

The microstructure of corroded amalgams

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One conventional amalgam and two amalgams with a high copper content were stored in 0.9% NaCl solution buffered with phosphate to pH 6. In one experimental series the amalgams were placed in contact with a gold alloy. Every 7 weeks the solutions were changed and analyzed with regard to elements released from the amalgams. The microstructure of the specimens was studied in a scanning electron microscope before immersion and after 7 and 35 weeks in the solution. All the amalgams corroded along the grain boundaries in the γ_1 phase. Corrosion was greatest in the γ_2 phase of ANA 68, in the η' phase of ANA 2000 and in the reaction zone ($\eta' + \gamma_1$) surrounding the Ag-Cu-eutectic particles of Dispersalloy. The microstructure of the corroded amalgams showed similarities to amalgams corroded in vivo. The change in microstructure observed in cross-sections of the corroded specimens was related to the amounts of corrosion products released into the saline solution. □ *Amalgam; corrosion; dental alloys; dissolution; metal release*

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Corrosion products from amalgams have been found in hard and soft tissues of the mouth (1, 2) and may cause allergy and lichen planus (3-6).

It would be of biological interest to quantify the elements released from the amalgam surface during corrosion in the oral cavity. However, measuring the amounts of metals released in vivo during a long period is not practicable. The microstructure of amalgams corroded in vitro in chloride-containing solutions has shown similarities with amalgams corroded in vivo (7-9). Therefore, the microstructure of amalgams, after corrosion in vivo, could give some indication of the amounts released.

The microstructure of amalgam has not, to our knowledge, previously been related to the amount of elements released from its surface during corrosion. In a previous study (10) the release of elements from amalgams in contact with acrylic and dental casting alloy plates was studied in vitro. The purpose of the present investigation was to study the changes in microstructure of the amalgams, quantitatively and qualitatively, after corrosion in relation to the corrosion products released into the saline solution.

Materials and methods

Three types of amalgam were used in the study, one conventional amalgam (ANA 68) and two amalgams with a high copper content (Table 1). Of the latter, one was a blended alloy (Dispersalloy) and the other a single-composition alloy (ANA 2000).

The amalgams were made as plugs, 4 mm long and 5 mm in diameter (1 cm² each), in steel molds, and the condensation was done by hand for 60 sec, 30 sec after trituration in accordance with ADA specification No. 1 (11). 24 h after condensation the amalgams were polished with a silicon-carbide wheel (600 grit).

Plates, 10 mm × 30 mm and 1 mm thick, with three holes, 5 mm in diameter, were made in type III gold alloy (Sjödings C; Sjödings, Spånga, Sweden) and acrylic. The casting specimens were polished down to 600 grit with silicon-carbide paper.

Three amalgam plugs were placed in the holes of the plates, and because of some conicity the plugs were stuck to the plates by friction. Five specimens of each combination were made.

Immediately after being polished the

Table 1. The amalgam alloys used in the investigation, their compositions, in percentage by weight, according to the manufacturers, and recommended mercury/alloy ratio

Metal	ANA 68*	Dispersalloy†	ANA 2000*
Mercury	1.5	—	1.6
Silver	68	70	42
Tin	26	18	29.4
Zinc	0.3	0.9	0.2
Copper	5.5	12.4	25
Mercury/alloy ratio	1/1	1/1	1.1/1
Batch no.	7903	OC 703	7-194

* Nordiska Affineriet ANA, Helsingborg, Sweden.

† Johnson & Johnson Dental Products Co., East Windsor, N.J., USA.

specimens were placed in glass beakers (25 ml) with 23 ml of sterilized 0.9% NaCl solution buffered to pH 6.0 with phosphate buffer (NaH_2PO_4 , 8.8 mM, and Na_2HPO_4 , 1.2 mM). The beakers were stored at 37°C and shaken once a day for a few seconds. The experiment was in progress for 35 weeks. Every 7 weeks the solutions were renewed. The corrosion products that precipitated on the surface of the specimens were removed by light brushing with a soft toothbrush in the solution. The solutions were analyzed with an atomic absorption spectrophotometer (Pye Unicam SP 190, Pye Unicam Ltd, Cambridge, England) with regard to Cu, Zn, Ag (air/acetylene flame), Sn (nitrous oxide/acetylene flame), and Hg (cold vapor).

The microstructure of the amalgam specimens was examined before immersion, and after 7 and 35 weeks in the saline solution using a scanning electron microscope (Philips SEM 501, Philips, Eindhoven, Holland) operating in secondary and back-scattered electron mode. The different phases in the structure were identified with an energy dispersive detector (EDAX). Cross-sections of the specimens were polished by standard metallographic techniques. The surfaces of some of the specimens were polished and marked with scribed lines before immersion in the solution, to make it possible to study the same spot before and after the corrosion test. To study an initial corrosion attack, the immersion lasted for only 7 weeks. The microstructure of 15 conventional and 7 high-copper amalgam restorations, 1–20

years old, taken from extracted teeth, was studied for comparison.

Results

The corrosion products in the analyzed solutions are shown in Fig. 1 and are discussed in detail in an earlier paper (10).

In different cross-sections of the amalgams the corrosion depth varied considerably. Corrosion at deeper levels was often associated with voids and cracks near the surface. In Table 2 the depth range is presented. No attempt was made to determine a mean corrosion depth—that is, by series of cross-sections of the specimens—or to order the three types of amalgams with regard to corrosion depth. However, a clear increase in corrosion depth was observed with the three groups studied in the order 1) immersed 7 weeks, 2) immersed 35 weeks placed in acrylic plates, and 3) immersed 35 weeks in contact with gold alloy plates. The release of corrosion products from the amalgams were larger per micrometer when the corrosion depth increased. The qualitative changes in the microstructure of the amalgams are described below.

Conventional amalgam (ANA 68) mounted in acrylic plates

Figs. 2a and b show the amalgam before corrosion in the saline solution. A γ particle (Ag_3Sn) in the bottom left-hand corner of Fig. 2b was penetrated by the γ_1 phase

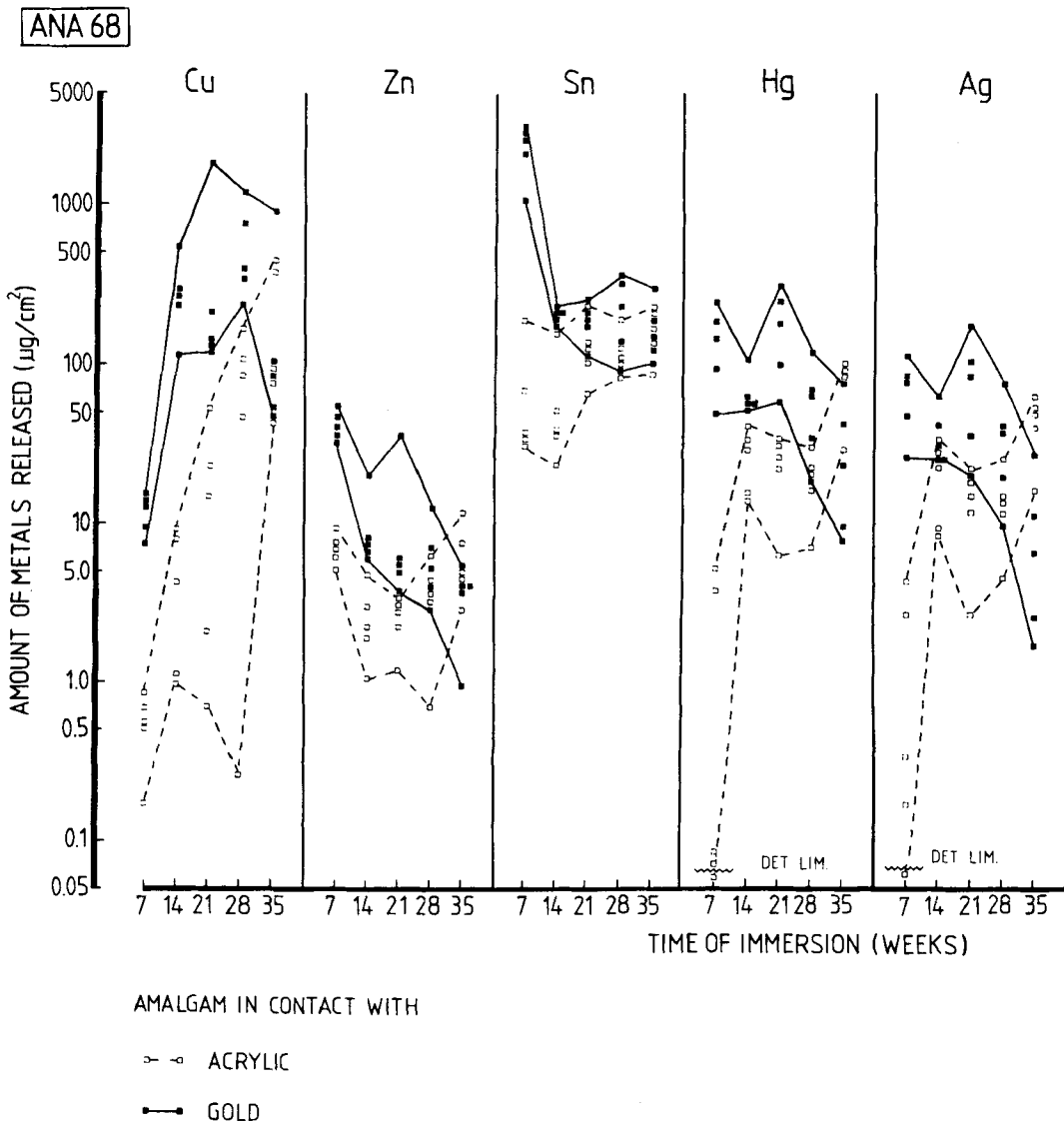


Fig. 1a. Amount of metals released from ANA 68 into the saline solution after 7, 14, 21, 28, and 35 weeks in contact with acrylic (□) and type III gold alloy (■). Five specimens of each group are presented, and the range is marked with lines. DET. LIM. = detection limit.

(Ag₃Hg₄) along its grain boundaries. After 7 weeks (Fig. 2c) corrosion of the γ_2 phase (Sn₈Hg) (12) was seen at the surface. Sn and Cl had accumulated on the γ_1 and ϵ phases (Cu₃Sn). Cross-sections showed heavily corroded subsurface areas containing high concentrations of Sn and Cl (Fig. 2d). Corrosion

of the γ_2 phase was most dominant and resulted in Sn-containing voids and pores.

After immersion of the amalgam in the saline solution for 35 weeks a surface layer of corrosion products was seen; however, in some places this was disrupted, leaving the superficial amalgam free. This layer of cor-

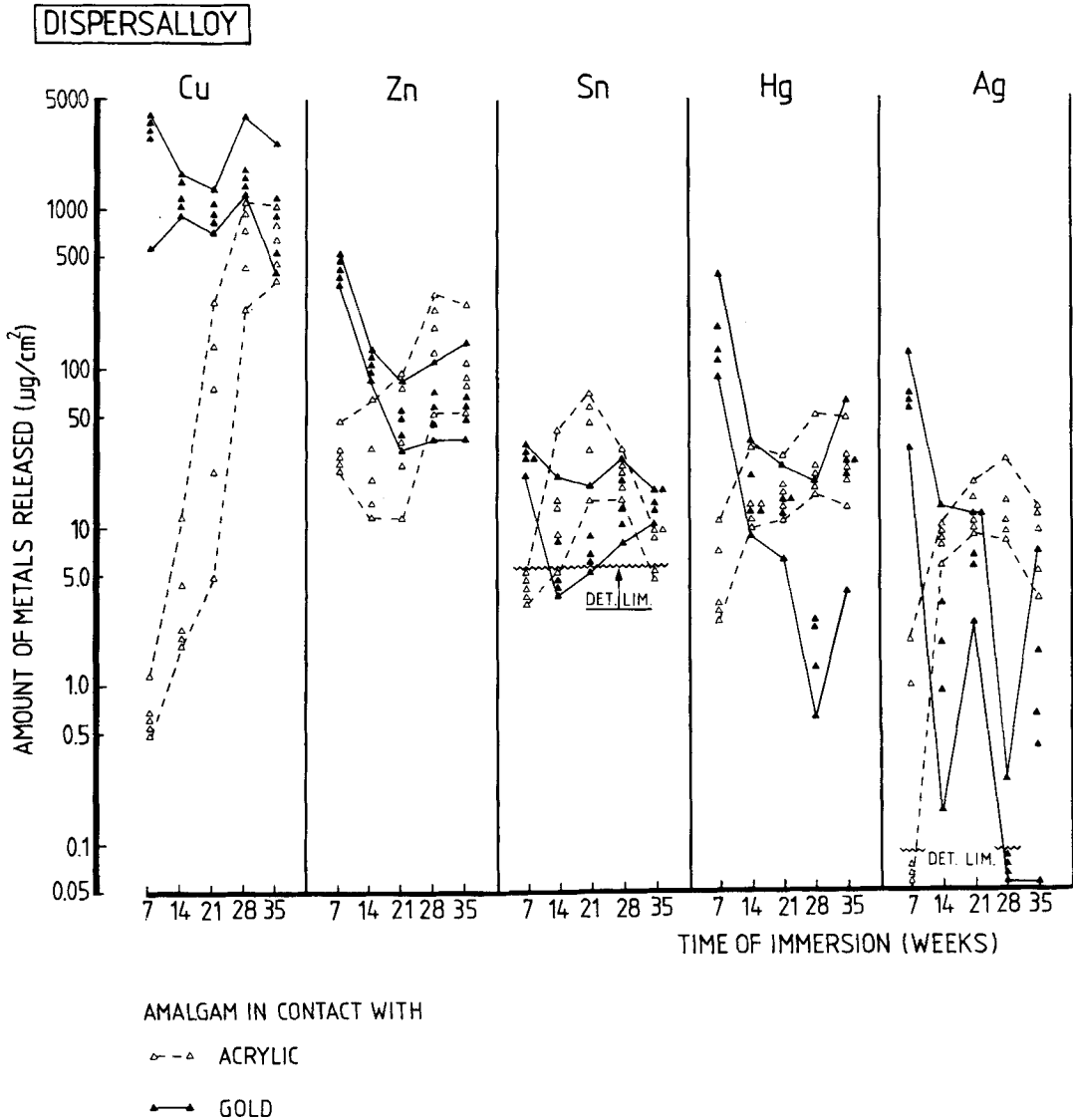


Fig. 1b. Amount of metals released from Dispersalloy into the saline solution after 7, 14, 21, 28, and 35 weeks in contact with acrylic (Δ) and type III gold alloy (\blacktriangle). Five specimens of each group are presented, and the range is marked with lines. DET. LIM. = detection limit.

rosion products contained high concentrations of Sn and Cl. Just below the surface a region rich in Sn and Cl was formed (Fig. 2e). At the amalgam surface above such a region cracks were sometimes seen. Similar regions, but smaller in size, were also seen deeper in the amalgam. There was less chlor-

ide in the corroded region near the surface than deeper in the amalgam. The amalgam, between the surface and the Sn-Cl-rich sub-surface region, showed heavy grain-boundary corrosion and an increased content of β_1 phase ($\text{Ag}_{4.5}\text{Hg}_4$), whereas the γ_1 phase was almost negligible. Deeper in the amalgam

ANA 2000

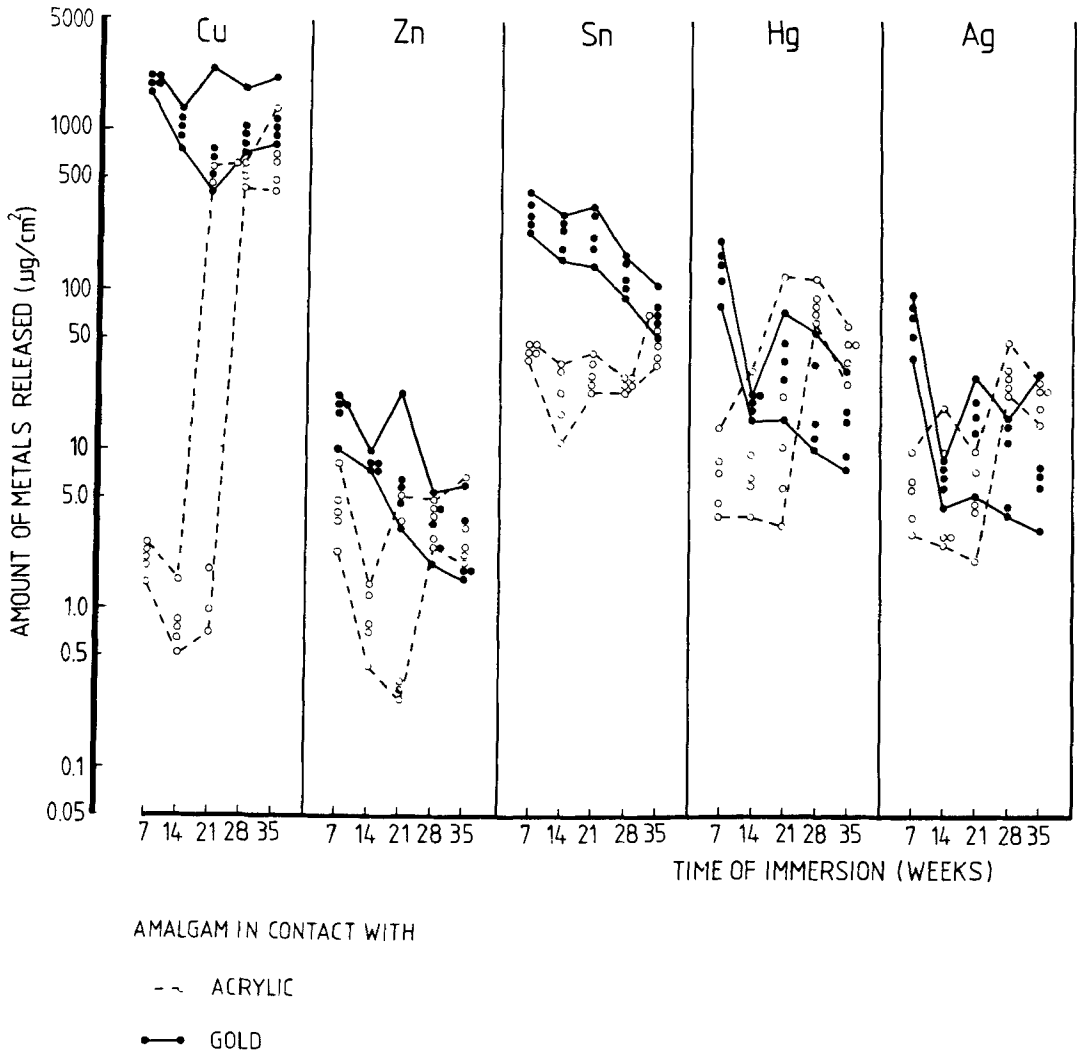


Fig. 1c. Amount of metals released from ANA 2000 into the saline solution after 7, 14, 21, 28, and 35 weeks in contact with acrylic (○) and type III gold alloy (●). Five specimens of each group are presented, and the range is marked with lines.

the grain boundaries of the γ_1 phase were heavily attacked by corrosion.

Tin dominated the metals released from ANA 68. When placed in acrylic plates, the Cu, Hg, and Ag release rate into the solutions was greatly increased during the experiment, whereas the release of Zn and Sn was steadier (Fig. 1a).

High copper, blended alloy, amalgam (Dispersalloy) mounted in acrylic plates

Figs. 3a and b show the amalgam before corrosion in the saline solution. After 7 weeks (Fig. 3c) pitting corrosion attacked the Ag-Cu-eutectic particles and the reaction zone surrounding the eutecticum and the

Table 2. The amounts of metals released from the amalgams after immersion in the solutions for 7 weeks and 35 weeks placed in acrylic plates and for 35 weeks placed in gold alloy plates (the amounts after 35 weeks are accumulated values from measurements every 7 weeks). The corrosion depth range observed in cross-sections is also presented

	Amount of metals released ($\mu\text{g}/\text{cm}^2$)					Total amount released ($\mu\text{mol}/\text{cm}^2$)	Corrosion depth (μm), range
	Cu	Zn	Sn	Hg	Ag		
ANA 68							
7 weeks	0.5	7.0	70	1.9	1.5	0.7	10-200
35 weeks	320	22	555	148	94	11.7	40-200
35 weeks, in contact with gold	2641	79	2701	1650	581	79.1	40-600
Dispersalloy							
7 weeks	0.7	32	1.7	5.5	0.6	0.5	10-180
35 weeks	1604	419	97	97	46	33.4	60-240
35 weeks, in contact with gold	10624	793	101	160	53	181	60-500
ANA 2000							
7 weeks	2.1	4.6	47	7.6	5.7	0.6	10-200
35 weeks	1495	14	177	179	80	26.9	40-240
35 weeks, in contact with gold	5627	94	921	291	115	100	40-550

grain boundaries of the γ_1 phase at the surface of the amalgam. Corrosion initially occurred in small spots, especially in irregularities such as voids and cracks. Sn and Cl were accumulated on the γ_1 phase. Cross-sections (Fig. 3d) showed corrosion from the surface along the grain boundaries of the γ_1 phase. Corrosion of the Ag-Cu particles and the reaction zone had a particularly uneven peripheral contour. Analysis of corroded areas in the reaction zone showed Sn and Cl, and γ_1 rods were also detected. The γ particles were attacked within the grains, and large voids in the matrix contained Sn and Cl.

Amalgams immersed for 35 weeks (Fig. 3e) showed heavier subsurface corrosion, which also propagated deeper into the amalgam than after 7 weeks. Corrosion along the grain boundaries of the γ_1 phase was still more pronounced. As in ANA 68, γ_1 transformed to β_1 near the surface.

Cu dominated the metals released into the solutions. As with ANA 68, the release rate of Cu, Hg, and Ag increased during the experiment (Fig. 1b).

High copper, single composition alloy, amalgam (ANA 2000) mounted in acrylic plates

Figs. 4a and b show the amalgam before corrosion in the saline solution. After 7 weeks in the saline solution corrosion products containing Sn and Cl located especially in connection with the γ_1 phase were seen at the surface (Fig. 4c). Fissures were formed in the phase boundaries between the γ_1 phase and the η' (Cu_6Sn_5) phase. Cross-sections of the specimen showed corrosion attack from the surface into the amalgam specimen mainly associated with the η' phase and the γ_1 grain boundaries (Fig. 4d).

After 35 weeks in the solution large areas of the η' phase and γ_1 phase boundaries were corroded (Fig. 4e). Grain boundary corrosion of the γ_1 grains was also seen. Close to the surface a region similar to the one seen in ANA 68 was observed, rich in Sn and Cl. The amalgam close to the surface was mainly transformed to β_1 , whereas the deeper amalgam was relatively unchanged.

The metals released into the solution were dominated by Cu and Sn. Cu, Hg, and Ag release rate increased with time during the 35 weeks.

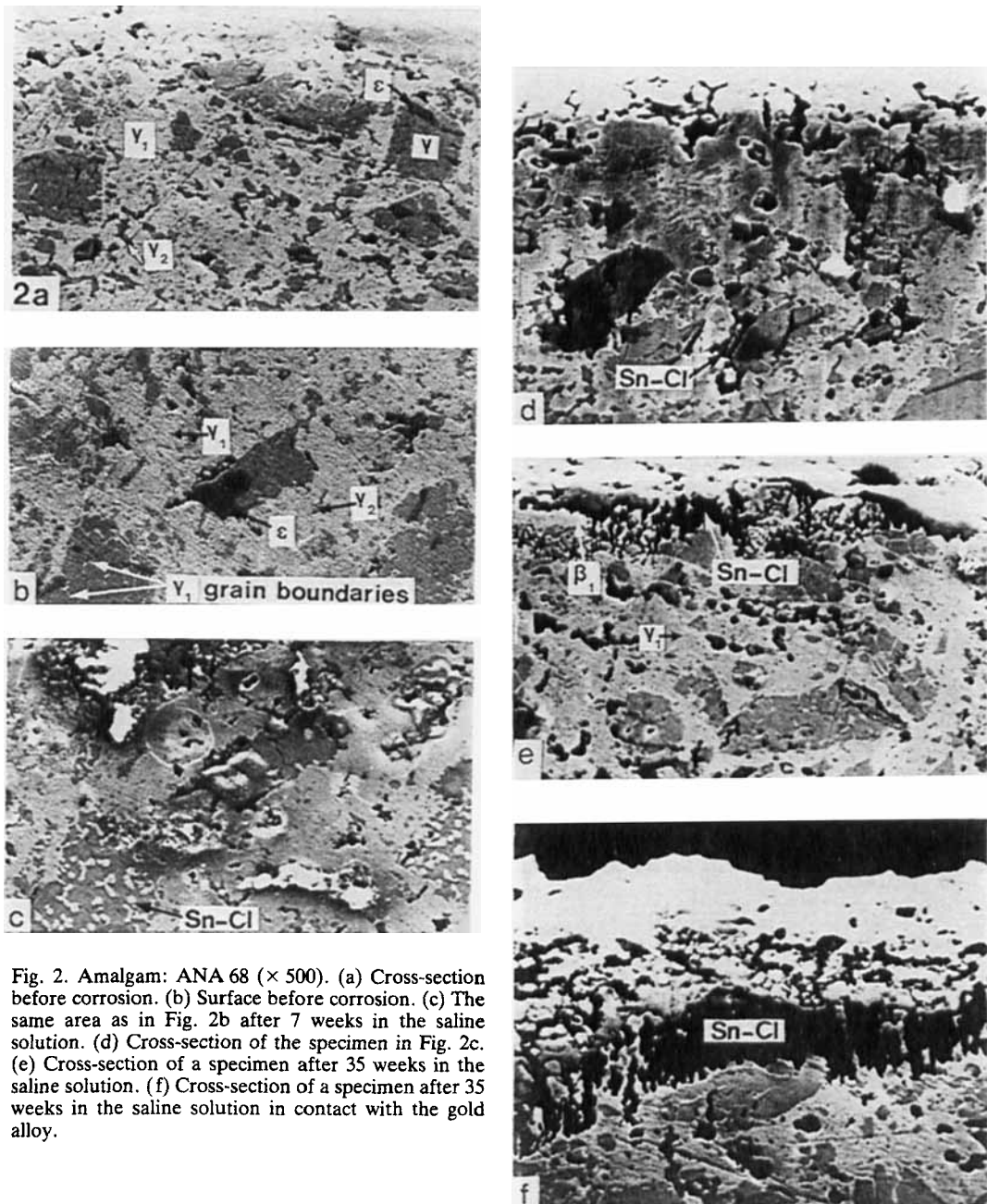


Fig. 2. Amalgam: ANA 68 ($\times 500$). (a) Cross-section before corrosion. (b) Surface before corrosion. (c) The same area as in Fig. 2b after 7 weeks in the saline solution. (d) Cross-section of the specimen in Fig. 2c. (e) Cross-section of a specimen after 35 weeks in the saline solution. (f) Cross-section of a specimen after 35 weeks in the saline solution in contact with the gold alloy.

The amalgams mounted in type III gold alloy plates

The microstructure of amalgams combined with the gold alloy (Figs. 2f, 3f, 4f) showed a more pronounced destruction of the γ_2 , η' , and ϵ phases, the Ag-Cu-eutectic,

γ_1 grain boundaries, and voids. The β_1 phase was more prominent. The corrosion attack also occurred deeper in the amalgams.

The release of metals from the amalgams into the solutions was high as compared with the amalgams not in contact with the gold

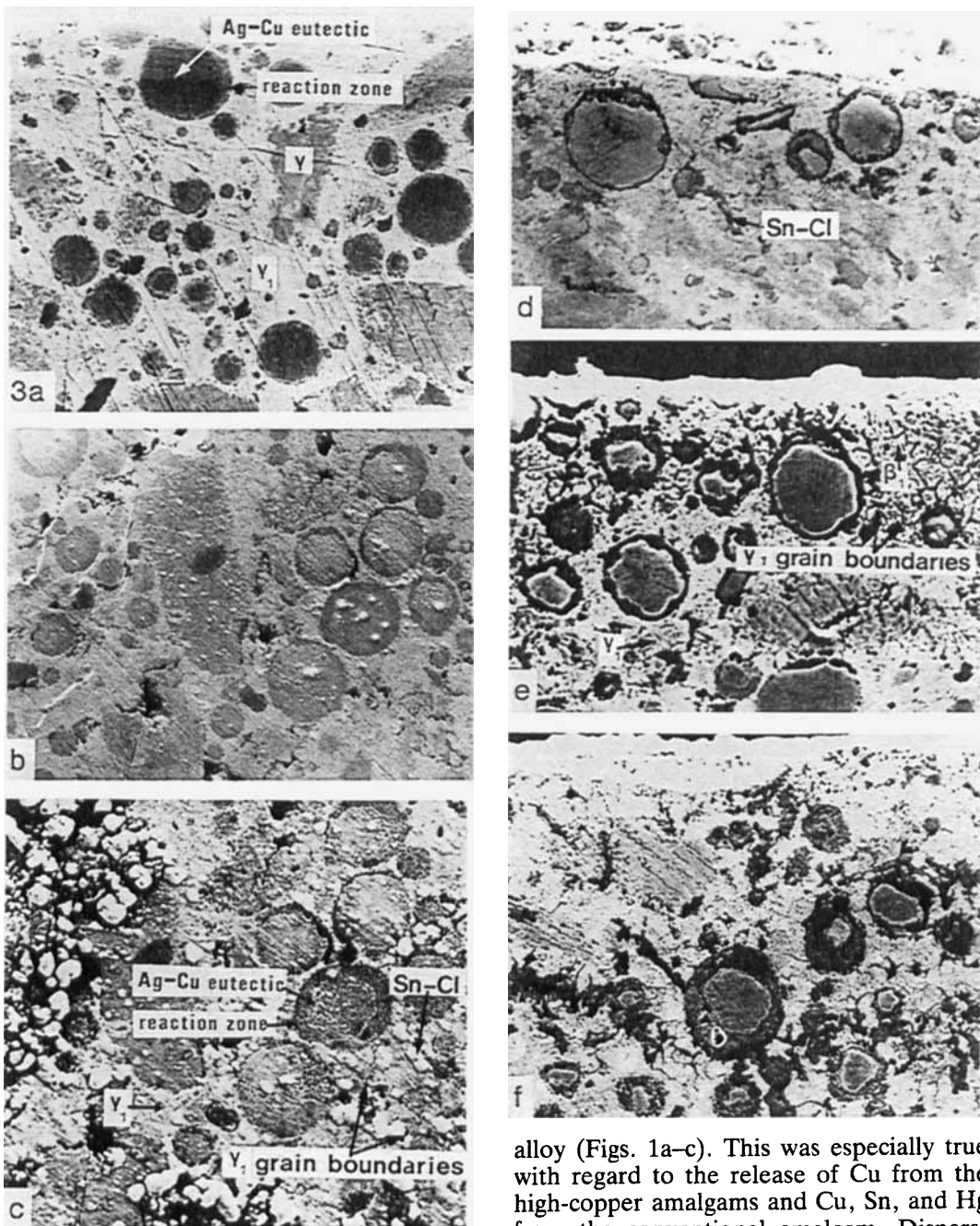
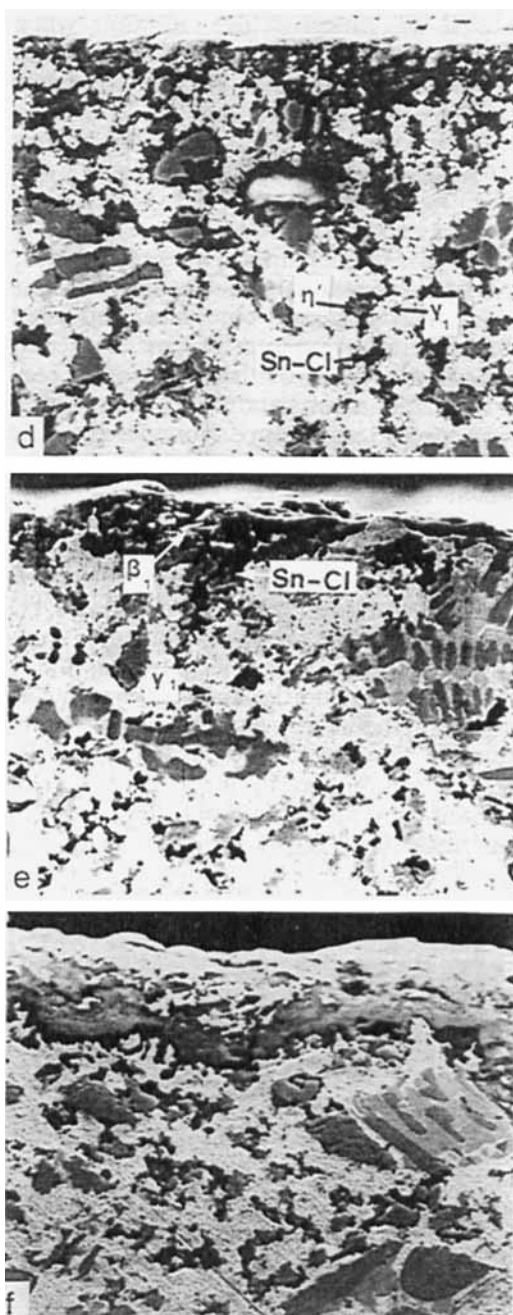
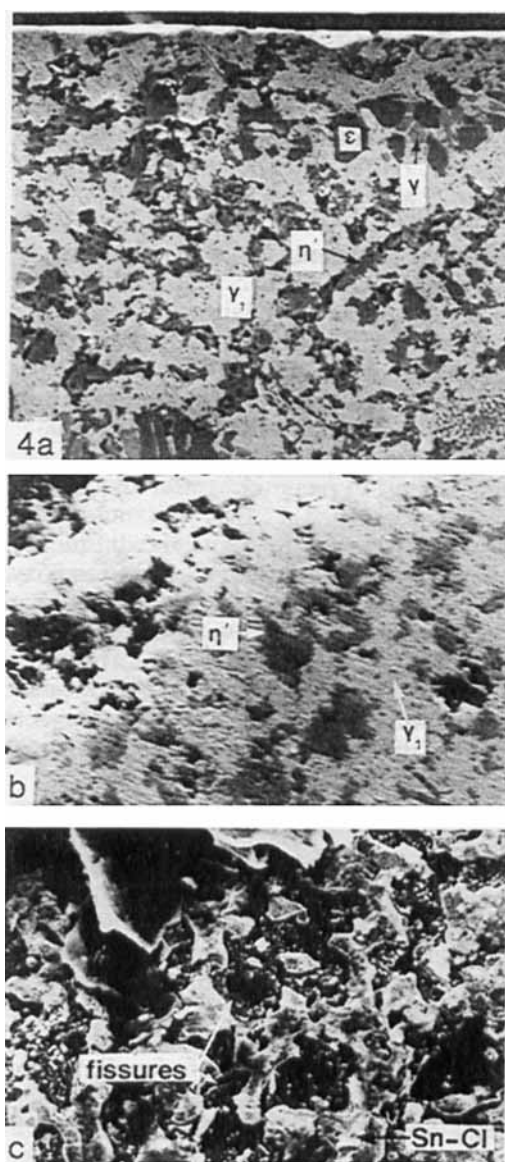


Fig. 3. Amalgam: Dispersalloy ($\times 500$). (a) Cross-section before corrosion. (b) Surface before corrosion. (c) The same area as in Fig. 3b after 7 weeks in the saline solution. (d) Cross-section of a specimen in Fig. 3c. (e) Cross-section of a specimen after 35 weeks in the saline solution. (f) Cross-section of a specimen after 35 weeks in the saline solution in contact with the gold alloy.

alloy (Figs. 1a-c). This was especially true with regard to the release of Cu from the high-copper amalgams and Cu, Sn, and Hg from the conventional amalgam. Dispersalloy released a larger amount of elements than ANA 68 and ANA 2000.

Expansion of the amalgam during corrosion

The formation of tin compounds,



especially in conventional amalgam, was associated with expansion. At regions with pronounced subsurface corrosion the amalgam surface was raised and often cracked. When ANA 68 was in contact with the gold alloy the expansion was more pronounced near the contact area and made the amalgam plugs stick harder to the gold plate. The diameter of the ANA 68 plugs near the contact area showed an increase of

Fig. 4. Amalgam: ANA 2000 ($\times 500$). (a) Cross-section before corrosion. (b) Surface before corrosion. (c) The same area as in Fig. 4b after 7 weeks in the saline solution. (d) Cross-section of the specimen in Fig. 4c. (e) Cross-section of a specimen after 35 weeks in the saline solution. (f) Cross-section of a specimen after 35 weeks in the saline solution in contact with the gold alloy.

$1.5 \pm 0.8\%$ (mean \pm SD; $n = 30$) when measured under a microscope (Leitz Wetzlar 17814-810R, Ernst Leitz GmbH, Wetzlar, FRG). No measurable change ($< 0.4\%$; $n = 30$) in diameter was found with Dispersalloy and ANA 2000.

Amalgam restorations

Some restorations showed almost no corrosion at all, whereas others were attacked throughout the whole restoration. In the latter case corrosion of the γ_2 phase in conventional amalgams and the η' phase in the high-copper amalgams dominated. The attack on the grain and phase boundaries was not as pronounced as in the *in vitro* study. Between the amalgam surface and the cavity wall a region rich in Sn and Cl was found. The boundary between this region and the amalgam underneath showed the same uneven contour as in the *in vitro* study (Fig. 5). The chloride concentration in corroded areas inside the amalgam was not as high as in the *in vitro* study. As in the saline solution, however, the chloride concentration was higher in the corroded areas located deep in the amalgam than near the surface.

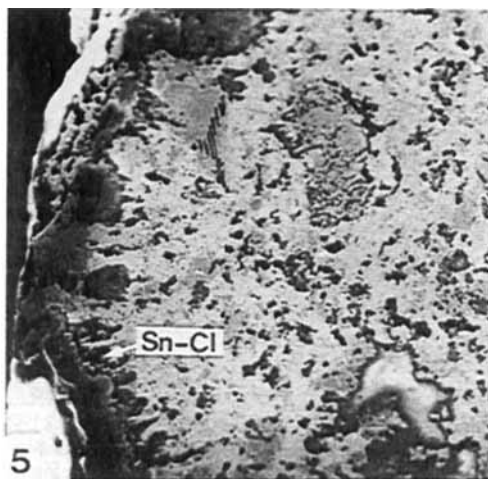


Fig. 5. Cross-section of a restoration made of conventional amalgam. To the left the amalgam surface earlier in contact with the cavity wall ($\times 500$).

Discussion

The results show that a passive layer preventing corrosion is not formed at the amalgam surface after exposure to a 0.9% NaCl solution buffered with $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ (8.8/1.2 mM).

The amounts of corrosion products increased exponentially with the corrosion depth. This was probably partly due to the grain and phase boundary corrosion, which increased with time in the corroded part of the amalgams and enlarged the area exposed to corrosion. The diffusion of elements out of and the diffusion of Cl^- into the amalgams were probably facilitated. In other solutions the corrosion may be different. Several mechanisms such as the inter- and trans-crystalline atomic diffusion, the diffusion of the surrounding solution, chlorides, and oxygen into the amalgam, and the formation of corrosion products with different solubilities will influence the corrosion products formed on and inside the amalgams. In ANA 68 mainly tin compounds were formed, which did not diffuse to the surface as easily as the copper in Dispersalloy and ANA 2000.

The initial deposition of corrosion products on the γ_1 phase has previously been demonstrated (13). It was analyzed and found to contain mainly tin-chloride. The main products in subsequent corrosion layers has been shown to contain tin or copper compounds (14, 15). Small amounts of Hg and Ag have also been found in the corrosion product layer after corrosion in a NaCl solution (16, 17). Brune (16) found the mercury release from a conventional amalgam and Dispersalloy in artificial saliva to be about $1.5 \mu\text{g}/\text{cm}^2$ after 4 weeks, which was within the range for ANA 68 and somewhat lower than for Dispersalloy after 7 weeks in the present study. However, this was without removing the precipitations from the surface.

With the conventional amalgam the surface corrosion started in the γ_2 phase and with the high Cu amalgams at the phase boundaries between the γ_1 phase and the ϵ and η' phases. In cross-sections corrosion of the γ_1 grain boundaries was seen. Grain boundary corrosion in ANA 68 may be explained by the boundaries containing a γ_2

phase (18). During setting of the amalgam Ag, Cu, and Sn diffuse into the Hg. At the grain boundaries of the γ_1 phase of Dispersalloy and ANA 2000 the corrosion-prone Cu-Sn phase could be precipitated.

Formation of the heavily corroded area in the matrix below the amalgam surface may start by degradation of the γ_2 phase in ANA 68 and the Cu_6Sn_5 phase in ANA 2000. Grain boundary corrosion of the γ phase above this area could contribute to β_1 transformation by Ag liberation. The γ phase almost disappeared in this area, and large irregular voids and broad corroded grain boundaries were frequent. Sn from the γ phase may diffuse towards the voids and corroded γ_2 phase to form oxygen and chloride compounds.

In all the alloys the γ phase fraction decreased while the Ag-Hg phases increased, with β_1 as the final stable phase. In ANA 68 corrosion of the γ_2 phase contributed to decreasing the γ content. In Dispersalloy the Ag phase in the Ag-Cu-eutecticum was suggested as a possible Ag source contributing to γ_1 - β_1 transformation (7).

Expansion of the conventional amalgam was pronounced, especially in contact with the gold alloy. Clinically, expansion increases the risk for tooth fracture and could also be an explanation for cracks in gold crowns built on amalgam restorations (19). Amalgams with a high copper content have been shown to resist marginal breakdown better than conventional amalgams (20, 21), probably due to the absence of the γ_2 phase. However, the release of corrosion products from high copper amalgams may contribute to pulpal damage (22).

The varying appearance of the microstructure of corroded amalgam restorations is in agreement with earlier investigations (9, 23). The microstructure of the corroded amalgams had an appearance similar to that found in amalgams corroded in vitro. However, the difference in chloride concentration inside the amalgams when they had been immersed in the 0.9% NaCl solution and had been situated in vivo probably depended on the concentration of Cl^- in saliva being lower than that in the saline

solution (about 1:6). This could also explain the more pronounced grain and phase boundary corrosion in the amalgam specimens.

In the present study a stagnant saline solution has been used to study the nature of corrosion over an extended period of time. In the oral cavity the situation is more complicated, since an interplay of corrosive and inhibiting agents and masticatory forces are active. This kind of in vitro study does, however, give an indication of the corrosion products released from the amalgam surface in relation to changes in the microstructure of the amalgam. The same type of study with other solutions is needed to gain additional information.

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References

1. Söremark R, Wing K, Olsson K, Golding J. Penetration of metallic ions from restorations into teeth. *J Prosthet Dent* 1968;20:531-40.
2. Möller B. Reaction of the human dental pulp to silver amalgam restorations. Mercury determination in the pulp by flameless atomic absorption spectrophotometry. *Swed Dent J* 1978;2:93-7.
3. Frykholm KO. Mercury from dental amalgam. Its toxic and allergic effects and some comments on occupational hygiene. *Acta Odontol Scand* 1957;15 (suppl 22).
4. Catsakis LH, Sulica VI. Allergy to silver amalgams. *Oral Surg* 1978;46:371-5.
5. Banoczy J, Roed-Petersen B, Pindborg JJ, Inovay J. Clinical and histologic studies on electrogalvanically induced oral white lesions. *Oral Surg* 1979;48:319-23.
6. Lundström IMC. Allergy and corrosion of dental materials in patients with oral lichen planus. *Int J Oral Surg* 1984;13:16-24.
7. Lin J-HC, Marshall GW, Marshall SJ. Microstructures of Cu-rich amalgams after corrosion. *J Dent Res* 1983;62(2):112-5.
8. Holland GA, Asgar K. Some effects on the phases of amalgam induced by corrosion. *J Dent Res* 1974;53:1245-4.
9. Marshall GW, Jackson BL, Marshall SJ. Copper-rich and conventional restorations after clinical use. *J Am Dent Assoc* 1980;100:43-7.

10. Moberg L-E. Long-term corrosion studies in vitro of amalgams and casting alloys in contact. *Acta Odontol Scand* 1985;43:163-77.
11. American Dental Association. Amalgam and mercury. In: Guide to dental materials and devices. 8th ed. Chicago: American Dental Association, 1976-1978:58-73.
12. Hansen M. Constitution of binary alloys. 2nd ed. New York: McGraw-Hill Book Co., 1958.
13. Katan T, Ryge G. Corrosion penetration in crevices of dental amalgam. *J Electrochem Soc* 1979; 126:903-8.
14. Marshall SJ, Lin JH, Marshall GW Jr. Cu_2O and $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ corrosion products on copper rich dental amalgams. *J Biomed Mater Res* 1982;16:81-5.
15. Sarkar NK, Marshall GW, Moser JB, Greener EH. In vivo and in vitro corrosion products of dental amalgam. *J Dent Res* 1975;54:1031-8.
16. Brune D. Corrosion of amalgams. *Scand J Dent Res* 1981;89:506-14.
17. Do Duc H, Tissot P, Meyer JM. Potential sweep and intensiostatic pulse studies of Sn, Sn_8Hg and dental amalgam in chloride solution. *J Dent Res* 1979;58:576-83.
18. Gjerdet NR, Espevik S. Corrosion and creep of dental amalgam. *J Dent Res* 1978;57:21-6.
19. Tullberg M, Odén A. Cracks in gold crowns built on amalgam restorations. *Acta Odontol Scand* 1985; 43:15-7.
20. Mahler DB, Terkla LG, Van Eysden J. Marginal fracture of amalgam restorations. *J Dent Res* 1973;52:823-7.
21. Rydinge E, Goldberg J, Sanchez L, Lambert K, Munster E. Clinical evaluation of high copper amalgam restorations. *J Oral Rehabil* 1981;8:465-72.
22. Mjör IA, Eriksen HM, Haugen E, Skogedal O. Biologic assessment of copper-containing amalgams. *Int Dent J* 1977;27:333-40.
23. McTigue D, Brice C, Nanda CR, Sarkar NK. The in vivo corrosion of Dispersalloy. *J Oral Rehabil* 1984;11:351-9.

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