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New high-tin phase found in electrolytic Sn–Ni deposits

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Using X-ray diffraction technique and transmission electron microscopy it has been demonstrated that multiphase Sn–Ni electrodeposits with 3–34 at.% Ni contain a new phase of composition close to $NiSn_9$. Its lattice parameters are specified as follows: $a_0 = 1.2621(7)$, $b_0 = 0.5231(4)$, $c_0 = 0.6213(4)$ (in nm), $\beta = 105.8(7)^\circ$ of the C 2/m space group. This new phase decomposes at 100°C into β tin and Ni_3Sn_4.

1. Introduction

Tin–nickel alloys are promising materials to be utilised as electrolytic coatings for decorative and functional use [1, 2]. As for now, coatings with 50 at.% of nickel are widely employed. However, their wider application is blocked as present deposition technology requires an aggressive hot fluoride–chloride bath. Therefore, as a replacement an environment friendly weak alkaline pyrophosphate solutions being used at ambient temperature were proposed [3–5].

Biestek *et al.* [6] have already presented some results on electrodeposition of Sn–Ni alloys with various Ni content from pyrophosphate solutions. The X-ray examination of these deposits revealed a set of lines, which do not correspond to any known phases in Sn–Ni system [7]. Therefore, it was suggested that a new phase might form during that process.

The aim of the present paper was to analyse both the morphology and crystal structure of this new phase in Sn–Ni deposits as well as to determine its sensitivity to heat treatment.

2. Experimental procedure

Coatings containing from 50 to 100 at.% Sn of a nominal thickness of 10 μm were electrodeposited from weak-alkaline (pH 8.2) pyrophosphate solutions at ambient temperature on copper plates as described in [6]. Tin to nickel ratios in surface layers were determined with electron spectroscopy for chemical analysis (ESCA).

X-ray measurements at ambient temperature were performed using Philips PW 1710 diffractometer with Co K_α radiation. The phase composition of selected electrodeposits during heat treatment was analysed in Philips X'PERT diffractometer (Cu K_α radiation, measuring range 2θ: 20–100°) equipped with Anton Paar HTK 16 high temperature camera.

Microstructure observations were performed using Philips CM (200 kV) transmission electron microscope equipped with Phoenix EDAX electron dispersive spectroscopy system (EDS). Thin foils were prepared in plan view by mechanical dimpling from the copper substrate side.

3. Results and discussion

The X-ray diffraction patterns of electrodeposits under investigation indicated that all specimens except tin (β-Sn) and pure NiSn intermetallic compound are multiphase mixtures. Diffraction lines from the hypothetical new phase referred to as the "X" phase were seen in the patterns of alloys containing between 3 and 34 at.% of nickel. The set of lines from the X phase dominated for deposits with 14.8–19.2 at.% Ni with the maximum of the X phase intensity obtained for a deposit containing 16.9 at.% Ni. At the last composition lines of β tin ($I_{\max\{101\}} = 33.3\%$) and a weak line from NiSn($I_{\{110\}} = 1.8\%$) were also recorded (Fig. 1A).

The specimen with the highest content of X phase was annealed and analysed as presented in Table I. First it was heated up to 110°C and kept at that temperature for 22.5 hours. Next, the specimen was heated to 120°C, annealed for 1 hour and cooled to ambient temperature. The X-ray patterns recorded during these experiments

TABLE I Description of in situ heating/annealing/cooling of Sn-Ni electrodeposit in X-ray diffractometer

No	Procedure[a]	Temperature (°C)	Time (min.)	Diffraction patterns (see Fig. 1)
1	S	20	60	A
2	H	110	30	
3	S	110	60	
4	A	110	120	
5	S	110	60	
6	A	110	120	
7	S	110	60	B
8	A	110	120	
9	S	110	60	C
10	A	110	120	
11	S	110	60	D
12	A	110	120	
13	S	110	60	
14	A	110	120	
15	S	110	60	E
16	A	110	120	
17	S	110	60	
18	H	120	30	
19	A	120	60	
20	C	20	30	
21	S	20	60	F

[a] S—scanning, H—heating, A—annealing, C—cooling.

(Cu K_α radiation) indicated that X phase slowly decomposes at 110°C into two stable phases β-Sn and Ni_3Sn_4 (Fig. 1). Similar but very slow decomposition of the X phase was also observed at 100°C.

Appearance of additional lines recorded during annealing (Fig. 1C–F) might have been caused either by recrystallization of NiSn or formation of another stable phase in this system like Ni_3Sn_2. The NiSn and Ni_3Sn_2 have similar crystal structure making them practically indistinguishable from each other with standard X-ray phase analysis. Therefore, as the presence of Ni_3Sn_2 was not verified it was omited in further analysis.

The microstructure observation of electrodeposit with 16.9 at.% Ni revealed that this material is built of submicron grains (Fig. 2). Some of them were roughly equiaxed (Fig. 3a), while others showed distinct pole like shape with rounded ends (Figs 4a, 5a). The selected area electron diffraction, presented in Figs 3b and 4b, indicated that while the equiaxed grains are of β-tin, though those from elongated grains did not match any of the known phases from Ni–Sn system. However, it was noted that the obtained diffraction patterns might be positively indexed with enlarged elementary unit cell of Ni_3Sn_4 ($a_0 = 1.22$ nm, $b_0 = 0.40$ nm, $c_0 = 0.52$ nm and $\beta = 105.2°$), i.e. $a_0 = 1.25$ nm, $b_0 = 0.53$ nm, $c_0 = 0.62$ nm and $\beta = 105.2°$. Crystallites of the new phase were also characterised by dense planar faults lying on {100} planes parallel to their long axis (Fig. 5).

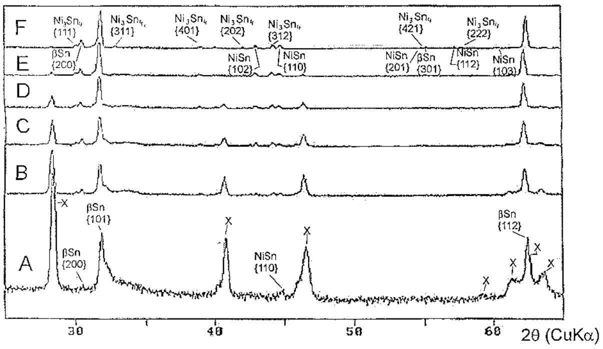

Figure 1 Selected X-ray diffraction patterns recorded during annealing of Sn-Ni electrodeposit (see Table I).

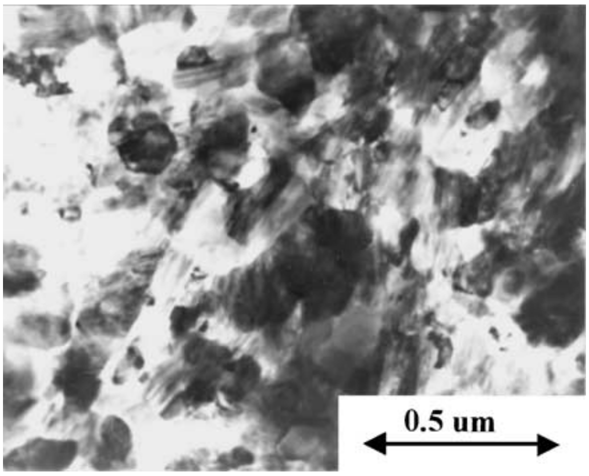

Figure 2 Microstructure of Sn-Ni electrodeposit of mixed morphology.

TABLE II Observed and calculated plane spacing for X phase

No	2Θ (Co K_α)	*d* (nm) Observed	*d* (nm) Calculated	Intensity Observed	Intensity Calculated	Mueller indices (h k l)
1	33,33	3,1211	3,112	100	100	(3 1 1)
2	43,08	2,4378	2,432	2	98	(2 0 2)
3	47,85	2,2074	2,203	33	85	(5 1 0)
4	54,09	1,9686	1,9653	3	11	(0 2 2)
5	54,78	1,9456	1,9423	18	2	(6 0 2)
6	72,81	1,5082	1,5064	2	3	(3 3 1)
7[a]	74,17	1,4833	1,4816	27	2 + 30	(3 1 4)
8[b]	75,60	1,4605	1,4589	5	1	(2 2 3)
9	114,00	1,0673	1,0667	10	2	(9 3 0)
10[c]	118,09	1,0430	1,0425	18	1	(1 5 0)

Possibility of coexistence with diffraction lines from βSn (ASTM;4-0673).

[a] $d = 1,484$; $I = 23\%$.

[b] $d = 1,458$; $I = 13\%$.

[c] $d = 1,0434$; $I = 3\%$.

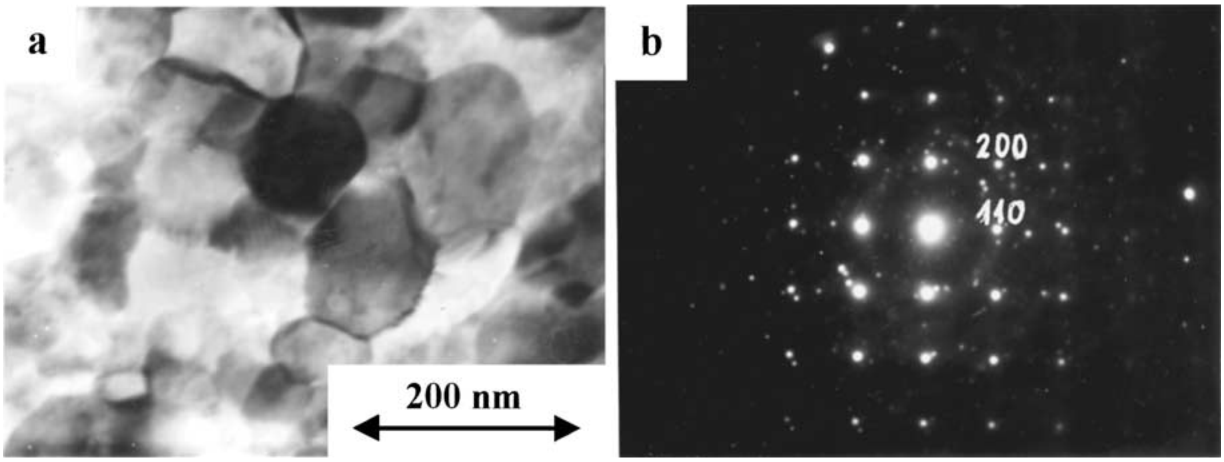

Figure 3 Microstructure of equiaxed grains in Sn-Ni electrodeposit (a) and corresponding selected area electron diffraction pattern (b).

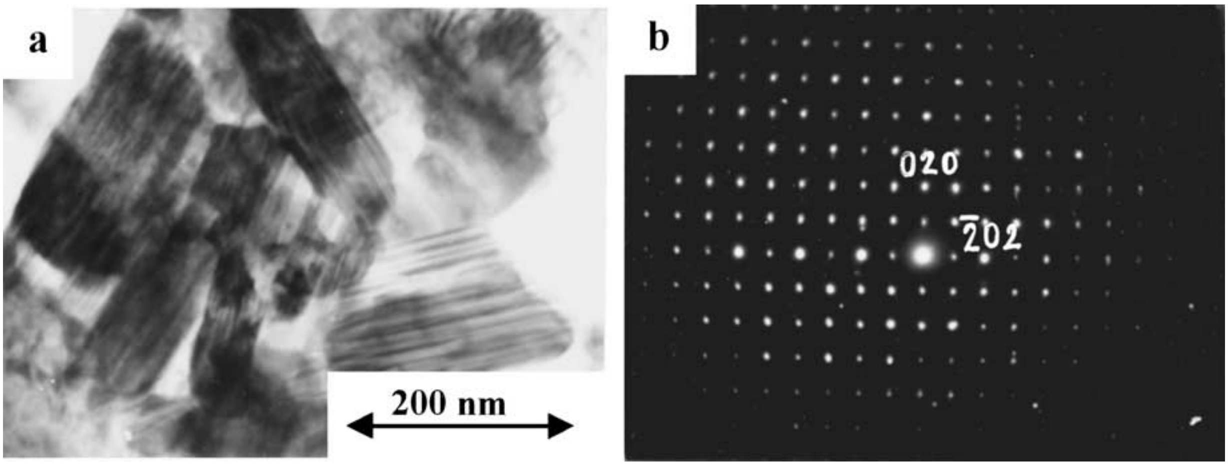

Figure 4 Microstructure of elongated grains in Sn-Ni electrodeposit (a) and corresponding selected area electron diffraction pattern (b).

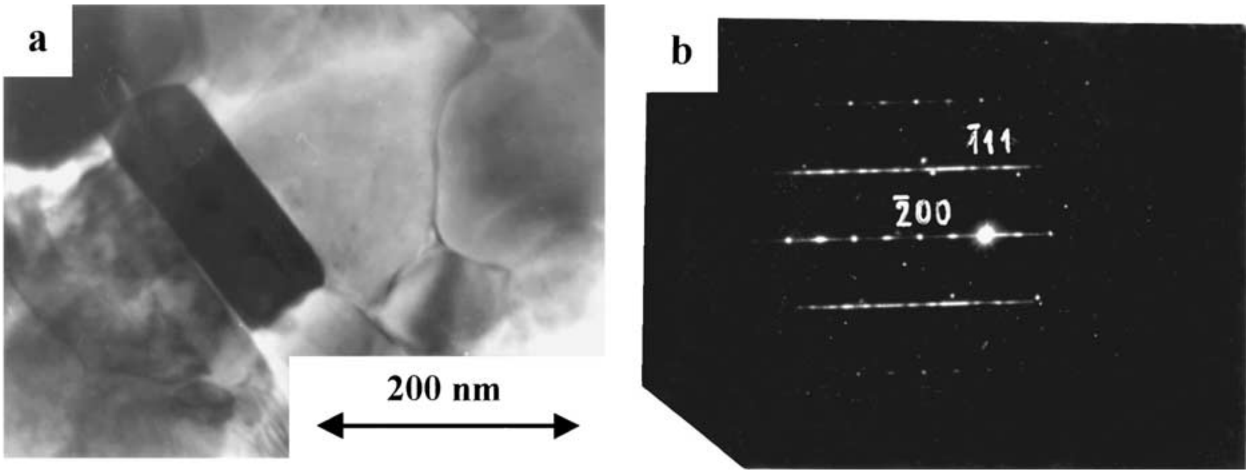

Figure 5 Defects in elongated grains (a) and corresponding selected area electron diffraction pattern (b).

The EDS microanalysis of the equiaxed β-Sn crystallites showed presence not only of tin but also traces of nickel, which might have been incorporated in it either during electrodeposition process or resulted just from sample preparation. The elongated crystallites of X phase showed consistently around 10 at.% of nickel, i.e. their chemical composition is close to $NiSn_9$. The above indicates that while the X phase preserved symmetry of the Ni_3Sn_4 compound, though some of the positions occupied in Ni_3Sn_4 by nickel are filled by tin in X phase instead. The 10 at.% of nickel might be obtained by substituting all nickel atoms with tin except those in {100} planes as presented in Fig. 6.

Using the lattice constants found by electron microscopy, X-ray powder diffraction patterns (Co K_α radiation) were indexed using programs of the PROSZKI system [8] (see Table II). The specified lattice parameters are as follows: $a_0 = 1.2621(7)$, $b_0 = 0.5231(4)$, $c_0 = 0.6213(4)$ (in nm), $\beta = 105.8(7)^\circ$ of the C 2/m space group.

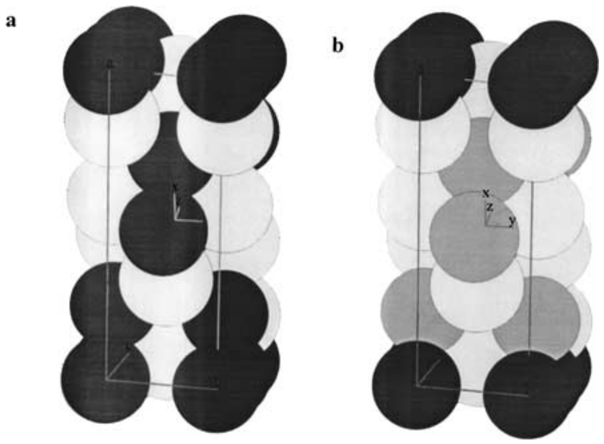

Figure 6 Original Ni_3Sn_4 cell with Ni and Sn atoms filled dark and light respectively (a) and proposed cell for $NiSn_9$ in which Ni positions substituted with Sn were marked by grey (b).

The proposed structure model fits the obtained X-ray spectrum well, while some differences between observed and calculated intensities might arise due to strong texture, occurring always in electrodeposited layers.

4. Summary and conclusions

The X-ray diffractometry and transmission electron observations indicated that electrodeposition of Sn-Ni alloys with 3–34 at.% Ni results in formation of multiphase deposits containing a new phase of composition close to $NiSn_9$. The set of diffraction lines from this phase dominated for deposits containing from 14.8 to 19.9 at.% Ni. This new phase has crystal lattice similar to Ni_3Sn_4, i.e. to C 2/m space group, but its unit cell dimensions are expanded to: $a_0 = 1.2621$, $b_0 = 0.5231$, $c_0 = 0.6231$ (in nm) and $\beta = 105.8°$. The expansion might result from substitution of some of the nickel atoms by the tin ones. During heating this new $NiSn_9$ decomposes at 100°C to β tin and Ni_3Sn_4.

Acknowledgement

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References

1. S. KARPEL, *Product Finish.* **44** (1991) 8.
2. T. BIESTEK, in Proc. Seminar "Surface Ingeneering," Institute of Precision Mechanics, 7–8th November 1995, Warsaw, p.155.
3. M. ISAKI, H. ENOMOTO and T. OMI, *Plating Surf. Finishing* **84** (1987) 6.
4. V. OREKHOVA and I. ROY, *Elektrokhimiya* **27** (1991) 706.
5. T. BIESTEK, W. RIESENKAMPF and W. OKUROWSKI, in Proc. Vth Int. Symp. "Forum for Chemistry 99," Warsaw University of Technology, April 1999.
6. T. BIESTEK, S. SAFARZYŃNSKI, W. RIESENKAMPF and W. OKUROWSKI, in Proc. of Seminar on "Protective Coatings," Inst. of Prec. Mechanics, Warsaw 1997.
7. P. VILLARS, A. PRINCE and H. OKAMOTO, "Handbook of Ternary Alloy Phase Diagrams," Vol. 10 (ASM International, Washington, D.C., 1995) p.12802.
8. W. ŁASOCHA and K. LEWIŃSKI, *J. Appl. Cryst.* **27** (1994) 437.

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