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

by Morten S. Jellesen^{*} & Per Møller

The electrodeposition of 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 exhibits surface passivation like stainless steel. The coating is decorative and non-allergic to the skin, can replace decorative nickel and nickelchromium coatings in many cases and decreases the risk for allergic contact dermatitis. A number 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.



Figure 1-NiSn phase diagram.²

More than 50 years ago, Parkinson¹ 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) referred to as 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 Fig. 1.²

Nuts & Bolts: What This Paper Means to You

The electroplating of tin/nickel (65/35 wt%) is unique because the deposit structure cannot be formed by any thermal metallurgical process. It also has unique corrosion properties and exhibits surface passivation like stainless steel. With recent concerns about nickel allergies, this decorative finish is non-allergic to the skin, decreases the risk for allergic contact dermatitis and can replace decorative nickel and nickel-chromium coatings in many cases.

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Early descriptions explained the NiSn phase as an extension of the composition range of the equilibrium phase Ni_3Sn_2 . This extension was explained by more favored nucleation kinetics at the deposition temperature and the resistance of this deposit to transformation at low temperature.³ Later the structure of an equiatomic NiSn deposit was interpreted by C.C. Lo,⁴ who proposed that the electrodeposited tin-nickel alloy consisted of Ni_3Sn_2 within each grain and extra tin atoms segregated on the grain boundary.

It is known that the NiSn phase will reveal its metastable character when heated, as, above 350°C (662°F), it decomposes into the two stable equilibrium phases Ni_3Sn_4 , and Ni_3Sn_4 .^{3.5,6}

In the late 1970s, a study was made into how the NiSn surface was protected from corrosion by a passive film which could be removed by mechanical wear.⁷ The authors found that if the substrate was exposed by wear-through or by brittle fracture of the NiSn, the corrosion resistance was determined by the substrate. It was also stated that freshly fractured edges of NiSn were severely corroded, while original NiSn surfaces and fractured edges exposed to air for three months were unaffected.

The effects of chloride, bromide or iodide ions on the passivity of NiSn alloys have also been studied.⁸ That work showed that the passive state of the NiSn alloy was not affected by halide ions up to the higher concentrations examined. In alkaline solutions containing chloride ions, the passivity of the NiSn alloy was far superior to that of both tin and nickel. Another study of the corrosion behavior indicated that a conversion of the metastable NiSn alloy did not degrade the corrosion stability of the deposit provided it remained coherent.⁹

In a 1987 study,¹⁰ it was stated that the NiSn alloy did not (or at least to a lesser 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. 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 greater stability of the protective oxide layer during electrochemical tests

than during the in-vivo tests. The oxide layer of NiSn has been studied using electron spectroscopy for chemical analysis (ESCA), estimating a thickness of 30 Å.² Other investigations, using low energy ion-scattering spectroscopy to determine the surface composition showed a clearly evident absence of Ni in the surface region (5 to 10 Å).¹¹ The results confirmed earlier Auger electron spectroscopy studies and were consistent with the idea that since tin is more readily oxidized than nickel, a tin oxide will form on the surface. Furthermore it was pointed out that a tin-rich surface may also form in the absence of oxygen due to differences in surface-free energies.

Nickel release can be evaluated according to European Standard EN 1811.¹² The method in this standard is to expose the substrate to synthetic sweat solution for a week. The nickel released is determined by atomic absorption spectroscopy and is related to the surface area. The upper limit for nickel release, according to a 2000 Danish regulation, is $0.5 \ \mu g/cm^2 (0.007 \ lb/in^2)$ per week. If the substrate has a surface layer, a suggested standard test is European Standard EN 12472,¹³ where the substrate is exposed to simulated wear prior to the EN 1811 test.

Experimental

NiSn has been deposited on copper alloys and solid nickel from a commercial galvanic bath with the composition: tin, 25 g/L (3.3 oz/gal); nickel, 65 g/L (8.7 oz/gal) and fluoride, 33 g/L (4.4 oz/gal). The bath was operated at a pH of 4.5 and a temperature of 70°C (158°F). Nickel was used as the anode. A cathode current density of 2.0 A/dm² (18.6 A/ft²) was applied. Further details concerning the deposition and thicknesses for various service conditions are described in ASTM Standard B605.¹⁴

The solution used for electrochemical testing was a synthetic sweat solution prepared according to European Standard EN 1811.¹² The solution composition was: sodium chloride, 0.3 wt%; lactic acid, 0.1 wt% and urea, 0.1 wt%. Ammonia solution (1%) was added to adjust the pH value to 6.50 ± 0.10 .

X-ray diffraction patterns of the as-electrodeposited NiSn layer are shown in Fig. 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. A total of 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 were *a* = 4.173 Å and c = 5.123 Å and resembled those found by Lo⁴ for electroplated NiSn with lattice parameters *a* = 4.15 Å and *c* = 5.10 Å (See the peak positions indicated in Table 1.). A few diffraction peaks could not be identified as Ni₃Sn₂, indicated by a question mark in Fig. 2. The results indicated that as-electrodeposited NiSn mainly consisted of Ni₃Sn₂ with a hexagonal structure of the NiAs type.



Figure 2—X-ray diffraction patterns (CuK α) of electrodeposited NiSn on a nickel substrate. The scan is repeated for eight different tilt angles. Nickel peaks from the substrate are marked with dotted lines.

Table 1 Observed peak positions consistent with structure proposed for Ni_xSn,

{hkl}	101	002	102	201	112	103	202	121	104	302	204
20	30.31	35.35	43.23	53.67	57.30	59.70	63.09	71.27	79.42	90.10	95.00

The composition of the alloy was determined using energy dispersive spectroscopy to be Sn/Ni 68.4/31.6 wt%, or 51.7/48.3 at% (Fig. 3).

Electrochemical tests

Electrochemical tests were all performed at room temperature in synthetic sweat solution with the composition described earlier. A standard three-electrode electrochemical setup was connected to a potentiostat.^{**} A wound platinum wire served as a counter electrode and a standard calomel electrode (SCE, +244 mV_{SHE}) as a reference electrode. The sample to be investigated was the working electrode. Samples were made of 2.0-mm thick (\emptyset 25 mm) [0.8-in.

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

thick (Ø1.0 in.)] discs mounted in polypropylene with epoxy. This allowed the working electrode to be used in a setup for tribocorrosion investigations.

Corrosion studies

Corrosion studies were performed with pure nickel, austenitic stainless steel AISI 304 and copper alloys plated with NiSn. Samples were polished to a 1000 grit finish, except for the NiSn deposit, which was unpolished after plating. The copper alloy substrates were already polished to a 1000 grit finish. Galvanic couplings between NiSn and brass (63% Cu, 37% Zn), ASTM A284 steel, AISI 304 and zinc were also investigated using zero resistance amperometry.

As shown in Fig. 4, the passivation behavior of NiSn exceeded 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 note that the deposit must be free of pores. A simple test to evaluate the existence of pores involved immersion of the plated substrate in concentrated nitric acid. Pores will reveal themselves after a few minutes through excessive bubbling.

Figure 4(a) shows the repeatability of polarization curves of NiSn





^{**} VoltaLab[®] PGZ 301 potentiostat, Radiometer Analytical, Lyon, France.

and how the deposit decreased its passive current after the first scan, suggesting a passivation after this initial scan. The curves of the second and third scans were similar. Figure 4(b) shows that the current density of the passive layer on AISI 304 and NiSn was comparable. However, the pitting potential of AISI 304 was approximately 520 mV_{SHE}, whereas the pitting potential for NiSn was still not reached at 1000 mV_{SHE}.

Galvanic couplings between NiSn, brass (63% Cu, 37% Zn), ASTM A284 steel, AISI 304 and zinc were carried out in synthetic sweat solution for comparison. Another environment where galvanic couplings could occur is drinking water where galvanic coupling between brass, steel and NiSn could be found in water pipe assemblies.

The increase in corrosion rate for the anodic part in various galvanic couplings is shown in Table 2. The data shows that when NiSn was coupled with zinc there was a risk of excessive degradation of zinc as it is the less noble part. Galvanic couplings between NiSn and brass (63% Cu, 37% Zn), ASTM A284 steel and AISI 304 did not seem to affect the corrosion rate excessively. NiSn did not degrade excessively in any of the investigated couplings since it acted as the cathode.

Tribocorrosion studies

Tribocorrosion studies were performed using the setup illustrated in Fig. 5. The apparatus consisted of a motor that rotated a polymer disk with a radius of 10 cm (3.9 in.). The disc was covered with synthetic washable leather. The motor rotated at a fixed speed of 150 rpm and the applied load was approximately 2.0 kg (4.4 lb.).

Washable leather was chosen as the wearing material, because it was comparable to the situation where human skin is in contact with the substrate. Electrochemical measurements could be made with the three-electrode setup, allowing potential and chronoamperometric studies of the substrate to be made with and without the influence of wear.

Prior to the tribocorrosion tests, the samples were briefly immersed in the solution until a steady open circuit potential was reached. The monitoring of the open circuit potential continued and after 10 min, the rotation of the washable leather was started. An abrupt decrease of the open circuit potential was observed (Fig. 6). When the motor was stopped (after 20 min), the open circuit potential increased, indicating a re-establishment of a passive film Table 2Galvanic couplings in synthetic sweat solution

Material coupling	Increased corrosion rate (mm/yr)
Ni-Sn + Brass (63% Cu, 37% Zn)	0.001
Ni-Sn + ASTM A284 steel	0.027
Ni-Sn + AISI 304	0.002
Ni-Sn + Zinc	1.047



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

on the NiSn and stainless steel. Based on the open circuit potential monitoring, nickel seemed to be the metal least affected by wear.

In the chronoamperometic studies, a constant potential with respect to the reference electrode was applied and the anodic current was measured. The results are shown in Fig. 7. The constant potentials applied were 220 mV_{SHE} for NiSn, 95 mV_{SHE} for stainless steel and 100 mV_{SHE} for nickel. It is important to note that the current densities were measured at different applied potentials for each sample. The potentials were fixed at approximately 25 mV above the individual open circuit potential for each sample to simulate minor oxidation. The individual potential was applied



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

at time zero. For NiSn, there was a rapid decrease in current after time zero due to passivation at this applied potential. After 10 min, there was a rapid increase in current density due to the start of the rotation of the washable leather. The increase in current was strongest in the case of NiSn at the applied potential 220 mV_{SHE}. As soon as the rotation stopped, the surface repassivated and the current decreased to a level similar to that before wear was introduced.

The increased corrosion rate observed under the wear test regime can explain the correlation discrepancy between *in-vivo* testing and electrochemical testing for Inconel[®] found earlier.¹⁰ The exposure to wear could have caused increased metal release and thereby nickel release. This could have caused the higher reactivity observed in the *in-vivo* test for Inconel.[®] It is also worth noticing that the European Standards EN 1811 and EN 12472 do not take the increased metal release during wear into account.

A comparison of the results indicates that NiSn was most susceptible to tribocorrosion at a constant potential of 220 mV_{SHE} when compared to austenitic stainless steel at 100 mV_{SHE} and nickel at 95 mV_{SHE}. Austenitic stainless steel seemed to be more susceptible to tribocorrosion than nickel. These findings are in accordance with the assumption that passive materials are more susceptible to altering corrosion behavior when exposed to wear, because of the destruction of the protective properties of the passive film.

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 was also a considerable change in the half-reaction standard potential when alloying the two elements.

The Pourbaix diagram shown in Fig. 8 is derived for a pressure of 1 bar (100 kPa; 14.5 lb/in²) and a temperature of 25°C (77°F). The diagram is derived for selected concentrations of ionic species (10⁻⁶M for nickel ions as well as tin, and 0.05M for chloride ions). Since X-ray investigations showed Ni₃Sn₂ to be dominant, Ni₃Sn₄, Ni₃Sn and nickel hydrides have been excluded from calculations, resulting in the diagram shown in Fig. 8.

The Pourbaix diagram shows stannic oxide (SnO_2) to be thermodynamically the most stable oxide. This does not necessarily mean that the oxide is of a protective (passivating) nature. Some kind



Figure 7—Chronoamperometric studies of nickel, AISI 304 and NiSn at a constant potential 25 mV above the corresponding individual open circuit potential.



Figure 8-Simplified Pourbaix diagram for the Sn-Cl-Ni-H₂O system at 25°C (77°F).

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

Reaction	E _{SHE} (mV)		
$Ni^{+2} + 2e^- \rightarrow Ni$	-238		
$\operatorname{Sn}^{+2} + 2e^{-} \rightarrow \operatorname{Sn}$	-141		
$3 \operatorname{Ni}^{+2} + 2\operatorname{Sn}^{+2} + 10e^{-} \rightarrow \operatorname{Ni}_3\operatorname{Sn}_2$	-42		

of passivating film is present on NiSn, accounting for its stability when exposed to concentrated nitric acid. At low pH values, Ni₃Sn₂ can transform into soluble tetrachlorostannate(II)⁻² ions (SnCl₄⁻²) or tin(II) chloride hydroxide (SnOHCl). At high pH values, tin(IV) hexahydroxide⁻² ion (Sn(OH)₆⁻²) is thermodynamically the most stable form. It should be emphasized that no information on corrosion kinetics is provided by this thermodynamically-derived diagram.

Conclusion

The structure of electrodeposited equiatomic NiSn alloy was determined by X-ray diffraction to consist mainly of Ni_3Sn_2 with a hexagonal structure of the NiAs type. The corrosion and tribocorrosion properties of the electrodeposited alloy were investigated in synthetic sweat solution by electrochemical techniques. The results show that NiSn had a passive behavior that exceeded that of stainless steel in synthetic sweat solution. Polarization curves also illustrated superior corrosion resistance for NiSn when compared to nickel. This was in accordance with earlier findings and is expected to be due to the passivity of NiSn alloys.

The passive film was studied earlier and was estimated to be approximately 30 Å thick, 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. This work demonstrated that the corrosion properties of NiSn changed considerably when the deposit was exposed to wear, even to such a small degree as rubbing with washable leather. Our wear test apparatus was set up to simulate wear from handling with human fingers. Prior work has shown that the NiSn alloy did not release remarkable amounts of nickel when exposed to synthetic sweat solution, but further investigations must be made to evaluate how the deposit behaves when exposed 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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