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Neutron activation analysis of corrosion products from gold coated ear piercing studs

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Abstract

Neutron activation analysis was applied to the determination of elements Au, Cr, Fe, Ni and Zn released in NaCl solution and in a culture medium in which gold coated studs were immersed for corrosion tests. The coating defects and corrosion effects on the stud surfaces were studied by scanning electron microscopy and energy dispersive spectroscopy analysis. The cytotoxicity assay of culture medium from corrosion test showed toxicity in a culture of mammalian cells.

Keywords: Neutron activation analysis; Cytotoxicity assay; Biomaterial corrosion; Gold coated ear piercing studs

1. Introduction

Gold is known as a metal having little or no toxicity and therefore it has been widely used for coating studs for ear piercing. However, for some people, gold coated studs have caused serious allergy and inflammatory problems. After piercing, the studs are usually kept in the ear lobes for at least one week and the surfaces in contact with the body fluids have been known to cause swelling, pain and redness of the skin. Consequently, it is important to assess whether the elements from the metallic substrate underneath the gold coatings migrate to the body fluids due to corrosion effect.

Therefore, it is interesting to characterize the corrosion products in order to investigate if there is a correlation between the elements released from gold coated studs and allergic contact dermatitis or inflammatory effects.

In this work, neutron activation analysis (NAA) was applied in the characterization of corrosion products, carried out by analyzing a simulated physiological solution and culture medium in which gold coated studs were immersed. A cytotoxicity assay was also carried out using the culture medium to determine the cytotoxicity index ($IC_{50(\%)}$). The presence of defects on coated stud surfaces and the corrosion products were also examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

2. Experimental

2.1. Material

The material used consisted of commercial gold coated ear piercing studs and their elemental composition (wt%) obtained by X-ray fluorescence analysis is

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Table 1
Concentrations of elements in NaCl solution

Element	Concentration and standard deviation (ng/ml)[a,b] after		
	11 days	22 days	30 days
Au	0.11 ± 0.02	0.14 ± 0.02	0.18 ± 0.02
Cr	120 ± 10	300 ± 15	410 ± 73
Fe	625 ± 182	2769 ± 138	3944 ± 276
Ni	277 ± 27	438 ± 37	570 ± 64

[a] Standard deviation calculated using statistical counting errors of sample and standard.
[b] Contribution from the blank was discounted.

presented below:

- Stainless steel substrate of butterfly backs: Cr = 16.7; Fe = 69.8; Mn = 2.5; Mo = 0.24; Ni = 10.5; Si = 0.16.
- Copper–zinc based alloy substrate of stem and stud: Cu = 50.1; Mn = 1.9; Ni = 6.8; Zn = 40.3.

2.2. Solutions for corrosion tests

Two solutions were prepared: (i) a 0.9 wt% NaCl solution in which a pair of studs was immersed for 30 days and (ii) a culture medium in which 12 pairs of studs were immersed in 60 ml of RPMI-FCS (RPMI 1640 culture medium supplemented with 10% fetal calf serum (FCS) and 1% penicillin–streptomycin solution), during 10 days at 37°C (Nakamura et al., 1989; ISO document 10993, 1992).

2.3. NAA of corrosion test solutions

500 μl solution was pipetted and dried in clean polyethylene capsules to be irradiated at the IEA-R1 nuclear reactor with elemental synthetic standards. Samples and standards were irradiated for 16 h by a thermal neutron flux of 10^{13} η cm^{-2} s^{-1}. After 10 and 20 days of decay times, gamma ray measurements were carried out using a hyperpure Ge detector coupled to EG&G Ortec ADCAM 918[A] Multichannel Buffer and this to a microcomputer. The gamma-ray spectra were processed using the VISPECT computer program. Radioisotope nuclides measured in this study (i.e. ^{198}Au, ^{51}Cr, ^{59}Fe, ^{58}Co for Ni analysis, ^{65}Zn) were identified according to their gamma-ray energies and half lives. The relative standardization method was used for analytical calculations. The blank of the solutions were also analyzed.

Table 2
Elemental concentrations in the culture medium and in blank

Element	Concentration and standard deviation (ng/ml)[a]	
	culture medium[b]	blank
Au	860 ± 2	3.84 ± 0.13
Cr	33 ± 7	625 ± 4
Fe	322 ± 82	288 ± 63
Ni	3452 ± 410	284 ± 21
Zn	1213 ± 11	601 ± 6

[a] Standard deviation calculated using statistical counting errors of sample and standard.
[b] Contribution from blank was discounted.

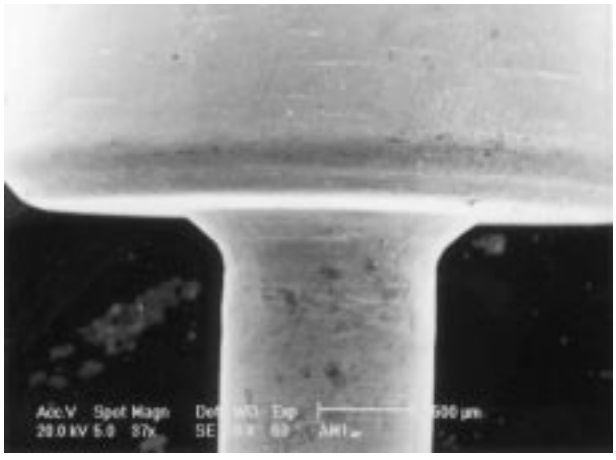

Fig. 1. SEM micrograph of stud surface before immersion in the culture medium.

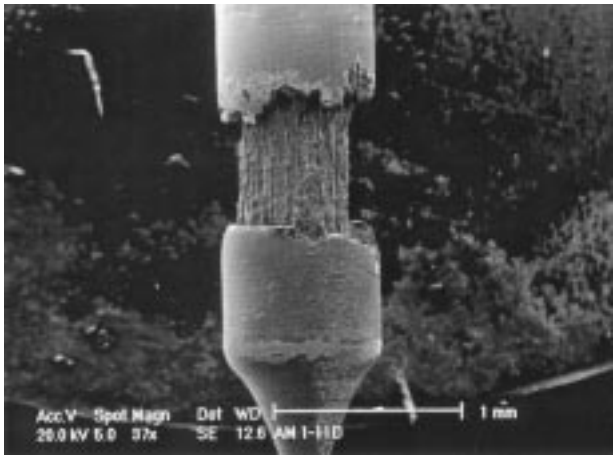

Fig. 2. SEM micrograph of attacked surface.

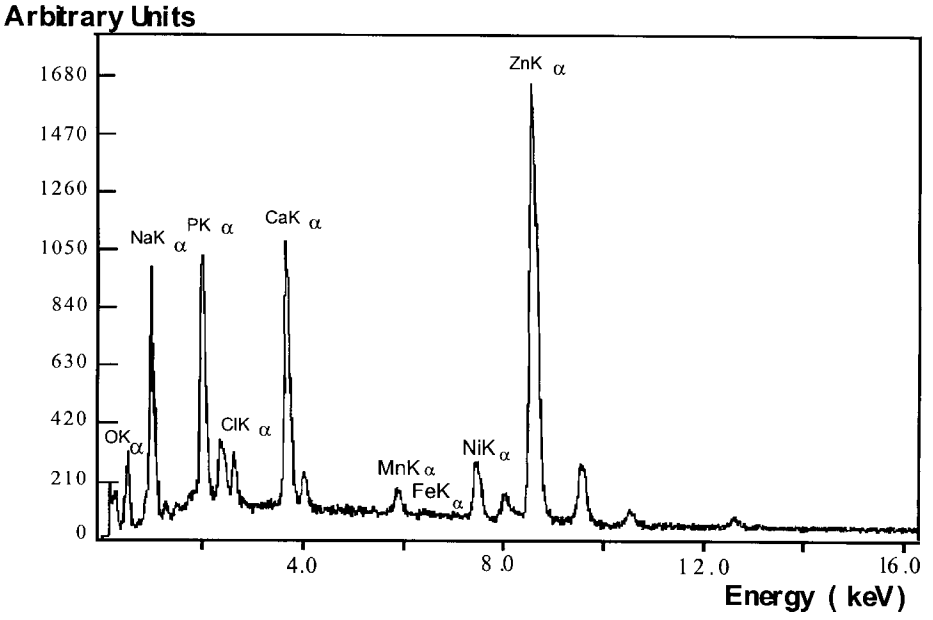

Fig. 3. EDS spectrum of the deposited product on the surface.

3. Results and discussion

Table 1 presents the results for Au, Cr, Fe and Ni found in the NaCl solution after 11, 22 and 30 days of immersion and Table 2 shows the results obtained for Au, Cr, Fe, Ni and Zn in the culture medium after 10 days of immersion. These findings indicate that the coated studs have defects which allowed the migration of elements from the substrate to the test solutions due to corrosion. The presence of defects on the stud surface, as well as the occurrence of the corrosion process were also confirmed by SEM and EDS analyses. In Fig. 1, defects (stains and small holes) can be seen on the surface. The test solution in contact with the exposed substrate initiates the corrosion process (Fig. 2). The EDS spectrum presented in Fig. 3 shows that elements from the culture medium, such as P, Ca, Cl and Na are present on the

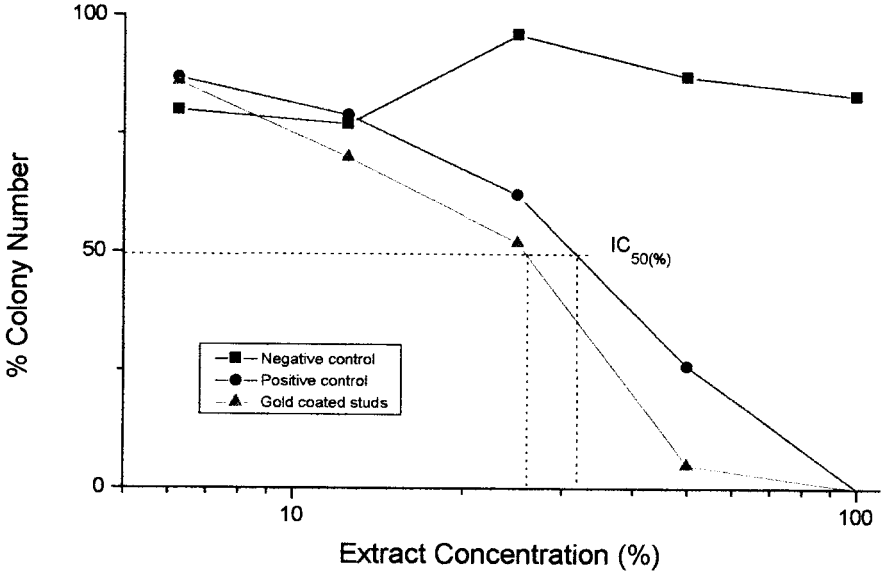

Fig. 4. Colony suppression curve of gold coated ear piercing studs.

surface as well as corrosion products constituted of Fe, Mn, Ni and Zn.

From the results obtained in the analysis of the test solutions, the high concentration of Ni found in the solutions could be associated to allergic and inflammatory reactions in the earlobes. Ni is known as the major cause of allergic contact dermatitis and recently nickel and cobalt sensitization has increased as the habit of ear piercing has become more popular (Meijer et al., 1995). The cytotoxicity assay results presented in Fig. 4 indicate the toxicity of the corrosion test solution, presenting $IC_{50\%} = 26$. This cytotoxic effect may be attributed to the high concentration of Ni in the test solution, as Ni itself has toxic effects in cell cultures and in tissues (Bordji et al., 1996).

This work indicates the viability of using the NAA for analyzing corrosion products from gold coated studs due to its simplicity and its high sensitivity for several elements. This method is well-suited to analyzing these products since elements released from the substrate of gold coated studs by corrosion are in very low concentrations.

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