The Electrochemical Deposition of Tin-Nickel Alloys and the Corrosion Properties of the Coating

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Tin/nickel (65/35 wt.%) is a unique coating process because of the deposition of an intermetallic phase of nickel and tin, which cannot be formed by any pyrometallurgical process. From thermodynamic calculations it can be shown that intermetallic phases can be formed through electrodeposition. The alloy has unique corrosion properties and shows surface passivation like stainless steel. The coating is decorative and non-allergic to the skin and can replace decorative nickel and nickel-chromium coatings in many cases and decrease the risk for allergic contact dermatitis. Anumber of electrochemical tests, including polarization curves, chronoamperometric studies and tribocorrosion tests have been performed to show the consequence of replacing nickel coatings with tin/nickel coatings.

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1. Introduction

More than 50 years ago Parkinson¹ (Tin Research Institute) published details describing a process to electroplate a deposit of nickel and tin with the composition of approximately 65/35 wt.% (1:1 atom ratio) from hereof called NiSn. This intermetallic phase of nickel and tin cannot be formed by any pyrometallurgical process and is not to be found in the phase diagram shown in Figure 1.

Early descriptions explain the NiSn phase to be an extension of the composition range of the equilibrium phase Ni_3Sn_2 . This extension is explained by more favoured nucleation kinetics at the deposition temperature, and the resistance of this deposit to transformation at low temperature.² Later the structure of equiatomic NiSn deposit is interpreted by C.C. Lo, who proposes that the electrodeposited tin-nickel alloy consists of Ni_3Sn_2 within each grain and extra tin atoms segregated on the grain boundary.³



Figure 1 NiSn phase diagram.⁴

It is known that the NiSn phase will reveal its metastable character when heated, as it above 350 °C (662 °F) decomposes into the two stable equilibrium phases Ni_3Sn_2 and Ni_3Sn_4 .^{2,5,6}

In the late seventies it was investigated how the NiSn surface is protected from corrosion by a passive film which can be removed by mechanical wear. The authors found that if the substrate is exposed by wear-through or by brittle fracture of NiSn the corrosion resistance is determined by the substrate. It was also stated that freshly fractured edges of NiSn were severely corroded; while three month air exposed fractured edges and original NiSn surfaces were unaffected.⁷

The effect of chloride, bromide or iodide ions on the passivity of NiSn alloys has also been studied.⁸ The study shows that the passive state of the NiSn alloy is not affected by halide ions up to the higher examined concentrations. In alkaline solutions containing chloride ions, the passivity of the NiSn alloy is far superior to that of both tin and nickel. Another study of the corrosion behaviour indicates that a conversion of the metastable NiSn alloy does not degrade the corrosion stability of the deposit provided it remains coherent.⁹

In a study from 1987 it was stated that the NiSn alloy does not or only to less extent cause allergic reactions on nickel sensitive persons, while 9 out of 14 nickel containing alloys caused medium to severe degrees of allergic reactions on nickel sensitive persons.¹⁰ The study also showed a reasonable correlation between in-vivo testing and electrochemical testing, except for Inconel[®] (77% Ni, 8% Fe, 15% Cr) which showed high reactivity when tested in-vivo. This is accounted for by the protecting oxide layer being more stable during electrochemical testing than during in-vivo tests.

The oxide layer of NiSn has been studied using electron spectroscopy for chemical analysis (ESCA) estimating a thickness of 30 Å.⁴ Other investigations using low energy ion-scattering spectroscopy to determine the surface composition shows a clearly evident absence of Ni in the surface region (5-10 Å). The results confirm former Auger electron spectroscopy studies and are consistent with the idea that since tin is more readily oxidized than nickel, a tin oxide will form on the surface. Furthermore it is pointed out that a tin-rich surface may also form in the absence of oxygen due to differences in surface-free energies.¹¹

Nickel release can be evaluated after European Standard EN $1811.^{12}$ The method in this standard is to expose the substrate to synthetic sweat for a week. The released nickel is determined by atom absorption and is related to the surface area. The upper limit for nickel release according to a Danish regulative from 2000 is 0.5 µg pr. cm² (0.007 lb pr. in²) pr. week. If the substrate has a surface layer a suggested standard test is European Standard 12472¹³, where the substrate is exposed to simulated wear prior to testing after European Standard EN 1811.

2. Experimental

NiSn has been deposited on copper alloys and solid nickel from a commercial galvanic bath with the composition: Tin 25 g/L, nickel 65 g/L and fluoride 33 g/L. The bath has a pH at 4.5 and is operated at 70 °C (158 °F) with nickel as anode and a current density of 2 A/dm² (19 A/ft²). Further details concerning depositing and thicknesses for various service conditions are described in ASTM Standard B605.¹⁴ The solution used for electrochemical testing is synthetic sweat prepared according to European Standard EN 1811. The composition of synthetic sweat in weight percent is: Sodium chloride 0.3%, lactic acid 0.1%, urea 0.1%. Ammonia solution (1%) is added to a pH value of 6.50 ± 0.10.



Figure 2 X-ray diffraction patterns (CuK_{α}) of electrodeposited NiSn on a nickel substrate. The scan is repeated in 8 different tilt angles. Nickel peaks from substrate are marked with dotted lines.

X-ray diffraction patterns of the as-electrodeposited NiSn layer are shown in Figure 2. Because of crystallographic texture effects the scan was repeated at different ψ -tilt angles to obtain as many identifiable {hkl} line profiles as possible. The various diffractograms are shown with offset on the intensity axis. In all 11 peaks were identified as being consistent with the crystal structure proposed for Ni₃Sn₂. The a and c lattice parameters determined from the peak positions of the {HK2} and {10L} line profiles, respectively are a = 4.173 Å and c = 5.123 Å and resemble those found by Lo² for electroplated NiSn with lattice parameters a = 4.15 Å and c = 5.10 Å (see peak positions indicated in Table 1). A few diffraction peaks could not be identified as Ni₃Sn₂; these are indicated by a question mark in Figure 2. The results indicate that as-electrodeposited NiSn mainly consists of Ni₂Sn₃ with a hexagonal structure of the NiAs type.

Table 1 Observed	peak positions co	nsistent with structure	proposed	for N	i,Sn,.
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{hkl}	101	002	102	201	112	103	202	121	104	302	204
2.0	30.31	35.35	43.23	53.67	57.30	59.70	63.09	71.27	79.42	90.10	95.00



Figure 3 Scanning electron micrograph and energy dispersive spectroscopy analysis of NiSn electrodeposited on copper alloy.

The composition of the alloy has been determined using energy dispersive spectroscopy to be Sn/Ni 68.4/31.6 wt.% or 51.7/48.3 at.%.

3. Electrochemical tests

Electrochemical tests are all performed at room temperature in synthetic sweat with the composition earlier described. A standard three-electrode electrochemical setup connected to a VoltaLab[®] PGZ 301 potentiostat from Radiometer is used. A wound platinum wire serves as a counter electrode and a standard calomel electrode (SCE, + 244 mV vs. SHE) as a reference electrode. The sample to be investigated is connected as the working electrode. Samples are made of 2 mm thick (ø25 mm) discs mounted in polypropylene with epoxy. This allows the working electrode to be used in a setup for tribocorrosion investigations.

3.1 Corrosion studies

Corrosion studies are performed with pure nickel, austenitic stainless steel AISI 304 and copper alloys plated with NiSn. Samples are polished down to a 1000 grit finish, except for the NiSn deposit which is unpolished after plating on copper alloys polished to a 1000 grit finish. Also galvanic couplings between NiSn and brass 63, AISI 304 and zinc are investigated using zero resistance amperometry.

As shown in Figure 4, the passivation behaviour of NiSn exceeds that of AISI 304 when polarized from -150 mV SHE to 1050 mV SHE at a scan rate of 0.5 mV/sec. It is important to notice that the deposit must be free of pores. A simple test to evaluate the existence of pores, is to immerse the plated substrate in concentrated nitric acid. Pores will reveal themselves after a few minutes by means of excessive bubbling.



Figure 4 Polarisation curve of electrodeposited NiSn, nickel and AISI 304 in synthetic sweat measured at a scan rate of 0.5 mV/sec. The scan for NiSn is completed three times on the same sample.

The current density of the passive layer on AISI 304 and NiSn is comparable, but the pitting potential of AISI 304 is at approximately 520 mV SHE, whereas the pitting potential for NiSn is still not reached at 1000 mV SHE (Figure 4). The repeatability of NiSn is adequate and it is worth noticing that the deposit decreases its passive current after the first scan, suggesting a passivation after this initial scan. The second and third scans are similar.

Galvanic couplings between NiSn, brass, steel 37, AISI 304 and zinc have been carried out in synthetic sweat in means of comparison. Another environment where galvanic couplings could occur is in drinking water where galvanic coupling between brass, steel and NiSn could be found in water pipe assemblings.

Material coupling	Increased corrosion rate [mm/year]		
NiSn + Brass 63	0.001		
NiSn + Steel 37	0.027		
NiSn + AISI 304	0.002		
NiSn + Zinc	1.047		

Table 2	Galvanic	couplings i	in synthetic	sweat.
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The increase in corrosion rate for the anodic part in presumed couplings to occur for NiSn is shown in Table 2. The galvanic couplings show that only when NiSn is coupled with zinc there is a risk of excessive degradation, but not for NiSn that acts cathodic in all cases.

3.2 Tribocorrosion studies

Tribocorrosion studies are performed using a setup as illustrated in Figure 5. The setup consists of a

motor that rotates a polymer disk with a radius of 10 cm. The disc is covered with synthetic washable leather. The motor rotates with a fixed speed of 150 rpm and the applied load is approximately 2 kg (4.4 lb).



Figure 5 Tribocorrosion setup with motor, washable leather, auxiliary and reference electrode. The mounted sample acts as the working electrode.

Washable leather is chosen as the wearing material, because it is comparable to the situation where human skin is in contact with the substrate. Electrochemical measurements are possible with the three-electrode setup and allows potential and cronoamperometric investigations of the substrate with and without the influence of wear.



Figure 6 Open circuit potential measurements for NiSn, nickel and AISI 304 with and without the influence of wear. The open circuit potential is measured for 10 minutes. and then the washable leather rotation starts. The rotation is stopped after 20 minutes.

Before starting the tribocorrosion tests the samples are immersed in the solution for a short period of time and a steady open circuit potential was reached. The monitoring of the open circuit potential continues and after 10 minutes the rotation of the washable leather is started and an abrupt decrease of the open circuit potential is observed (Figure 6). When the motor is stopped (after 20 minutes) the open circuit potential increases, indicating a re-establishment of a passive film in the case of NiSn and stainless steel. Based on the open circuit potential monitoring, nickel seems to be the metal least affected by wear.

In cronoamperometic studies a constant potential in respect to a reference electrode is applied and the anodic current is measured. The results are shown in Figure 7.



Figure 7 Cronoamperometric studies of nickel, AISI 304 and NiSn at constant potential 25 mV above individual open circuit potential.

The constant potentials applied are 220 mV SHE for NiSn, 95 mV SHE for stainless steel and 100 mV SHE for nickel. It is important to notice that the current densities are measured for different applied potentials for each sample. The potentials are fixed at 25 mV above the individual open circuit potential for each sample to simulate a minor oxidation. The individual potential is applied at time zero. For NiSn there is a rapid decrease in current after time zero due to passivation at this applied potential. At 10 minutes there is a rapid increase in current density due to rotation of the washable leather is started. The increase in current is strongest in the case of NiSn at applied potential 220 mV SHE. As soon as the rotation stops the surface repassivates and the current decreases to a similar level as before wear was introduced.

An increased corrosion rate when exposed to wear can explain the discrepancy in correlation

between in-vivo testing and electrochemical testing for Inconel[®] as found earlier.¹⁰ The exposure to wear can cause increased metal release and hereby nickel release causing higher reactivity when in-vivo tested as the study showed for Inconel[®]. It is also worth noticing that the European Standards 1844 and 12472 do not take increased metal release during wear into account.

A comparison of the obtained results indicates that NiSn is most susceptible to tribocorrosion at a constant potential of 220 mV SHE compared to austenitic stainless steel at 100 mV SHE and nickel at 95 mV SCE. Austenitic stainless steel seems to be more susceptible to tribocorrosion than nickel. These findings are in accordance with the assumption that passive materials are more susceptible to alter corrosion behaviour when exposed to wear, because of destroying the protective properties of the passive film.

4. Thermodynamic considerations

It is known that the NiSn alloy has properties that are not the average properties of nickel and tin separately, such as hardness and tarnish resistance. Table 3 shows that there is also a considerable change in half-reaction standard potential when alloying the two elements.

Reaction	E [mV SHE]
$Ni^{2+} + 2e^- \rightarrow Ni$	-238
$\mathrm{Sn}^{2+} + 2\mathrm{e}^{-} \rightarrow \mathrm{Sn}$	-141
$3Ni^{2+} + 2Sn^{2+} + 10e^{-} \rightarrow Ni_3Sn_2$	-42

Table 3 Half-reaction standard potentials at 20 °C (68 °F).

The Pourbaix diagram shown in Figure 8 is derived for a pressure of 1 bar and a temperature of 25 °C (77 °F). The diagram is derived for selected concentrations of ionic species (10^{-6} M for nickel as well as tin, and 0.05 M for chloride ions). Since X-ray investigations show Ni₃Sn₂ to be dominant Ni₃Sn₄, Ni₃Sn and nickel hydrides have been excluded from calculations resulting in the diagram showed in Figure 8.



Figure 8 Simplified Pourbaix diagram for a Sn, Cl, Ni, H,O-system at 25 °C (77 °F).

The Pourbaix diagram shows stannic oxide (SnO_2) to be the thermodynamically most stable oxide. This does not necessarily mean that the oxide is of a protective (passivating) nature. Some kind of passivating film is present on NiSn; hence its stability when exposed to concentrated nitric acid. At low pH values Ni₃Sn₂ can transform into soluble tetrachlorostannate(II)-2 ions $(SnCl_4^{-2})$ or tin(II)chloride hydroxide (SnOHCl). At high pH values tin(IV)hexahydroxide-2 ion $(Sn(OH)_6^{-2})$ is the thermodynamically most stable form. It should be emphasised that no information on corrosion kinetics is provided by this thermodynamically derived diagram.

5. Conclusion

The structure of electrodeposited equiatomic NiSn alloy was indicated in an X-ray diffraction pattern to mainly consist of Ni_2Sn_3 with a hexagonal structure of the NiAs type. The corrosion and tribocorrosion properties of the electrodeposited alloy were investigated in synthetic sweat by electrochemical techniques. The results show that NiSn has a passive behaviour that exceeds that of stainless steel in synthetic sweat. Polarization curves also illustrate superior corrosion resistance of NiSn compared to nickel. This is in accordance with earlier findings and is expected to be due to the passivity of NiSn alloys.

The passive film has been studied earlier and is estimated to be approximately 30 Å with a tin-rich oxide formed on the surface. Other investigations have shown that freshly fractured edges corrode severely compared to a passivated NiSn surface in the same environment. Investigations carried out in this work demonstrate that the corrosion properties of NiSn change considerably when the deposit is being exposed to wear; even in a small degree like rubbing with washable leather. This setup was used to simulate wear from handling with human fingers. Prior investigations have

shown that the NiSn alloy does not elicit remarkable nickel amounts when exposed to synthetic sweat, but further investigations must be made to evaluate how the deposit behaves when exerted to tribocorrosion.

The risk of increased metal release as a consequence of tribocorrosion can explain previous findings concerning discrepancies in electrochemical testing and in-vivo testing. This possible increased metal release is not taken into account in present European Standards evaluating nickel release.

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