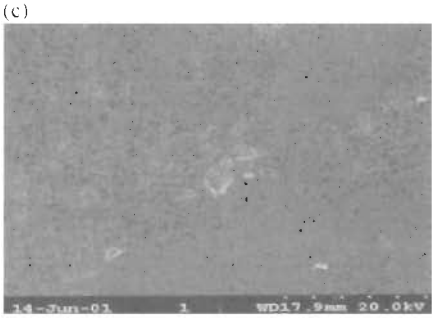
(a)



(b)



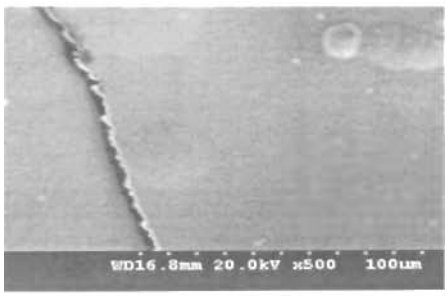
(c)



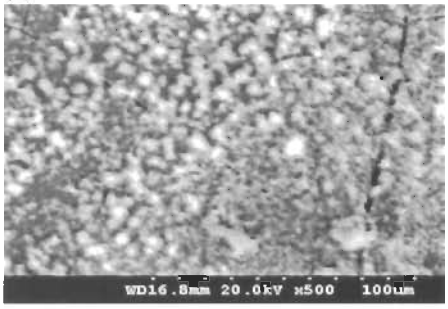
(d)

(e)

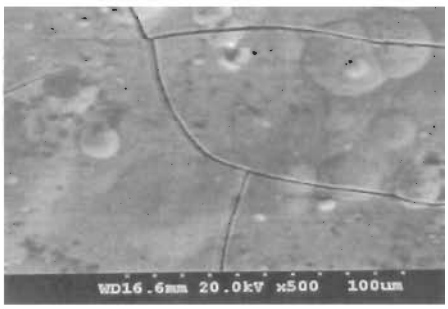
Figure 8. SEM Photomicrographs of alloy deposits with additives: (a) SAC (b) NTS (c) VBSA (d) TU (e) ATU



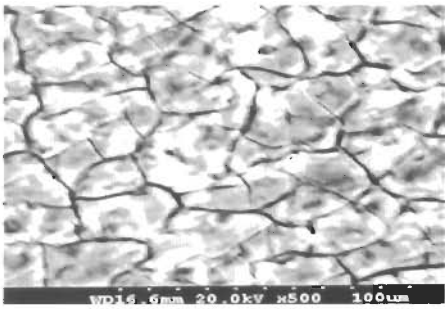
(a)



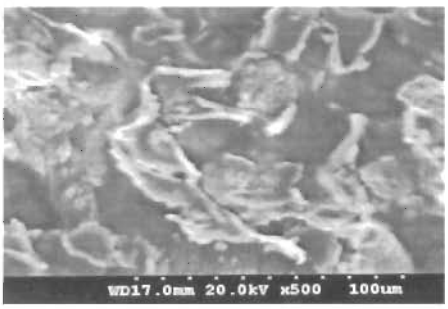
(b)



(c)



(d)



(e)

Figure 9. SEM Photomicrographs of alloy deposits after heat treatment, with additives: (a) SAC (b) NTS (c) VBSA (d) TU (e) ATU

VBSA is found to give deposits of desire composition with high efficiency, unifor composition and thickness with a fine-graine structure.

ACKNOWLEDGEMENTS

The authors wish to express their since thanks to the Director, Centr Electrochemical Research Institute f permission to publish this work.

REFERENCES

1. A. Brenner, "Electrodeposition of Alloy Principles & Practice", Academic Pres N.Y., 1963.
2. M. Van Schilfgraarde, I.A. Abrikosov an B. Johansson , *Nature* , 1999, **400** (7) 4
3. D.L. Grimmet, M. Swarrtz and K. Nob *Plat. Surf. Fin.*, 1998, **75** (6) 94.
4. N. Phan, M. Schwartz, and K. Nob *Plat. Surf. Fin.*, 1998, **75**(8) 46.
5. D.L. Grimmet, M. Schwartz and K Nobe, *J.Electrochem. Soc.*, 1990, 13 3414.
6. D.L. Grimmet, M. Schwartz and K. Nob *J. Electrochem. Soc.*, 1993, **140** 973.
7. R. Brugger, "Nickel Plating", Robe Draper Ltd., Teddington, U.K., 1970.
8. J.K. Dennis and T.E. Such, "Nick Chromium Plating", Butterworths, 198
9. A. Bodonevas and J. Zahavi, *Plat. Su Fin.*, 1994, **81**(12) 75.
10. K. Nakamura, M. Umetani and Hayashi, *Surf. Technol* ., 1985, **25** 111
11. J. Edwards, *Trans. Inst. Met. Fin.*, 196 **39** 33.
12. J. Edwards, *Trans. Inst. Met. Fin.*, 196 **39** 52.
13. T. Osaka, M. Takai, Y. Sagawa, T. Momm K. Ohashi, M. Sato and K. Yamuda, *Electrochem. Soc.*, 1999, **146** 2092.
14. T. Osaka, T. Sawaguchi, F. Mizutani, Yokoshima, M.Takkai and Y. Okinaka, *Electrochem. Soc.*, 1999, **146** 3295.
15. I. Tabakovic, S. Riemer, V. Inturi, Jallew and A. Thayar, *J. Electroche Soc.*, 2000, **147** 219.
16. F. Czerwinski, *Electrochim. Acta*, 197 **126** 186.
17. B.N. Popov, S.N. Popova , Ken-Mi Yin and R.E. White, *Plat. Surf. Fin.*,199 **81**(3) 65.
18. J. Horkans, *J. Electrochem. So* 1979,**126** 186.
19. H. Dahms and I. Croll, *J. Electroche Soc.*, 1965, **112** 771.
20. K.M. Yin, J.H. Wei, J.R. Fu, B.N. Popo S.N. Popova and R.E. White, *J.App Electrochem.*, 1995, **25** 543.
21. T.C.Franklin, *Plat. Surf. Fin.*, 1993, 80 53.
22. J. Bielinski and J. Przyluski, *Su Technol.*, 1979, **9** 65.