

Exposure of nickel in used and unused gold-plated earrings: a study using scanning electron microscopy and X-ray microanalysis

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Nickel is the most common contact sensitizer in the female population. The aim of the present study was to examine closely the surface of both used and unused gold-plated earrings by scanning electron microscopy, and to ascertain the distribution of nickel on the surface of these earrings qualitatively and quantitatively by X-ray microanalysis. The clasps of 4 sets of used earrings causing nickel dermatitis and of the 3 sets of unused earrings were examined. In backscattered electron images obtained by scanning electron microscopy, a large number of scratches and pits were found on the surface of the used earrings. Cross-sections of the surfaces confirmed that the gold plating was defective in some areas, exposing the nickel. Nickel was readily detected and quantitatively determined in the scratches and pits by X-ray microanalysis. We also found that, even in unused earrings, numerous scratch marks and pits were present, again exposing the nickel. Clearly, even in unused earrings, nickel exposed at the surface sensitizes the skin and causes contact dermatitis.

Key words: nickel; allergic contact dermatitis; earrings; pits; scratches; surface structure; interliner; gold-plated; prevention; legislation. © Munksgaard, 1997.

Accepted for publication 18 April 1996

Nickel is one of the commonest causes of allergic contact dermatitis. The prevalence of nickel sensitivity among females in the general population today is around 10% (1-3) and is increasing (4), especially in schoolchildren (5). The nickel interliner beneath the gold plating of various metal accessories becomes exposed with the use, and sensitizes the skin, leading to contact dermatitis. However, the surface structure of such metal articles and the distribution of nickel in them have not been closely examined.

The purpose of the present study was to observe the surface structure of the clasps of used and unused gold-plated earrings by scanning electron microscopy, and to determine qualitatively and quantitatively the distribution of nickel on their surface by X-ray microanalysis.

Materials and Methods

The clasps of 4 sets of used gold-plated earrings causing nickel dermatitis were provided by 4 patients. These earrings were all made in Japan,

though by different companies. All 4 patients who provided their earrings had positive reactions to nickel on patch testing. 3 sets of unused gold-plated earrings bought in a shop for the present study were also examined. All the unused ones examined were of different Japanese brands.

A JSM-5410 LV scanning electron microscope (JEOL), equipped with a Links ISIS energy dispersive spectrometer (EDS) (Oxford), and a JMS-5310 LV scanning electron microscope (JEOL), with a JED-2100 energy dispersive spectrometer (JEOL), were used. To examine the surface of the clasps, backscattered electron images were obtained using scanning electron microscopy. In X-ray microanalysis, point analysis was used to study metal elements on the surface of the clasps both qualitatively and quantitatively (wt %), and, to ascertain the distribution of gold and nickel on their surfaces, a colour map image technique was used. The condition of the plated gold and interliner of nickel was clarified by examining the cut surface in backscattered electron images.

We measured the thickness of the gold plate in

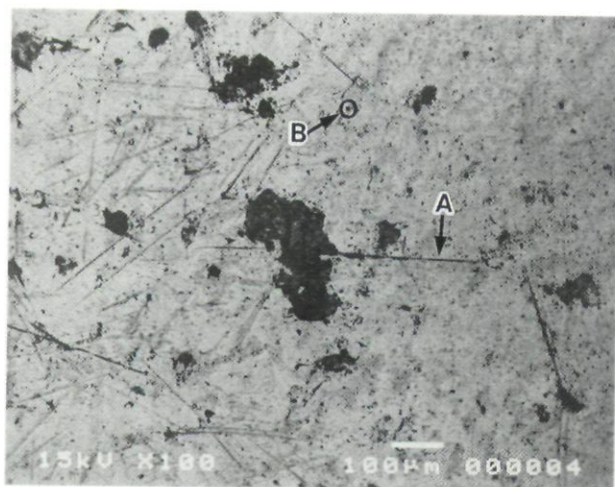


Fig. 1. Scanning electron microscopy: backscattered electron image of the surface of a used earring. There are numerous scratches and small pits in the surface. A: scratch mark. B: pit. $\times 3500$.

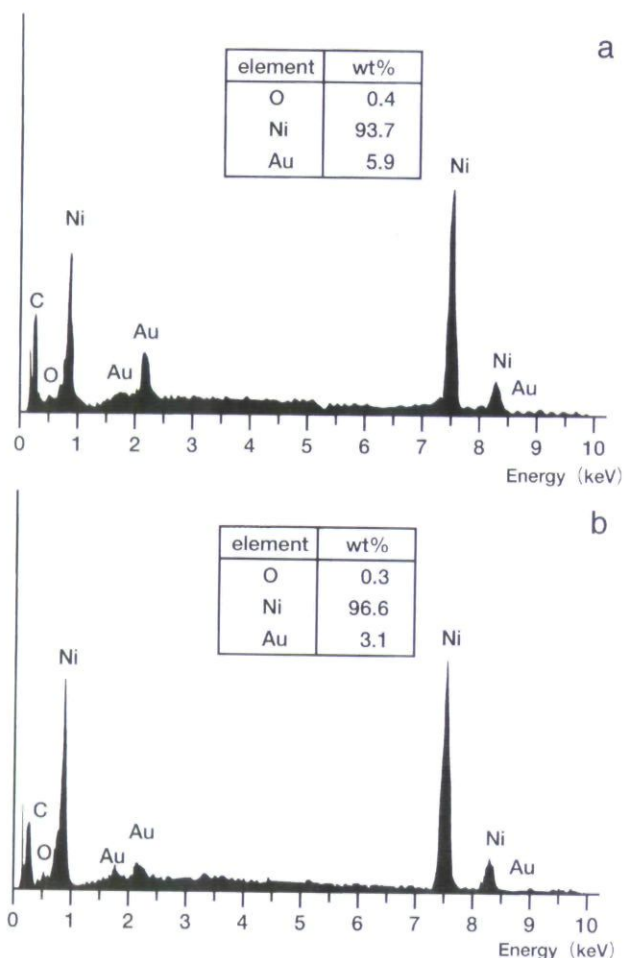


Fig. 2. X-ray microanalysis: point analysis. High peaks are seen for nickel in a scratch (A in Fig. 1) and a pit (B in Fig. 1). More than 93 wt% of the metal on the pit was found to be nickel (a) and the scratch (b). The %s of elements by weight are shown in the insert table.

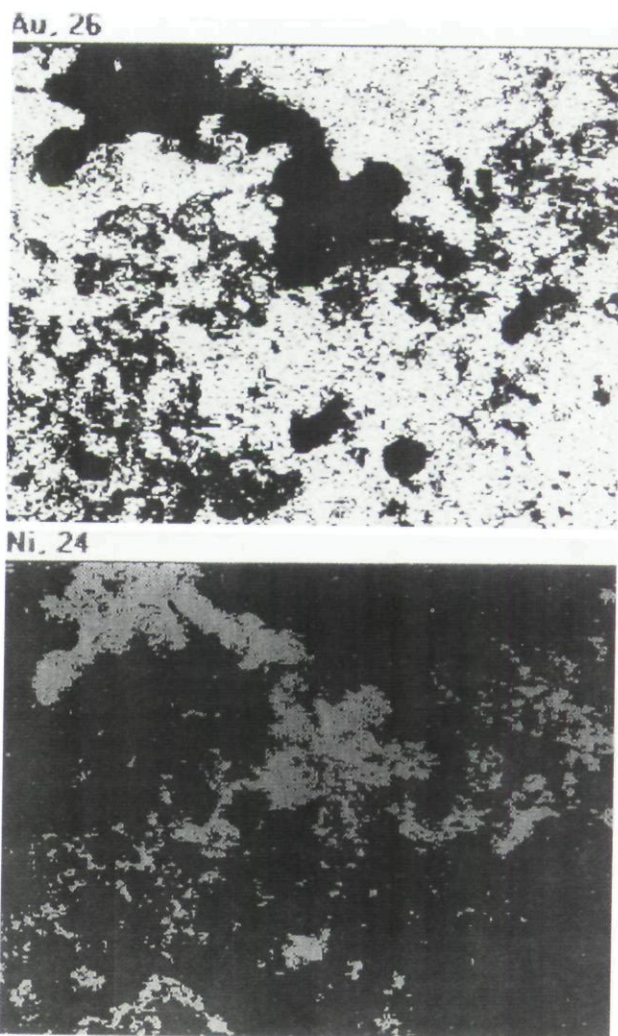


Fig. 3. X-ray microanalysis: colour map image. Gold is displayed in clear (a) and nickel in gray (b). The areas of nickel exposure correspond to those where the gold plating is defective. $\times 700$.

2 used and 2 unused earrings with a fluorescent X-ray coating thickness gauge (Seiko).

Results

Used gold-plated earrings

Numerous scratch marks and pits of various sizes were recognized on the surface of the clasps in the backscattered electron images (Fig. 1). On X-ray microanalysis, large nickel and small gold peaks were detected in a scratch (A in Fig. 1) and a small pit (B in Fig. 1) by point analysis (Fig. 2). The results are summarized in Table 1. The composition of the base alloys was not analyzed. Quantitatively, more than 93 wt% of the metal revealed in both the small pits and the scratches was nickel. It was confirmed in colour map images (Fig. 3) and in backscattered electron images of cross-sections

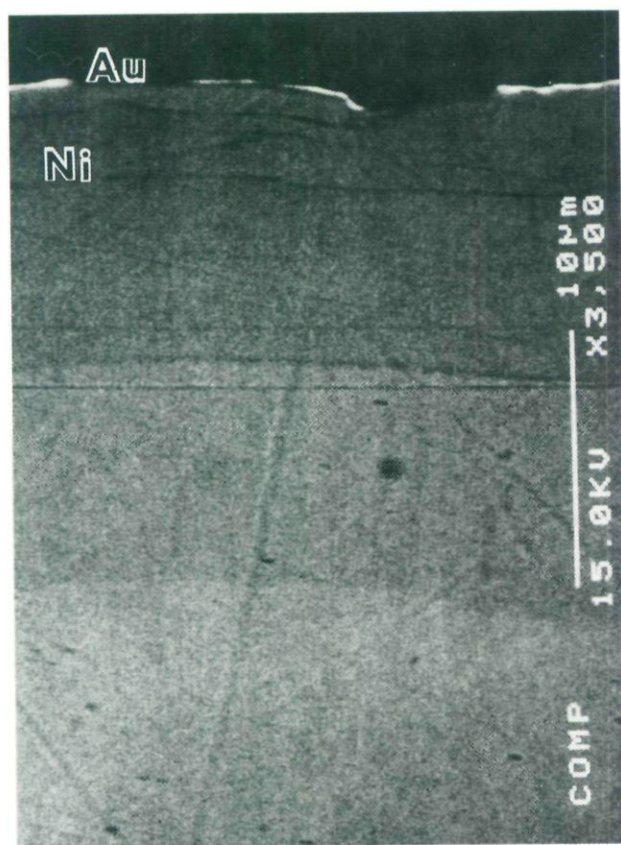


Fig. 4. Scanning electron microscopy: backscattered electron image of cross-section of surface of used earring. The thin layer of gold plating (Au) is clearly observed as the outermost layer, where it is defective, the layer of nickel plate (Ni) is exposed; $\times 18,000$.

(Fig. 4) that the nickel of the interliner was exposed at the surface. In the former, gold appears clear (Fig. 3a) and nickel, gray (Fig. 3b). The nickel was observed in the areas where the gold plate was defective. In a cross-sectional backscattered electron image (Fig. 4), a layer of gold plate was clearly seen on the surface of the clasp, with a layer of nickel plate present beneath it. In many areas, this gold layer was defective and the nickel

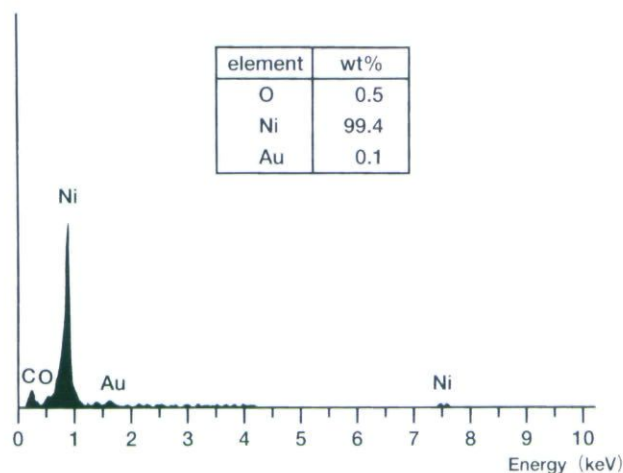


Fig. 5. X-ray microanalysis: point analysis. High nickel peaks are detected at the scratches, where 99 wt% of the metal found was nickel. The %s by weight of elements are shown in the insert table.

was exposed. The thickness of the gold plating was approximately $0.05\text{--}0.08\text{ }\mu\text{m}$ in all the earrings examined.

Unused gold-plated earrings

A large number of scratches and pits of various sizes were seen on the surface of the clasps in backscattered electron images. X-ray microanalysis of these clasps revealed large peaks of nickel in the scratches and pits (Fig. 5), just as on the clasps of the used earrings. In the scratches and pits, nickel accounted for more than 99 wt% of the metal detected. The composition of the base alloys was not analyzed. The thickness of the gold layer was about $0.05\text{--}0.08\text{ }\mu\text{m}$. These results are summarized in Table 1.

Discussion

In gold-plated accessories, there is usually an interliner of nickel beneath the gold plating to enhance

Table 1. Summary of the results of scanning electron microscopy (EM), X-ray microanalysis and thickness of gold plating of earrings examined

Used or unused	Specimens	Scanning EM		X-ray microanalysis Metal elements in scratches and pits	Thickness of gold plating*
		Scratches	Pits		
used	1	numerous	numerous	Large peaks of Ni, small peaks of Au, more than 93% of the defective surface of Ni	not measured
	2	numerous	numerous		$0.05\text{--}0.08\text{ }\mu\text{m}$
	3	numerous	numerous		not measured
	4	numerous	numerous		$0.05\text{--}0.08\text{ }\mu\text{m}$
unused	5	numerous	numerous	Large peaks of Ni, small peaks of Au, more than 99% of the defective surface of Ni	not measured
	6	numerous	numerous		$0.05\text{--}0.08\text{ }\mu\text{m}$
	7	numerous	numerous		$0.05\text{--}0.08\text{ }\mu\text{m}$

*The fluorescent X-ray coating thickness gauge technique was used.

the gloss and prevent oxidation and corrosion of the base alloy. However, the gold layer may easily be stripped off the surface, and, in the present study, in both used and unused earrings, numerous scratches conspicuously marked the surface, and the nickel of the interliner was exposed. Nickel in contact with the skin of the earlobes is a source of allergic contact dermatitis. The gold layers examined in the unused earrings were very thin (approximately 0.05–0.08 μm in thickness). It is difficult to plate metal articles with a layer of gold thicker than 0.05 μm , even if an interliner of nickel is present beneath it. Therefore, the nickel is exposed where pits and scratches in the base material of the article remain in the finished product.

We (6) indicated that the gold plating gradually flaked off, so that, under normal wearing conditions, the interliner of nickel became partially exposed, and large quantities of nickel ions were released by the sweat. Santucci et al. (11) indicated that the clasps and clips commonly used in earrings released high quantities of nickel ions. It was suggested that the nickel exposed in the scratches and small pits in the clasps, and the resulting high daily absorption of nickel ions through the skin during wear, cause allergic contact dermatitis.

In the present study, it was observed that, even in unused earrings, the nickel of the interliner was already exposed at the many scratch marks and pits. It appears that these exposed areas of nickel enlarge easily as a result of friction and exposure to sweat. We concluded that even new, unused gold-plated earrings can cause allergic contact dermatitis from nickel, as well as used ones.

Fischer et al. (7) stored gold-plated ear piercing kits and earrings at room temperature in 0.5 ml of synthetic sweat at pH 6.4 for 1 week. They observed that both of these articles released nickel and that neither gold nor silver plating prevented this release. Our data suggest that nickel was probably released through the pits and scratches into the synthetic sweat. Nickel ions released from metal articles become attached to specific high-molecular-weight proteins. This combination of the nickel ion (the hapten) with proteins generates the antigen. The latter is recognized and processed by antigen-presenting cells such as the Langerhans cells (8).

Nowadays, many women and young girls have been sensitized by nickel. Recent data from Denmark reported positive results in 11.1% of nickel patch tests in females and in 2.2% in males (9). Other studies (1, 2) have estimated that, in the general population, the prevalence of nickel sensitivity in women is about 10%. However, women generally are unwilling to give up making themselves more attractive by self-adornment. Recently,

men have also taken to wearing earrings and are having their ears pierced in increasing numbers. The prevalence of nickel allergy among both may therefore increase. In Europe, new legislation will lead to the replacement of nickel interliners by nonallergic interliners (9). It is necessary to improve both plating methods and the materials that are used for gold-coloured accessoires. McDonagh et al. (10) stated that jewellery suppliers should be encouraged to provide nickel-free earrings to reduce the frequency of this easily avoidable problem.

Acknowledgements

This work was supported in part by a grant from the QP Co., Ltd., Japan.

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