

Effects of Ion Active Agents on the Electrodeposition of Ni-Sn Alloys

By

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Abstract

The effects of three kinds of active agents, e. g.

Anion: $(C_{17}H_{33}COONa)$

Nonion: $\left(R-N \begin{array}{c} (CH_2CH_2O) \ nH \\ (CH_2CH_2O) \ nH \end{array} \right),$

and

Cation: $\left(\left[\begin{array}{c} CH_3 \\ | \\ R - N - CH_3 \\ | \\ CH_2 - \text{C}_6\text{H}_5 \end{array} \right]^+ Cl^- \right)$ on the deposit were examined.

The experiments of electrodeposition of a Ni-Sn Alloy were carried out in the Hull-cell which used a current of 2 A. The cathode was steel or copper plate and the anode was Sn- and Ni-plates.

The composition of the electrolytic bath was $NiCl_2 \cdot 6H_2O$ 300 g/l; $SnCl_2 \cdot 2H_2O$ 50 g/l; H_3BO_3 30 g/l; $NH_4F \cdot HF$ 56 g/l. The temperature of the bath was 65°C.

The structure of the deposits was observed and determined by means of Microscope, Scanning Electron Microscope, X-ray Diffractometry, and Electron Probe Micro Analyser.

The results obtained were summarized as follows:

1) All ion active agents influence the surface condition and the structure of the deposits.

2) The electrodeposited alloys from the solution without additional agents are mainly Ni_3Sn_4 , and from the bath with the anion active agent are mostly Ni_3Sn_4 on copper, and on steel, respectively. The solution added non-ionic addition agent which gives a β -Sn deposit only on steel, but on copper gives Ni_3Sn_4 . Moreover, the solution added cation active agent which gives a β -Sn deposit only either on steel or on copper.

3) The effects of ion active agents on the structure of the deposits are independent of the current density.

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1. Introduction

The electrodeposited *Ni-Sn* alloys containing intermetallic compounds have so many interesting characteristics such as hardness, color, metallic luster, wear resistance, abrasion resistance, and corrosion resistance, etc. that they have been used in many industrial fields such as automobiles, electronics, and decorations.

The scientific and technological interests in the electro-deposition and the properties of the alloys have continued since being introduced by Monk and Ellingham, who were interested in improving the hardness and abrasion resistance of tin coatings in 1935⁽¹⁾. Very many research results on the electrolytic conditions for the deposition and on the structures and properties of the deposits have been reported⁽²⁾⁽³⁾, but the reports about the effect of surface active agents are very few. The work by Parkinson⁽⁴⁾ who found that in the deposition of *Ni-Sn* alloys from a fluoride bath, additional agents usually decrease the percentage of nickel content in the deposit is encouraging us to study much more about that.

This paper deals with the effect of three kinds of ion active agents namely anion, nonion, and cation on the structure and composition of *Ni-Sn* alloys electrodeposited from a fluoride bath using a Hull-Cell.

2. Experimental

The effects of ion active agents on the electrodeposition of *Ni-Sn* alloys were studied using a thermostatic Hull-Cell under the standard electrolytic condition as shown in *Table 1*.

The three kinds of ion active agents added to the standard bath are shown in *Table 2*, and the amount of the agent added is shown in *Table 3*.

The surface conditions and the structure of the deposit were observed using

Table 1. Standard Electrolytic Condition

<i>Bath Composition :</i>	
NiCl ₂ • 6 H ₂ O	300 g/l, SnCl ₂ • 2 H ₂ O 50 g/l, NH ₄ HF ₂ 56 g/l, H ₃ BO ₃ 30 g/l,
Hull-Cell : 267 ml.	
<i>Electrolysis ;</i>	
Total current 2A, Temperature 65°C, Duration 6 min., Cathode plain carbon steel plate, or copper plate Anode tin and nickel plates, without agitation	

Table 2. Ion Active Agent

Anion	: Oleic Acid Sodium Salt	$C_{17}H_{33}COO Na$
Nonion	: Polyoxy Ethylene Alkyl Amine	$R-N \begin{cases} (CH_2CH_2O) nH \\ (CH_2CH_2O) nH \end{cases}$
Cation	: Alkyl Benzyl Ammonium Chloride	$\left(\begin{array}{c} CH_3 \\ \\ R - N - CH_3 \\ \\ CH_2 - \text{C}_6\text{H}_5 \end{array} \right)^+ Cl^-$

Table 3. Amount of Addition Agent Added

Bath No.	A	N	C
0	0 g/l	0 g/l	0 g/l
1	4×10^{-3} g/l	4×10^{-3} g/l	4×10^{-3} g/l
2	2×10^{-2} g/l	4×10^{-2} g/l	7×10^{-2} g/l
3	2.1×10^{-1} g/l	2.0×10^{-1} g/l	2.6×10^{-1} g/l
4	1.0×10^0 g/l	1.0×10^0 g/l	1.0×10^0 g/l

Bath A : Standard bath + Anion agent

Bath N : " " + Nonion agent

Bath C : " " + Cation agent

an optical microscope ($\times 200$ or $\times 400$) and a scanning electron microscope ($\times 2000$, HITACHI Type-S-40). The composition of the surface was analyzed by a scanning electron microanalyzer (HITACHI Type X-650), and the crystal structure was identified by the X-ray diffraction pattern of $Co \cdot K_{\alpha}$ with Joint Committee Powder Diffraction Standard Card. (X-ray generator PHILIPS Type PW 1729, Gonio meter Type 42266.)

3. Results and discussion

As shown in *Fig. 1*, naked eye observation showed that all the active agents (anion, nonion and cation) gave effects to the appearance of the deposit either on steel or on copper.

A small amount of active agent increased the brightness of the deposit at

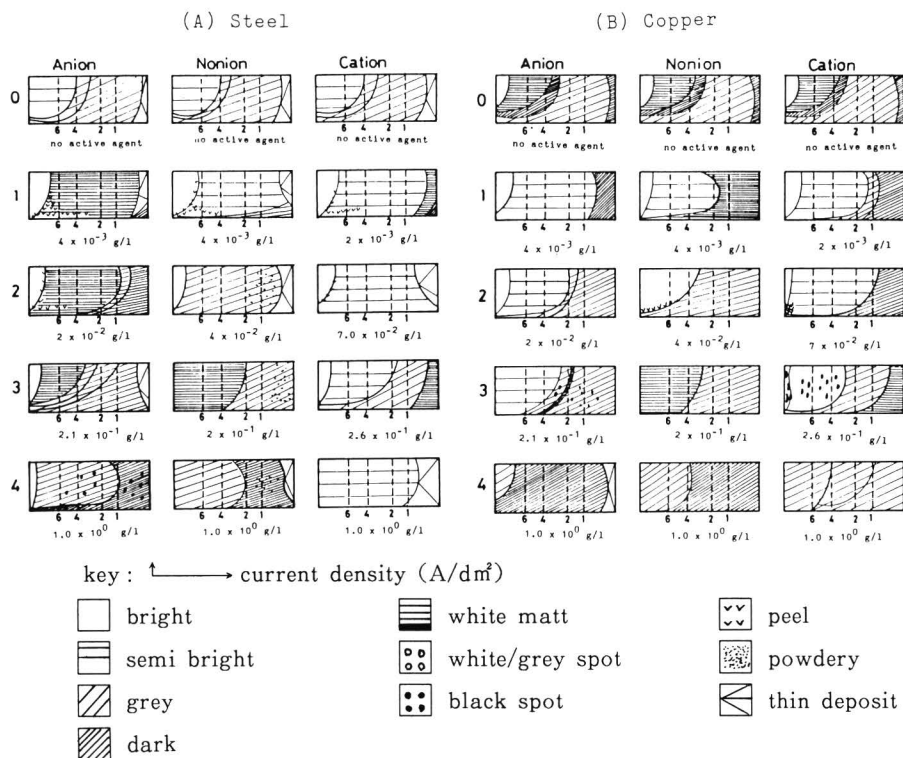


Fig. 1 Naked eye observation

the high current density area. When the addition was continued, on the other hand, the bright area decreased gradually.

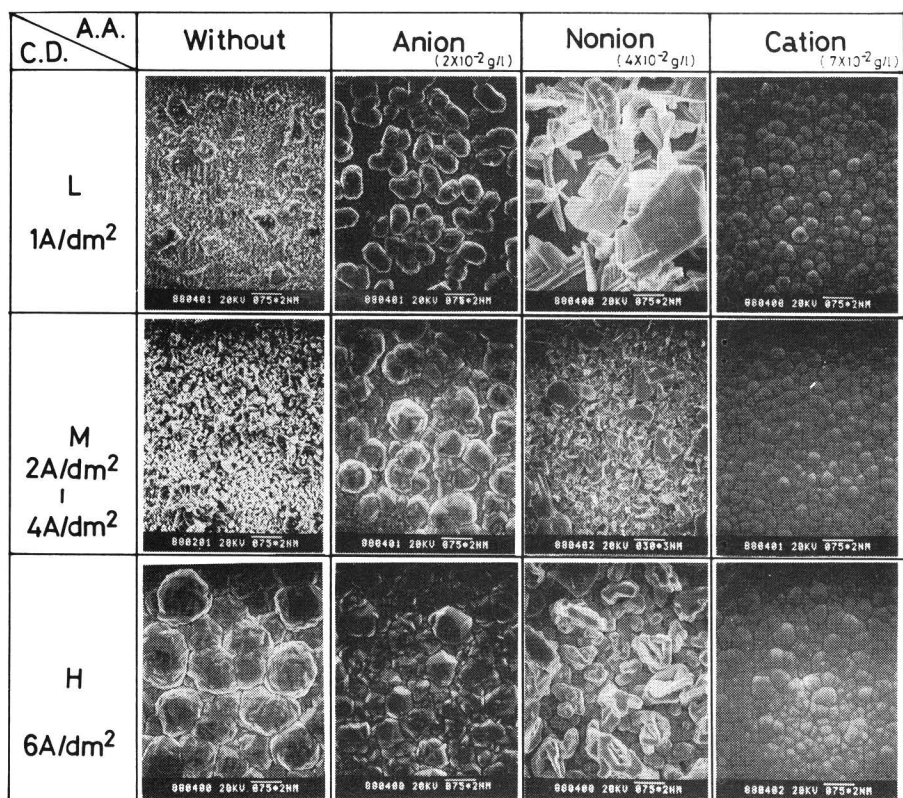
The highest concentration on the active agent in this experiment (1 g/l) resulted in a deposit which had no bright area, except the anion active agent on steel.

Peeling occurred on the boundary of the bright area and next to it. A thin deposit could be found at the low current density area especially on steel.

The anion active agent resulted in a black spot deposit on steel at the 1 g/l concentration at the medium and low current density areas.

The addition of the 4×10^{-2} g/l nonion active agent caused a powdery deposit at the low current concentration on steel. This powdery deposit also occurred on the next grade concentration (2×10^{-1} g/l, and 1 g/l).

The cation active agent gave a white spot on copper at the 2.6×10^{-1} g/l concentration at the high current density area.

Fig. 2 SEM observation of deposit on steel ($n \times 10^{-2} \text{ g/l}$)

As mentioned before, the observation was also done by means of an optical microscope by magnification $\times 200$ and $\times 400$. The results are as follows; if to the standard bath was added the ($n \times 10^{-3} \text{ g/l}$) active agent, much the same crystal size and shape (small and round) were obtained compared with the deposit from the standard bath.

Further addition was found to produce a significant change of the crystal size and shape.

Those tendencies could be observed clearly when observation was done by SEM ($\times 2000$). The results are summarized in Fig. 2, 3, 4, and 5.

As shown in Fig. 2, the standard bath produced a mixture of round and sharp crystals at the low current density (1 A/dm^2) and the medium current density ($2-4 \text{ A/dm}^2$). At the low current density the size was smaller than at the medium current density. At the high current density (6 A/dm^2) big and round crystals were found. The EPMA observation of those specimens gave

information that the deposits contained nickel and tin at all current density areas, and the X-ray pattern showed that the deposit had a $NiSn$ structure at the $8-10 A/dm^2$ area and a Ni_3Sn_4 structure was found at the lower current density area ($1-6 A/dm^2$).

The addition of the anion active agent resulted in an ellipsoidal shape at the low current density, and the shape changed to a round shape when the current density increased. The EPMA observation shows that the deposit contained nickel and tin at all current densities, and the X-ray pattern shows that the deposits had a Ni_3Sn_4 structure at all current densities.

The addition of the nonion active agent resulted in big and sharp crystals at the low current density, the same shape but rather small occurred at the medium current density and a mixture of sharp and round crystals was found at the high current density area. From the EPMA observation, the deposit was found to be tin only, and the X-ray pattern showed that the deposit had a $\beta-Sn$ structure at all current densities.

The addition of the cation active agent produced a deposit which had the same round shape at all current density areas. The deposit contained nickel and tin as observed by EPMA, and had a $NiSn$ structure at the high current density, but Ni_3Sn_4 at the medium and low current densities.

The effect of the deposit on steel caused by the addition of the $1 g/l$ active agent can be seen in *Fig. 3*.

The anion active agent produced small size crystals at the low current density, but at the medium and high current densities round crystals were found. The deposit contained nickel and tin, and the X-ray pattern showed a Ni_3Sn_4 structure in all current density areas.

The deposit effected by the addition of nonion had sharp and large crystals at the low current density, sharp and tiny crystals could be found at the medium current density, and again round crystals occurred at the high current density. The EPMA observation showed that the deposit consisted of tin only at all current densities and the X-ray pattern showed that it had a $\beta-Sn$ structure at all current densities.

The addition of the cation active agent altered the crystals which became big and round at the low current density. At the medium current density sharp crystals were found, and round crystals occurred at the high current density. The result from EPMA showed that the deposit contained tin only, and the X-ray examination gave a $\beta-Sn$ structure.

The SEM observation of the deposits on copper by adding $n \times 10^{-1} g/l$ of active agents can be seen in *Fig. 4*.

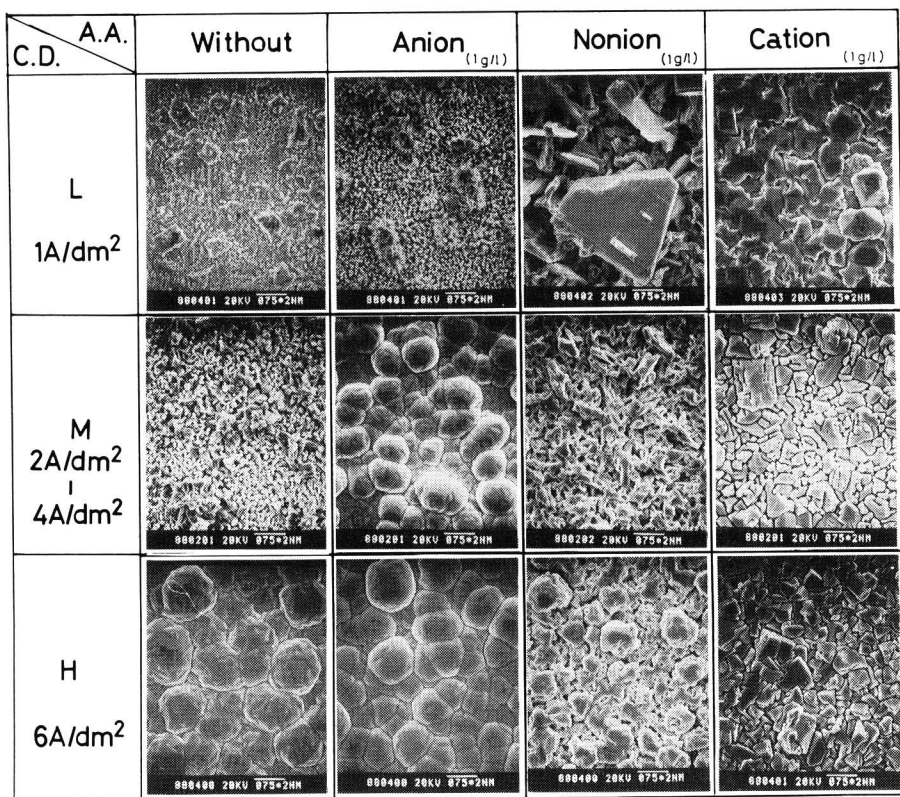
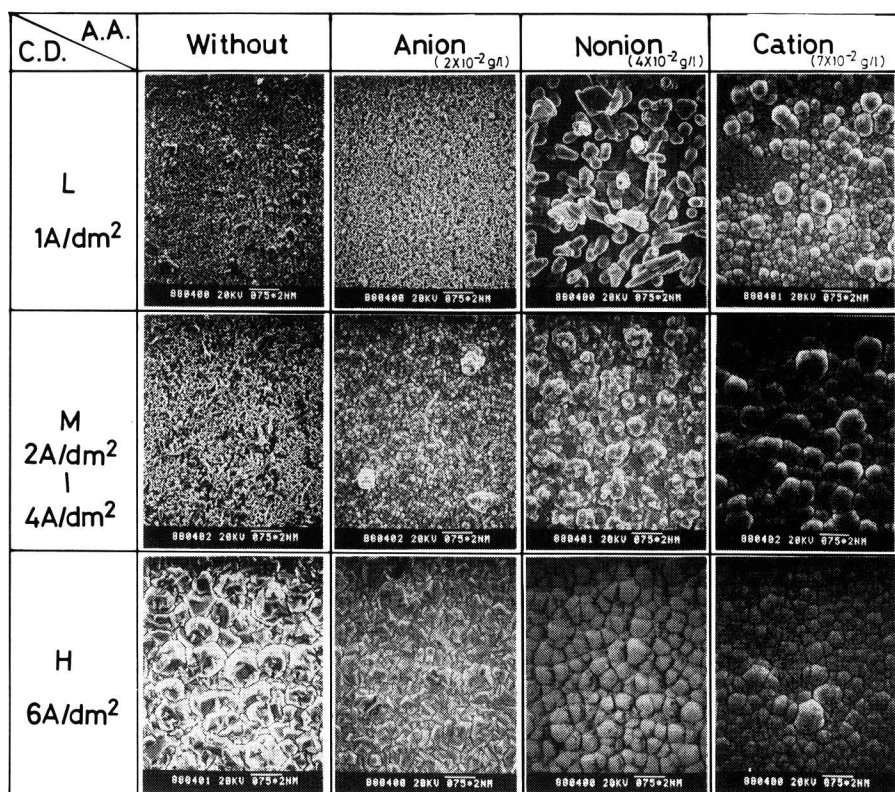


Fig. 3 SEM observation of deposit on steel (1g/l)

The crystals produced by the standard bath had the same figure with deposits on steel at all current density areas. It was found that the deposits contained nickel and tin after EPMA, and by X-ray it was a Ni_3Sn_4 structure.

The anion active agent had no effect on the crystal size and shape at the low current density. It had almost the same condition as the crystals produced by the standard bath. However, at the medium current density the shapes of crystals became round, and at the high current density the size of the crystals was smaller than that of the standard bath. The EPMA showed that the deposits contained nickel and tin, and the X-ray showed the deposits had a $NiSn$ structure at the high current density and Ni_3Sn_4 for the rest of the current densities.

The addition of the nonion active agent resulted in a deposit which had some crystals which looked like bullets at the low current density. At the medium current density round crystals were found and at the high current

Fig. 4 SEM observation of deposit on copper ($n \times 10^{-2}$ g/l)

density round crystal occurred. The EPMA showed the deposits contained nickel and tin, and the X-ray showed that the deposits had a $NiSn$ structure at all current density areas.

The cation active agent produced deposits which had round crystals at all current density areas. However, the size was different at the low current density where big and small round crystal mixtures were found having a somewhat coarse structure. The EPMA showed the deposits contained nickel and tin at all current density areas and the X-ray pattern showed Ni_3Sn_4 at the low and medium current densities and $NiSn$ at the high current density.

The SEM observation of the deposit on copper by adding 1 g/l of active agents can be seen in Fig. 5.

The anion active agent resulted in short stick shape crystals at the low current density area, and at the medium current density small and round crystals looking like marbles but not massive occurred. Very small sized crystals

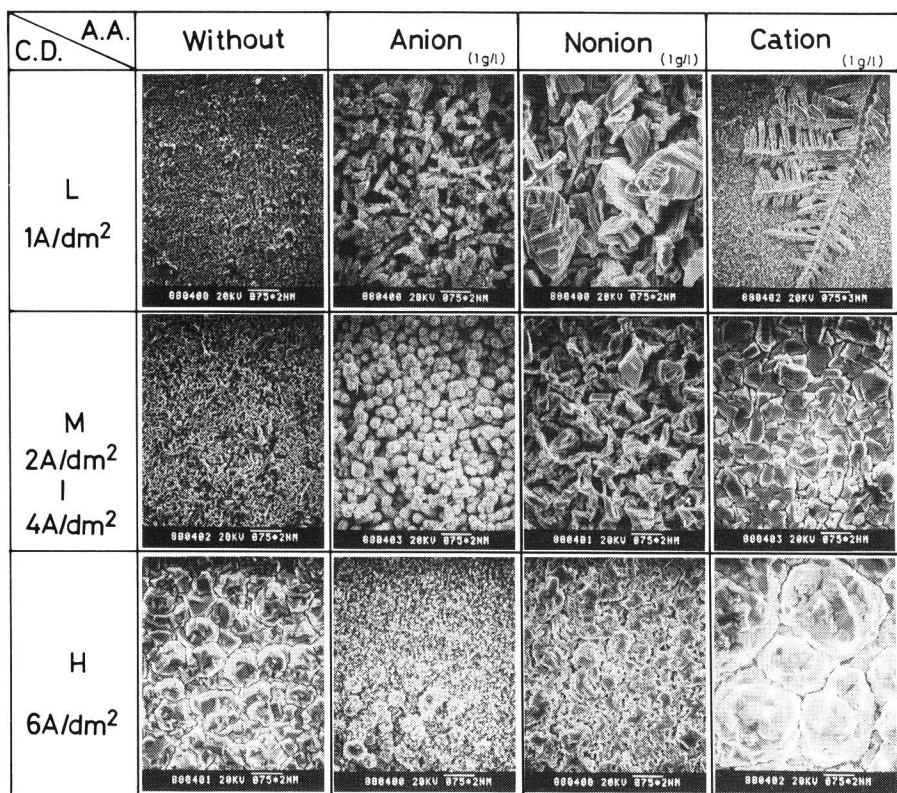


Fig.5 SEM observation of deposit on copper (1g/l)

could be found at the high current density area. The EPMA showed that the deposits contained nickel and tin at all current densities and the X-ray pattern showed a Ni_3Sn_4 structure.

The nonion active agent effected deposits which had big and sharp crystals at the low current density, and almost the same shape but smaller crystals could be found at the medium current density area and also at the high current density. The EPMA showed that the deposits contained tin only and a β -Sn structure appeared on the X-ray.

The cation active agent gave very small crystals with a tree-like shape at the low current density. Rather big and sharp crystals were found at the medium current density and at the high current density very big crystals looking like cauli-flowers occurred. The EPMA observation showed that the deposits contained tin only, and also the X-ray examination identified that they had a β -Sn structure.

By the EPMA, it could be noted that the nickel content decreased by a decreasing current density if to the bath was added cation or a nonion active agent, e.g., addition of 7×10^{-2} g/l cation active agent resulted in a deposit which had 61% atomic weight of Sn and 39% of Ni at the high current density, 64.5% Sn and 35.5% Ni at the medium and 72% Sn, 28 %Ni at the low current density on copper.

4. Conclusion

The electrodeposition of Ni-Sn alloys from a mixed bath of nickel-, tin-chloride and fluoride using a Hull-Cell was studied by adding three kinds of ion active agents: oleic acid sodium salt as anion, poly ethylen alkyl amine as nonion, and alkyl benzyl dimethyl ammonium chloride as cation.

The results obtained for the same amount of addition (1 g/l) were summarized as follows:

- 1) All ion active agents influence the surface condition and the structure of the deposit.
- 2) The electrodeposited alloys from the bath without additional agents are mainly Ni_3Sn_4 , and from the bath with the anion active agent are mostly Ni_3Sn_4 on both steel and copper. The bath with the nonion active agent gives β -Sn on steel and also appears on copper. The bath with the cation active agent gives a β -Sn deposit on both steel and copper.
- 3) The nickel content of the deposit decreases by a decreasing current density if to the bath is added a relatively small amount of cation or nonion active agent.

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6. References

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