Alloys at Low Nickel-release: Pd-Ni Coatings on Copper

G. Moretti, F. Guidi & R. Tonini

Allergies created by metals in contact with the human body are becoming an increasingly important problem. Nickel is known to be an allergy-causing factor and Ni-containing alloys of coated items coming into direct and prolonged contact with the skin have to be tested to verify their Ni release before commerce. Samples coated with thin layers (0.3 µm and 0.04 µm and 0.04 µm Ar$^+$ ion implanted [I.I.]) of a Pd-Ni alloy (90-10 wt%) were electrochemically tested in an alkaline (pH=12.4) solution. The coated samples were also tested in synthetic sweat solution, using the European EN 1811 test method. The electrochemical tests (potential vs. time, potentiodynamic test) and the synthetic sweat tests confirmed the good corrosion behavior of the very thin coatings. After the synthetic sweat test, it is possible to affirm that the Pd-Ni coatings are in accordance with the law proposed by the European Committee for Standardization (CEN) given that the nickel release was lower than 0.5 µg/cm^2/week.

***Keywords*: Pd-Ni coatings on copper, ion implantation, Ar$^+$ ion beam mixing, release of nickel from products coming into direct and prolonged contact with the skin, synthetic sweat test method (European Law EN 1811).**

Allergies caused by metals in contact with the human body are a well-known problem in the galvanic field.[1] In recent years, several works have demonstrated that nickel-release from objects containing this metal has provoked allergies (eczemas, dermatitis, etc.) in an average of about 15 percent of the population.[2-5]

Nickel-release, therefore, can be a problem for all industries (galvanic and other industries) producing metallic items in contact with the human body (Table 1). In recent years, more and more research centers have begun to address the problems connected with nickel release. From a legal point of view, the measures taken to limit the use of nickel in objects coming into direct and prolonged contact with the skin are relatively recent.

The European Community was initially oriented toward prohibiting the use of nickel in objects in contact with the skin. However, after considering industry requirements, in particular the galvanic industry, it revised this position and on October 27, 1993, the European Parliament promulgated a law fixing the limit of nickel-release at 0.5 µg/cm^2/week. Subsequently, it has also sought to establish criteria to verify and certify the release of nickel by a particular object.

After numerous proposals (dimethylglioxime test, synthetic sweat test), the Final Draft, EN No. 1811 (June 1998), was approved.[1] At the same time, numerous proposals were made in Europe regarding wear tests (*e.g.*, draft prEN 12472—rev. June 1998) to be made before the synthetic sweat test to simulate aging of at least two years. Therefore, it does not seem hazardous to affirm that in the near future, at least in Europe, coatings containing high percentages of nickel (>20%) used as a bright substrates in objects in direct contact with the skin will have to be replaced.

Among the various alternative coatings, the palladium-nickel (Pd-Ni) alloys are known for their aesthetic appearance, as well as their resistance to corrosion, especially when the layer thickness is on the order of microns.[6-7]

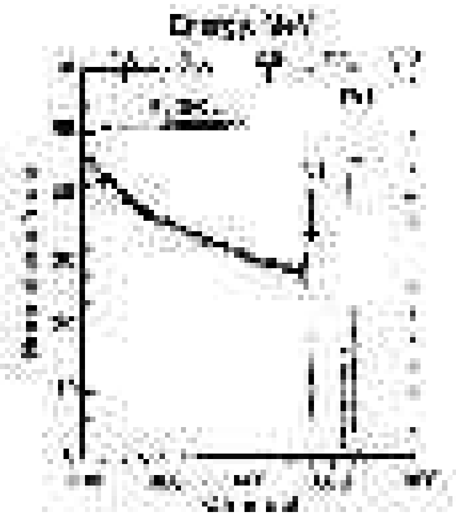

Fig. 1—RBS spectrum of Pd-Ni sample obtained with 3 MeV of $^4He^+$ particles. The simulation spectrum [using a RUMP code (9)] is also shown.

The aim of the present paper is to verify the corrosion behavior of a Pd-Ni alloy (theoretically 95/5 wt%) electroplated in different, very thin layers (400 Å and 0.3 µm) on copper plate (20 µm thick) and ion-beam mixed (Ar$^+$) copper plate. Corrosion behavior tests on the various coatings in standard solutions were carried out using the usual electrochemical techniques (potential vs. time, potentiodynamic tests). All the various specimens were then analyzed with the synthetic sweat test method.

Experimental Procedure

Copper Specimens

In all the experimental tests, the specimens consisted of commercial copper (99.8 wt%) obtained from the same 0.5 mm-thick plate with an exposed surface of about 10.5 cm x 10.5 cm. As the result of preliminary tests on commercial copper plates that revealed the non-homogeneity of this material, a 20-µm coating of leveling acid copper was electrodeposited over the surface. The copper-coated copper plate was then electrocoated with Pd-Ni alloy layers, and the specimens painted with a strippable varnish to preserve them from wear during cutting and handling. Discs 11.3 mm in diameter were then cut from the plates.

Galvanic Depositions

Pre-treatment. Before plating, all copper substrates were degreased in an ultrasonic bath at 60°C for 30-120 sec. After being rinsed in deionized water, they were electrolytic-etched to remove the oxides, using a solution containing K_2CO_3, NaOH, silicates, phosphates, ionic and non-ionic biodegradable surfactants (operating conditions: temperature, 30-60°C; immersion time, 30-120 sec; current density, 1-4 A/dm^2; voltage, 3-5 V). After being rinsed again in deionized water, the plates were then activated in acid salts to remove every basic residual product of the electrolytic etching from the metal surface.

Table 1
Products with Surface Coatings Containing Ni that can Provoke Allergic Effects

Earrings, hair clips & hairpins
Necklaces, bracelets, chains, ankle bracelets, rings
Wristwatch enclosures, normal & elastic watchbands
Eye-glass frames
Buttons, automatic buttons, snaps & zippers

Table 2
Comparison Between the Average E_{corr} Obtained with Different Samples (From E-time & Potentiodynamic Tests)

	E_{corr} time mV$_{sce}$	E_{corr} Tafel mV$_{sce}$
Commercial Cu	-197 ± 14	-201 ± 14
Electrolytic Cu	-217 ± 3	-217 ± 3
0.3µm Pd-Ni	-15 ± 5	-16 ± 6
0.04µm Pd-Ni	-29 ± 8	-27 ± 8
0.04µm (I.I.) Pd-Ni	-25 ± 4	-23 ± 4

Acid copper plating. As previously mentioned, an electrolytic copper coating (20 µm thick) was deposited to eliminate surface irregularities and obtain a good substrate before alloy deposition. The galvanic bath was composed of inorganic salts and some additives, as follows:

Copper sulfate ($CuSO_4.5H_2O$)	175-210 g/L
Sulfuric acid (H_2SO_4) (ρ = 1.84 g/mL)	32-38 mL/L
Chlorides	60-110 mg/L
Brighteners	0.5 mL/L
Leveling agent	0.5 mL/L
Anti-pitting compounds	10 mL/L

The operating conditions were as follows:

Temperature	24-26°C
Cathodic current density	1-4 A/dm^2
Voltage	1-4 V
Deposition rate	0.7 µm/min at 3 A/dm^2
Air blow	12-20 m^3/hr/meter of cathodic bar
Anodes	Copper/phosphorus 0.03-0.06%
Anode bags	Meraklon®
Filtration	Continuous, 2-3 volumes/hr
Filters	Polypropylene 5 µm
Efficiency	About 100%

Pd-Ni electroplating. The bath composition and operating conditions for the Pd-Ni electrodeposition is given below. The bath also contained brighteners, non-ionic biodegradable surfactants, stabilizer and conductive salts.

Palladium (as metal)	5.0 g/L
Nickel (as metal)	0.5 g/L
pH	7.5-8.5
Density	10° Bé
Temperature	30°C
Cathodic current density	1 A/dm^2
Deposition rate	0.25 µm/min at 1 A/dm^2
Efficiency	27 mg/A-min

Fig. 2—Some typical E-time curves obtained with Pd-Ni coatings compared with that of electrolytic copper (pH 12.4, 25°C, aerated solution).

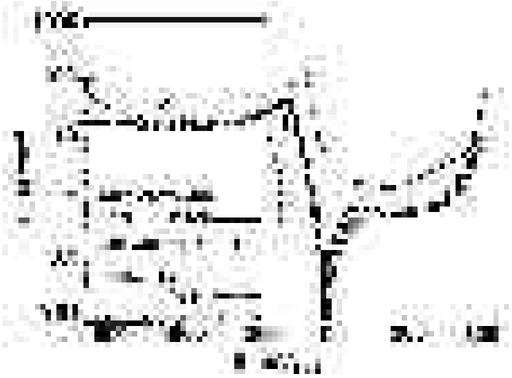

Fig. 3—Some typical potentiodynamic curves obtained with different Pd-Ni coatings compared with that of electrolytic copper (pH 12.4, 25°C, aerated solution).

The ratio of the two elements in the bath generally allows electrodepositing an average theoretical layer of Pd-Ni = 95-5 wt%. The electrodeposition was formulated and carried out to obtain layers of Pd-Ni alloys with a composition ratio of 90-10 wt% so as to verify the behavior of the coating by means of the synthetic sweat test in less favorable conditions. This was achieved by electrodeposition at high current density (1 A/dm^2).

The homogeneity and composition of the alloys obtained under these experimental conditions were tested by scanning electron microscopy (SEM), Rutherford back-scattering (RBS) and chemical analyses. The effective percentage ratio of the elements in the alloy was 90/10 wt%. The hardness of the deposited alloy was 450-500 VHN.

Ion Implantation

The samples of Pd-Ni coated copper were ion implanted at room temperature in two different ways: 1) with Ar^+ at 110 keV and $6x10^{15}$ at/cm^2 and 2) with Ar^+ at 95 keV and $6\ x10^{15}$ at/cm^2, respectively. The implantation energy was chosen to place the maximum Ar^+ profile at the Pd/Ni–Cu interface and was evaluated with a Monte Carlo simulation program (SRIM98).[8] The RBS measurements used to measure the film composition were performed with a 3 MeV $^4He^+$ beam with a detector scattering angle of 160°.

This technique is usually considered non-destructive, and the interaction of the probe beam and the sample is so mild that no changes are induced by the beam itself. [9] Figure 1 shows the RBS spectra of Pd (90 wt %) - Ni (10 wt %) film. The resulting thickness is 450Å.

Electrochemical Tests

All the electrochemical tests were carried out in an alkaline medium [borate/boric acid plus NaOH (10%) yielded pH = 12.4], a test solution already in use in evaluating corrosion behavior of copper and other metallic materials.[10-11] All reagents were “pure for analysis” chemicals. The working electrode, a reference saturated calomel electrode (SCE) inside a Haber-Luggin’s capillary probe and two platinum counter electrodes were placed inside a Pyrex glass ASTM cell filled with 700 mL of aerated borate/boric acid solution. The specimen, used as the working electrode, was placed inside a Teflon holder with the electrode contact made by an inner metal rod. A 0.50 cm^2 surface was exposed.

Anodic and cathodic polarization curves were carried out at 25°C using an AMEL (Italy) apparatus consisting of a potentiostat, a signal generator, an interface and a PC for data acquisition. The temperature was regulated within ±0.1°C of the required value (25°C) using a thermostatically controlled water bath. All the potential values are referred to the SCE electrode. Potentiodynamic tests were carried out in accordance with already established methodology.[12-13]

Table 3
Electrochemical Data Obtained from the Potentiodynamic (& E-time) Curves with Different Surface Treatments

	i_L (µA/cm²)	i_p (µA/cm²)	i_{corr} (µA/cm²)	R_{corr} (mdd)
Commercial Cu	16.1 ± 2.6	1.9 ± 0.2	1.5 ± 0.4	4.2 ± 1.1
Electrolytic Cu	15.7 ± 1.9	1.8 ± 0.1	1.8 ± 0.2	5.0 ± 0.6
0.3µm Pd-Ni	18.7 ± 0.7	0.60 ± 0.05	0.06 ± 0.01	0.27 ± 0.03
0.04µm Pd-Ni	17.7 ± 0.8	0.60 ± 0.05	0.09 ± 0.01	0.41 ± 0.07
0.04µm (I.I.) Pd-Ni	16.8 ± 0.8	0.60 ± 0.05	0.05 ± 0.01	0.23 ± 0.06

R_{corr} is in mdd, mg/dm²/die (pH 12.4, 25°C, aerated solution)

The following electrochemical parameters were obtained from polarization curves:

E_{corr}, free corrosion potential
i_L, limit current density of the O_2 diffusion
i_{corr}, corrosion current density (directly correlated to the corrosion rate, R_{corr}) and
i_p, passivation current density.

Synthetic Sweat Test

This test was performed according to the recent European standard corrosion test procedure which requires objects to be immersed for 168 hr (one week) in an aerated 0.5-wt% NaCl, 0.1-wt% lactic acid and 0.1-wt% urea solution in deionized water, at pH 6.5 (adjusted with 0.1-wt% NH_3) and at T=30°C.

Some small spill-proof bottles were used to carry out the synthetic sweat test (nine per metal sample). These bottles were equipped with screw caps and ring-shaped seals. The metal sample was put between the cap and the seal, leaving a 0.50-cm^2 metal surface exposed to the test solution.

Before use, all the bottles were immersed for 8 hr in nitric acid (10%) to eliminate all traces of nickel. After rinsing and drying, the bottles were filled with 0.5 mL of synthetic sweat prepared immediately before use (1 mL of test solution/cm^2 of exposed metal surface, as established by the European method). All the bottles were then turned upside down and immersed in a thermostatic bath at (30.0 ± 0.1°C).

After 168 hr, the solution contained in each tube was analyzed and the results compared with those of the "blank" solution, expressed in "µg Ni/cm²/week" by means of:

$$d = \frac{(C_1 - C_2)}{a \cdot 1000} V \qquad (1)$$

where:
d = Ni - release (µg/cm²/week);
a = exposed surface of the sample (cm²)
V = final volume of the test solution (mL)
C_1 = concentration of nickel after 168 hr (µg/L)
C_2 = concentration of nickel in the "blank" solution after 168 hr (µg/L)

Results & Discussion

Electrochemical Tests

Potential vs. time test. Tests were carried out on commercial (99.8 wt%) electrolytic copper (before the Pd-Ni deposition) and on Pd-Ni alloy- and copper-coated copper.

The electrolytic copper reached stable values of E_{corr} after 10 min, whereas the commercial copper did not reach a steady-state situation even after a relatively long time. This supported the validity of the choice to pretreat all the commercial plates before the deposition of the alloy. Table 2 indicates that the E_{corr} of the electrolytic copper reached more negative average values than did the commercial one.

Figure 2 shows typical "E vs. time" curves obtained with Pd-Ni coatings compared with those of electrolytic copper. The trend of the curves obtained with the Pd-Ni samples was very similar. E_{corr} was slightly more negative for the thinner layer [-15 to -16 mV_{sce} for 0.3µm, -29 to -27 mV_{sce} 0.04µm and –25 to –23 mV_{sce} for 0.04µm (I.I.)] but both were around 200 mV more noble than copper.

Potentiodynamic tests. Potentiodynamic tests allowed various electrochemical data to be drawn out. In particular the corrosion current density, i_{corr}, directly correlated with the corrosion rate of the different surface treatments.

Figure 3 shows typical potentiodynamic curves obtained immediately after the immersion of the different Pd-Ni coatings, compared with a typical curve for electrolytic copper under the same experimental conditions. Similar trends in the 0.3 µm Pd-Ni and 0.04 µm Pd-Ni curves substantially differed from that obtained with the copper. Table 3 reports the more significant electrochemical data.

From a comparison between the copper and Pd-Ni coatings one can point out the more noble character of the Pd-Ni alloys over the copper substrate. Values of R_{corr} were significantly lower than that of copper even at thicknesses of 0.04 µm (0.3 µm Pd-Ni, 0.27 mdd; 0.04 µm Pd-Ni, 0.41 mdd and 0.04 µm Pd-Ni (I.I.), 0.23 mdd in comparison with commercial copper, 4.2 mdd and electrolytic copper, 5 mdd).

The average i_L values of the coatings were also higher than that of copper, even if not considerably (17-19 vs. 16 µA/cm²), thus indicating the slight influence of the surface treatment in the range of the cathodic potentials. In any case, the ion implanted (I.I.) specimens showed a behavior similar to that of 0.3 µm Pd-Ni coatings (R_{corr} 0.23 and 0.28 mdd, respectively). The R_{corr} of the ion-implanted material is around half of that of 0.04 µm Pd-Ni. Further analyses are underway to investigate the degree of modification induced by the ion implantation process.

Synthetic sweat test. It must first be noted that the synthetic sweat test was not preceded by a wear test because the substrate did not contain high percentages of nickel (>20 wt%). In the latter case, in fact, European law establishes that a wear test must be carried out immediately before the synthetic sweat test to simulate two years of normal use of the object in question.

In any case, the wear test generally results in higher values of nickel-release than the successive synthetic sweat test (at least one order of magnitude greater than the value obtained without wear treatment), so much so that the law allows multiplying the data obtained from equation (1) by a factor

Table 4
Values of Ni-release μg/cm^2/week) Obtained with the Pd/Ni Samples After 168 hr (1 week) of Immersion in Synthetic Sweat

Coating	μg/cm^2/week
0.3μm Pd-Ni	0.074 ± 0.005
0.04μm Pd-Ni	0.056 ± 0.005
0.04μm (I.I.)Pd-Ni	0.049 ± 0.005

of 0.1. However, there is more than one opinion on this approach and many researchers from various European Nations do not agree with this method.[14]

The synthetic sweat test allowed us to verify the nickel-release of the Pd/Ni samples after 168 hr (1 week) of immersion in synthetic sweat. The results obtained are summarized in Table 4. The nickel-release of all the Pd-Ni coatings was lower than the limit established by the European 1811 rule (0.5 μg/cm^2/week). As a result, these treatments seem to be a consistent alternative to those traditionally used and can constitute final coatings of a limited thickness for products coming into direct and prolonged contact with the skin because the calculated nickel-release is around one order of magnitude lower than that provided by European law. It cannot be ignored, however, that allergic phenomena may arise, especially in particularly sensitive subjects, even when the nickel-release is lower than the limit fixed by the law.

In conclusion, it is worth remembering that, over the past years, the large use of nickel as a brilliant substrate in the galvanic field polarized attention on its allergenic impact. This use is now limited by law and reasonable alternative treatments will have to be adopted.

Furthermore, if the allergic reactions from nickel-release are well known and statistically consolidated, the possibility of similar allergic episodes occurring with other metallic materials cannot be excluded. Indeed, some studies are underway to verify the allergenic effects of cobalt and chromium, which are probably responsible for allergic phenomena comparable to those caused by nickel.

Conclusions

Seeing that the European Law 1811 (June 1998) fixes the limit of nickel-release in 0.5 mg/cm^2/week, one can conclude that:

1. Electrochemical tests carried out in a standard solution [pH 12.4 (borate-boric acid + NaOH (10%)); 25°C; aerated solution] showed that thin galvanic coatings (0.04-0.3mm) of Pd-Ni (90-10 wt%) alloys not only ennobled the E_{corr} of the substrate (copper electrolytically coppered – 20mm) of around 200 mV, but also reduced the R_{corr} of more than one order of magnitude.
2. The ion implanted Pd-Ni 0.04-mm specimens behaves like those of the non-implanted Pd-Ni 0.3 mm, showing that after the implantation treatment the R_{corr} of the implanted samples was around half of that of those not implanted Pd-Ni 0.04 mm.
3. The results of the "synthetic sweat test" indicated that the nickel-release of all the Pd-Ni coatings was lower than the limit provided by the European Law 1811 (0.5 mg/cm^2/week). So, these treatments seem to be an alternative to those traditionally employed and can constitute final coatings of limited thickness for products coming into direct and prolonged contact with the skin.

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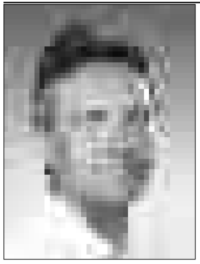

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