CORROSION RESISTANCE OF MATERIALS USED IN EAR PIERCING STUDS

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Abstract: **Nickel containing alloys have been widely used as substrates in the manufacture of ear piercing studs. Unfortunately, skin sensitization has been related to Ni^{+2}, which can leach out into body fluids in corrosion reactions. Defect free coatings are very difficult to produce, hence nickel free materials should be used as substrates. In this study two kinds of commercial studs and a laboratory made titanium stud were investigated. Corrosion resistance of the studs in the culture medium was determined using potentiodynamic polarization measurements and electrochemical impedance spectroscopy as a function of immersion time. The elements that leached out into the medium were analyzed by instrumental neutron activation analysis. The surfaces of the commercial gold-coated studs were examined by scanning electron microscopy and analyzed by energy dispersive spectroscopy, before and after exposure to the culture medium. The cytotoxicity of the tested studs was also determined.**

Keywords: Corrosion, gold coated studs, electrochemical impedance spectroscopy, titanium, nickel.

Introduction

Nickel containing alloys are widely used in the manufacture of ear piercing studs. On their surfaces, gold coatings are applied for aesthetic reasons, corrosion resistance and because gold has little or no cytotoxicity[1]. These coatings should be compact and adherent to the substrate, to prevent contact between alloying elements in the substrate and body fluids while the pierced earlobes are healing. However, in practice, the coating process introduces defects in the coat, which allow corrosion of the substrate to take place and this releases nickel ions. Nickel is the main cause of allergic contact dermatitis[2-7] and is caused by Ni^{2+} ions, which bind to tissue and interstitial fluid proteins[3].

In a previous study, neutron activation analysis was used to determine the elements leached out during corrosion of two alloys used for producing ear piercing studs[8]. This paper presents the corrosion resistance of two commercial gold coated ear piercing studs, one with a copper-zinc based alloy substrate and the other with a stainless steel substrate, as well as a laboratory made Ti stud, determined by electrochemical impedance spectroscopy and potentiodynamic polarization testing.

This investigation is a contribution to the study of alloys that are being used in the manufacture of ear piercing studs and that are being linked to allergic reactions. Besides, a laboratory made Ti stud was tested as a potential material for ear piercing studs.

Materials and Methods

Materials

Three types of ear piercing studs have been studied: gold coated austenitic stainless steel (St); gold coated copper-zinc alloy (Pf) and titanium (Ti). Figure 1 shows an ear piercing stud.

Figure 1 – Photograph of an ear piercing stud.

The compositions of the materials used as substrates were determined by instrumental neutron activation analysis (INAA) and the results are given in Table I. In these analyses, the stems and butterfly backs of the studs were analysed separately after removing the gold coating.

Table I. Elemental composition of ear piercing studs determined by instrumental neutron activation analysis

Element	Substrate of Pf studs	Substrate of St studs	Ti ear piercing studs
As $\mu g\ g^{-1}$	8.1 ± 0.5	57.4 ± 0.8	17.7 ± 0.3
Co $\mu g\ g^{-1}$	27.4 ± 0.4	2203 ± 11	≤ 1
Cr %	0.0070 ± 0.0005	16.1 ± 0.2	0.0096 ± 0.0001
Cu %	36.5 ± 1.2	0.35 ± 0.01	≤ 0.04
Fe %	9.0 ± 0.2	67.9 ± 0.2	≤ 0.04
Mn %	2.34 ± 0.07	1.81 ± 0.02	0.0007 ± 0.0002
Mo %	≤ 0.2(*)	0.394 ± 0.002	≤ 0.0003
Ni %	6.80 ± 0.07	7.86 ± 0.07	0.009 ± 0.001
Ti %	≤ 23	≤ 23	97.4 ± 6.4
V $\mu g\ g^{-1}$	≤ 77	987 ± 26	33 ± 3
Zn %	36.4 ± 3.3	≤ 0.7	≤ 0.002

* - For the elements not detected, the detection limit values were evaluated according to Currie[9].

Corrosion tests

The corrosion performance of the three types of studs was investigated by electrochemica impedance spectroscopy (EIS) and potentiodynamic polarization testing. The perturbatior amplitude of voltage for the EIS tests was 10mV and the frequency range, from 50kHz tc 5mHz. These measurements were carried out in a MEM culture medium at roorr temperature, at the open circuit potential. A three-electrode cell arrangement was used foı the electrochemical tests, with a graphite rod as the auxiliary electrode, a saturated calome electrode (SCE) as the reference electrode and cold resin mounted studs as the workinc electrodes. The studs were mounted in an epoxy resin exposing only their stems to the culture medium.

The specimens were immersed in the culture medium for various times (from one to nine days) and the EIS test was carried out as a function of time. Polarization tests were carriec out on the Pf and St studs, after removing their gold coatings with Hg. They were polarizec from the corrosion potential (E_{corr}) up to +1300 mV(SCE) after 5 days of immersion. The coating was removed to avoid localized corrosion at the defects in the coating, and to permit comparison of the corrosion resistances of the different substrates.

Chemical analysis

Twelve pairs of studs were immersed in the MEM culture medium for 10 days. After this period the studs were removed and the medium was analysed by instrumental neutron activation analysis (INAA), according to a procedure described elsewhere[8]. 500 µL of each extract solution was pipetted and dried in a clean polyethylene capsule for irradiation in the IEA-R1 nuclear reactor. The gamma ray spectra obtained were processed using appropriate software and the concentrations of the elements calculated by a comparative method. Also, the blank of the culture medium was analysed to determine the elements in this medium.

Cytotoxicity test

The cytotoxicity assay was carried out according to Rogero et al[10] and the International Standards Organization (ISO)[11] by adding diluted culture medium in which the studs remained immersed to Chinese Hamster Ovary cells culture (ATCC CHO k1). The determination of cytotoxicity, according to ISO, can be either qualitative or quantitative. In this study, cytotoxicity was determined quantitatively, based on cell viability.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

The surfaces of the studs were examined in a scanning electron microscope (SEM) and analysed by energy dispersive spectroscopy (EDS), before and after ten days immersion in the culture medium. The studs were examined for defects in the coating, which could expose the substrate, and for reaction products on the surface.

Results

Polarization tests

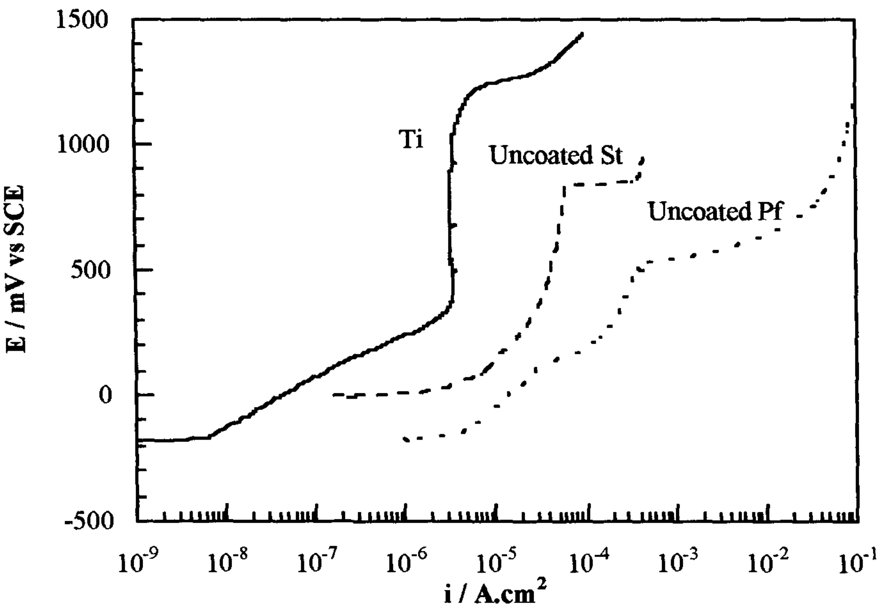


Figure 2 – Polarization curves of different stud substrates after 5 days in the culture medium.

The results of polarization tests carried out on specimens immersed for 5 days are shown in Figure 2. The highest corrosion current density, among the materials tested, was that of Pf substrate. It also showed a pitting potential at around 500 mV (SCE). Low corrosion current densities were observed for St substrates, up to high overpotentials, and a slight increase was seen at approximately 850 mV (SCE). The Ti stud showed a behaviour typical of an active corrosion reaction (anodic Tafel behaviour), in a large range of overpotentials, (approximately 550 mV). However, the very low current densities (order of $\mu A.cm^{-2}$) up to the oxygen evolution reaction potential, indicated that it was passive.

EIS tests
The EIS results shown in Figure 3 revealed large differences in the corrosion response of the three studs after 1 day of immersion. Only one time relaxation constant was observed, associated with the St stud, whereas two time relaxation constants were observed, related to the Ti and Pf studs. The St stud showed a capacitive behavior in a large frequency range (from 10^3 to 10^{-2} Hz), suggesting that the gold coating on this stud was of good quality.

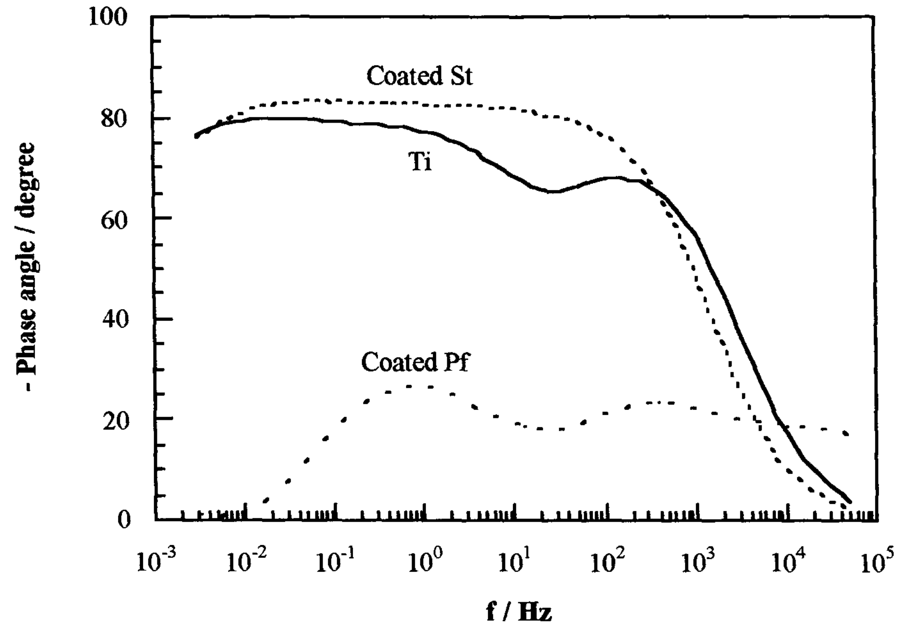


Figure 3 – Bode phase angle plots of the studs after 1 day of immersion in the culture medium.

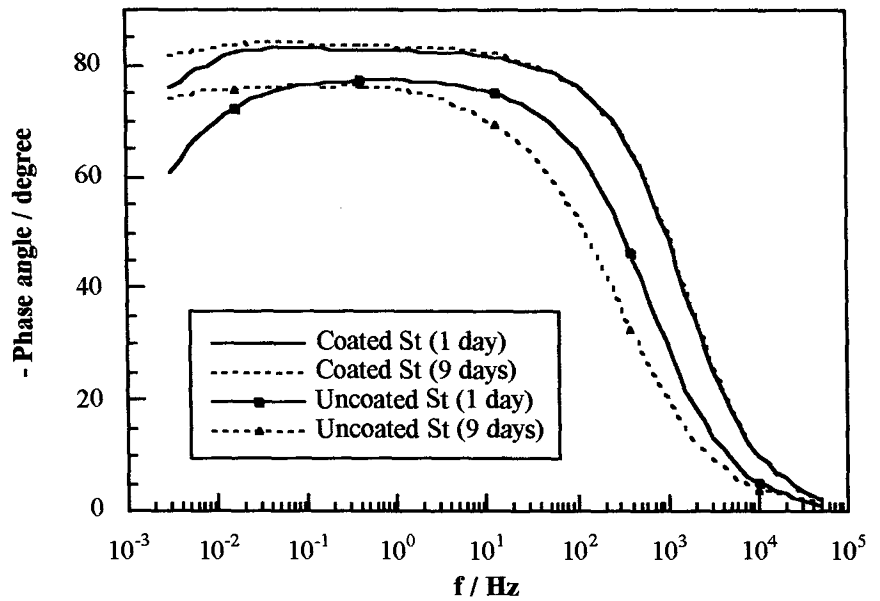


Figure 4 – Bode plots of coated and uncoated St studs after 1 and 9 days in the culture medium.

Increasing the time of immersion caused only slight changes in the EIS response of the coated St stud, Figure 4, lending further evidence of the good quality of the coating. It is important to remember that the substrate of this coating (austenitic stainless steel) also showed a high corrosion resistance in the culture medium, as revealed by the polarization tests. In the case of the uncoated St stud, the increase in immersion time caused the double layer capacitance to increase. A capacitive behaviour was also indicated at low frequencies in the EIS results of uncoated St stud.

The effect of increasing the immersion time of Ti studs, was mainly on the relaxation process at high frequencies, Figure 5. This was probably due to the oxide on the Ti stud surface. Upon increasing the immersion time from one to three days, the EIS results indicated a decrease in the resistance of this oxide, possibly due to an increase in its porosity. Further increase in immersion time from three to nine days, indicated an increase in its capacitance. The observation of a relaxation process at the low frequency range suggests that this oxide was porous, and that the electrolyte had reached the metallic substrate at the base of the pores. A capacitive behaviour was seen at low frequencies during the whole test period, indicating a high corrosion resistance of the Ti stud in the culture medium.

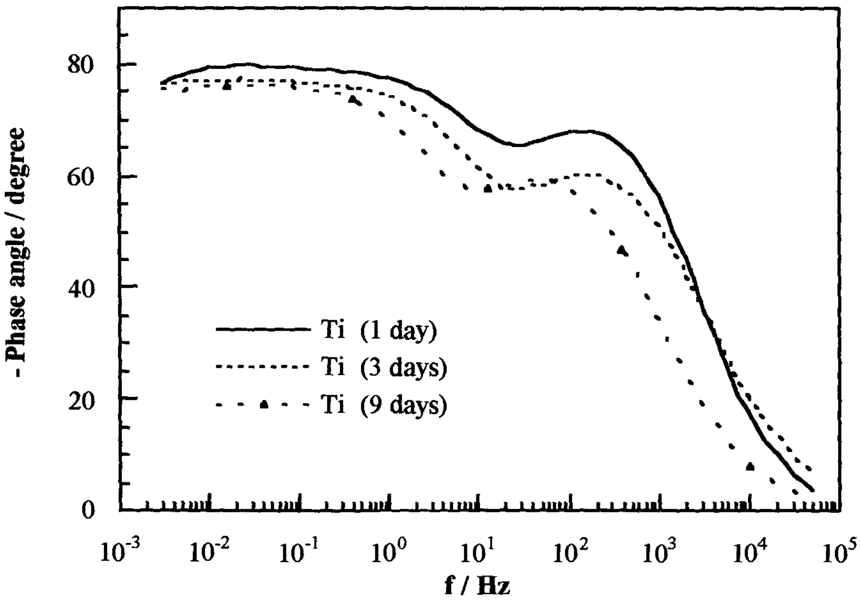


Figure 5 – Bode plots of Ti studs immersed in the culture medium for varying periods.

Significant changes occurred in the EIS results of the Pf stud with increasing immersion times, both at high and low frequencies, Figure 6(a). The high frequency relaxation process was likely related to the coating and the low frequency response to the corrosion process at the base of the defects in the coating.
After two to three days of immersion, the peak at low frequencies was broad, indicating interaction of two time constants. These two time constants were separate after nine days of immersion.

The relaxation process at frequencies from 10^2 Hz to 10^{-1} Hz, was possibly due to the precipitation of corrosion products in the defects of the coating. The thickening of these products, leading to an increase in resistance, and an associated decrease in the charge transfer resistance, may have caused the separation of the two time constants upon increasing the immersion time from three to nine days. A diffusion controlled process through this layer was also indicated in the EIS results. The response relative to the metallic material/electrolyte interface, seen at low frequencies, after corrosion products had formed in the defects, suggests that these products were porous, allowing electrolyte to reach the metallic substrate. These results indicate that the Pf studs were continuously corroding during the whole test period, even after corrosion products had deposited in the defects.

Nyquist plots of Pf studs immersed in the culture medium for periods corresponding to one to three days, showed depressed semicircles at high frequencies, figure 6 (b). This indicated the interaction of various time constants, possibly due to heterogeneities, such as defects, in the coating.

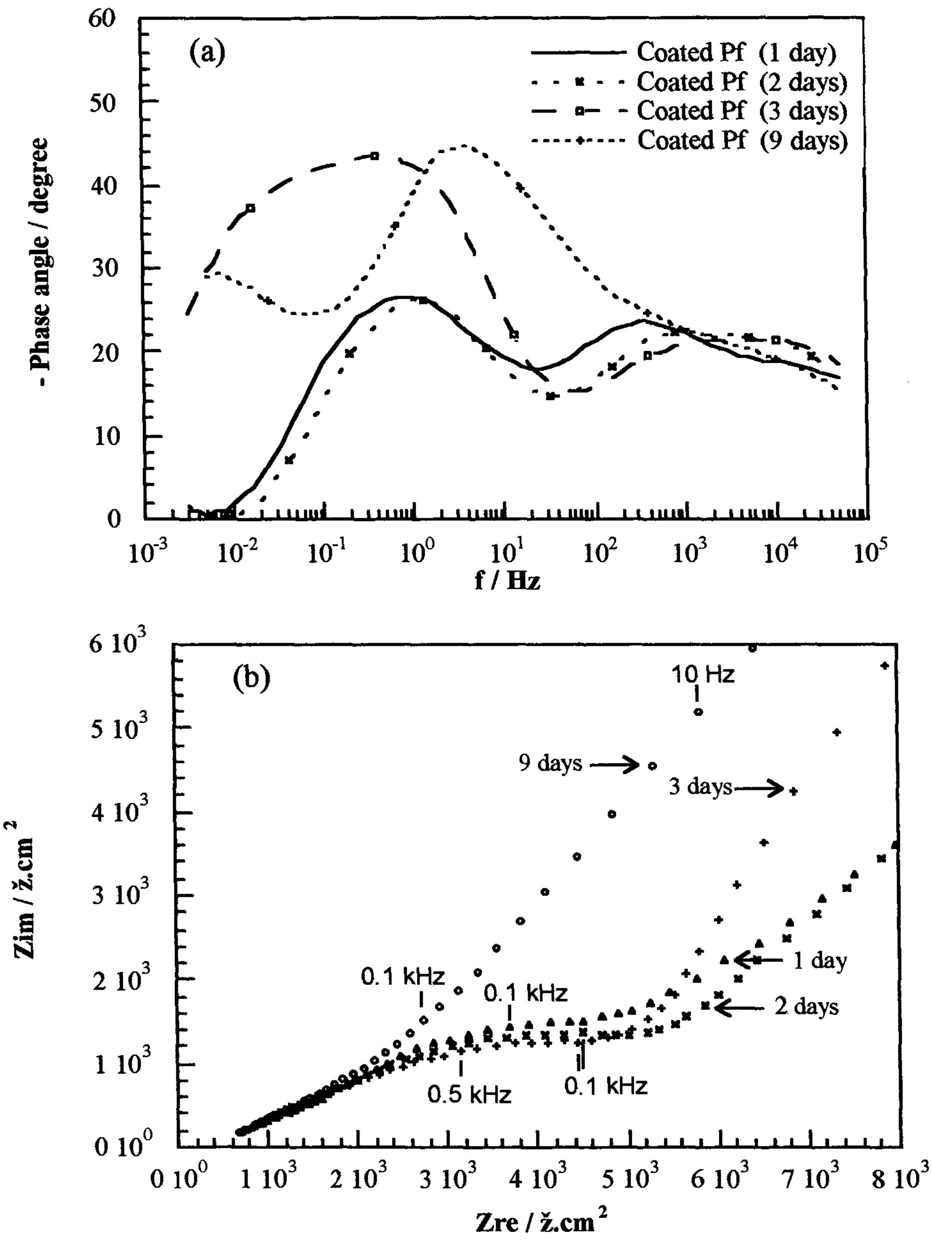
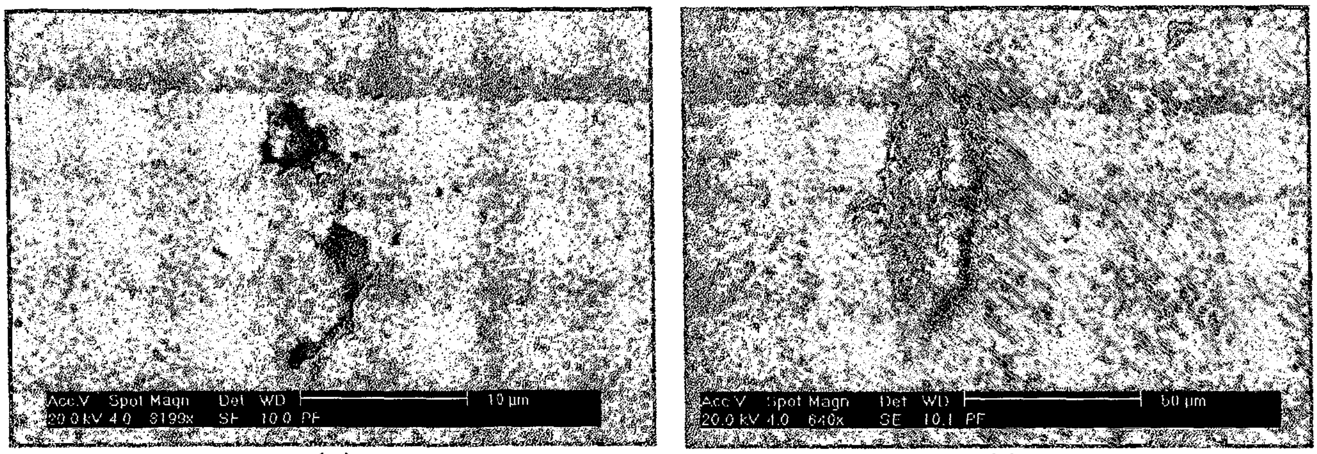


Figure 6 – (a) Bode plots and (b)Nyquist plots of coated Pf studs after different immersion times.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

Defects were observed in the coating on Pf studs before immersion in the culture medium, figure 7 (a). After a few days of immersion, corrosion products were seen on the Pf stud surface, at regions with defects in the coating, figure 7 (b). EDS analysis indicated this product to be zinc phosphate, figure 8. It is important to mention that phosphate is a component of the culture medium.



(a) (b)

Figure 7 - (a) Defects in the coating before corrosion, (b) corrosion products on a corroded area.

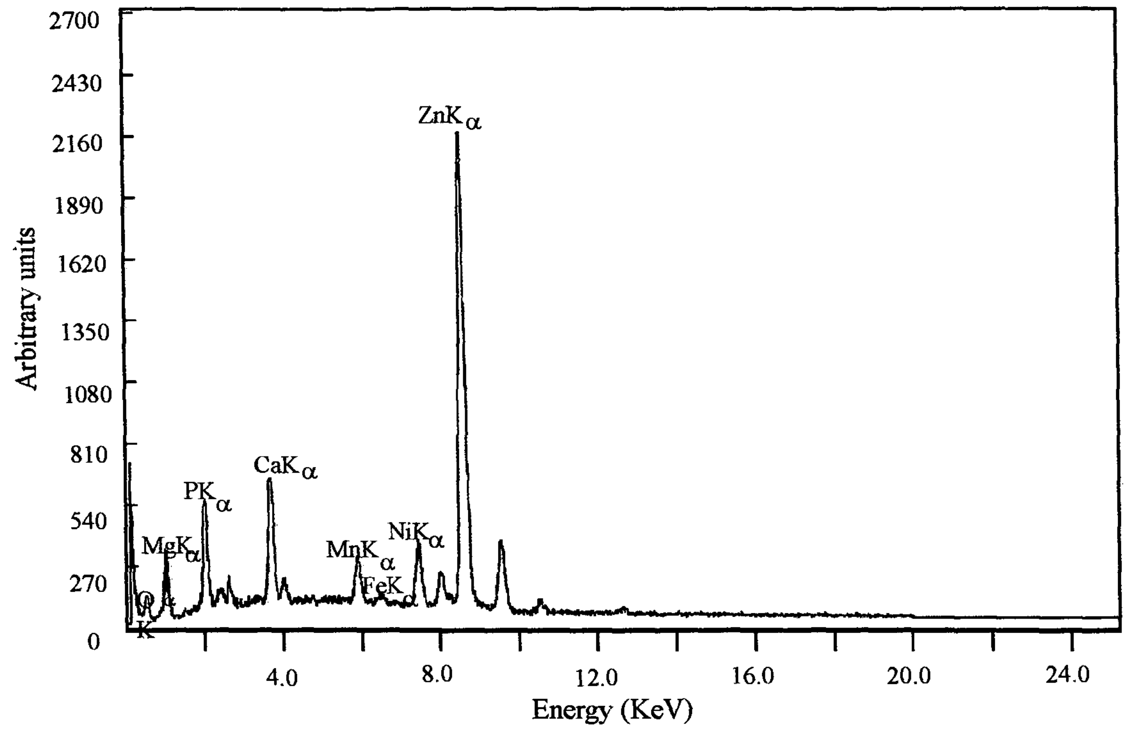


Figure 8 – EDS on corroded area.

Chemical analysis of the culture medium after corrosion

The elements present in the culture medium after ten days of exposure of studs and in the blank culture medium solution are presented in Table II.

Ni was released from both the gold-coated studs. This indicates that despite the good characteristics of the gold coating on St stud, Ni is released into the corrosive medium. In normal use, this can lead to allergic reactions. The culture medium in which stem substrates of Pf studs were immersed, presented a high concentration of Zn and where the St studs were exposed, high levels of Fe. The high zinc content, (six times that of the blank) in the culture medium after ten days of immersion of studs indicates that this element was leached from the substrate alloy, because of significant corrosion, and this observation was supported by the EIS results. In the solution in which Ti studs were immersed, the elements detected were of the same order of magnitude as that in the blanks, indicating passivation of the Ti surfaces in the culture medium.

Table II. Elemental concentrations in the culture media and in the blank

Element	Blank	Culture medium after 10 days of immersion of studs		
		Pf	St	Ti
Co ng/mL	12.1 ± 1.2	61.6 ± 0.5	99 ± 10	53.8 ± 2.1
Cr µg/mL	0.72 ± 0.02	0.73 ± 0.04	0.73 ± 0.03	0.75 ± 0.03
Fe µg/mL	0.60 ± 0.09	0.61 ± 0.08	4.03 ± 0.31	0.43 ± 0.11
Ni µg/mL	N.D.*	0.96 ± 0.09	0.66 ± 0.06	N.D.
Zn µgmL	0.58 ± 0.05	3.84 ± 0.41	0.61 ± 0.01	0.75 ± 0.10

* N.D. – Not detected

Cytotoxicity test

The cytotoxic potential can be quantitatively expressed as cytotoxicity index ($IC_{50(\%)}$). This is the concentration of the extract necessary to suppress colony formation to 50% of the control value. St and Pf commercial studs showed cytotoxicity, presenting $IC_{50(\%)}$ = 78 and 44, respectively, and the latter, Pf , higher toxicity. On the other hand, Ti studs were not cytotoxic, $IC_{50(\%)} > 100$.

Conclusions

The results have shown that the studs investigated here had large differences in their corrosion resistance. The stud with the highest corrosion resistance was St. This was partially attributed to the good quality of the gold coating on this stud and partially to the high corrosion resistance of its substrate (stainless steel). Nevertheless, nickel was leached from the St stud substrates into the culture medium and it was cytotoxic. The Pf stud on the other hand, had the lowest corrosion resistance, and released a significant amount of Ni, due to corrosion, and revealed higher cytotoxicity. The Ti stud showed the best combination of properties, it had high corrosion resistance, has no Ni in its composition and therefore, no cytotoxicity. These results emphasise further the importance of using Ni free materials for the manufacture of ear piercing studs.

Acknowledgements

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