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Corrosion of gallium alloys *in vivo*

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The aim of this work was to study the corrosion of gallium alloys *in vivo*. Three gallium alloys were tested: GF alloy, Galloy and an experimental GaIn alloy. An amalgam was applied as a control. After ageing for a minimum of two weeks, one disc of each of these alloys was mounted with the polished side up in the buccal surfaces of 17 acrylic dentures. Eight sets of the specimens were retrieved after exposure to the oral cavity for 2–4 months, and another seven were retrieved after 6–9 months. Corrosion of the polished cross-sections of the specimens was studied using scanning electron microscopy (SEM). Only the $CuGa_2$ phase was found to corrode substantially in all three of the alloys investigated, leaving behind holes up to 20 μm deep. This is consistent with the corrosion reported after immersion tests in a solution of 0.1 mol lactic acid and 0.1 mol NaCl for 7 days. Such *in vitro* tests are also reported to cause distinct corrosion of the Sn phase in the gallium alloys. However, a salient feature of the corrosion *in vivo* was the lack of detectable dissolution of this phase. Thus, for gallium alloys, the accelerated *in vitro* immersion method produced results which did not agree with clinical observations. Large variations in the corrosion of the $CuGa_2$ were observed from patient to patient. The amount of corrosion on the Galloy specimens appeared to be less and on a finer scale than on specimens of the two other alloys. The depth of corrosion was thus shallower than for this alloy. This finding indicates that there is room for further improvement of the corrosion resistance by modifying the microstructures. Less overall corrosion was found for the amalgam control than for the gallium alloys.

1. Introduction

The application of gallium alloys as a filling material and an alternative to amalgam has received increased attention in recent years [1, 2]. Two gallium alloys have appeared on the market; one of them has been approved by the Japanese government for clinical use. The strength properties of both commercial and experimental gallium alloys have been reported to be comparable to those of amalgam [1, 3]. However, concern has been expressed regarding their biocompatibility [4, 5] and corrosion resistance. Accelerated immersion tests in saline (0.9% NaCl) or solutions of 0.1 mol/l lactic acid + 0.1 mol/l NaCl at a pH of 2.5 have indicated substantial dissolution of the Sn phase in particular, and to some extent, also of the $CuGa_2$ phase of gallium alloys [6–8]. Correlation of the corrosion found *in vitro* with that occurring in the oral cavity has not been reported so far. The aim of the present work was to study the corrosion of gallium alloys *in vivo* and to compare the corrosion occurring under such conditions with that of amalgam.

2. Materials and methods

The four alloys used in this study are presented in Table I. Three of them were commercial products, and their chemical compositions are listed according to the information from the manufacturers. Three of the alloys were gallium-based on the fourth was an alloy for amalgam (GC Lumi Alloy, GC Corp., Tokyo, Japan) which was used for comparison. The two commercial gallium alloys were Gallium Alloy GF (Tokuriki Honten Co., Ltd., Tokyo, Japan; GF) and Galloy (Southern Dental Industries, Bayswater, Victoria, Australia). The microstructures of these two commercial alloys have been previously reported [2]. The third gallium alloy was an experimental alloy in which the powder consisted of 49% Ag and 51% Cu (m/m), and the gallium liquid was alloyed with 24.5% In (m/m); this alloy will be designated as "GaIn". Mixing ratios (powder/liquid) for both GF and GaIn were 1.0/0.65, 1.0/0.49 for Galloy, and 1.0/0.83 (m/m) for Lumi Alloy.

Cylindrical specimens (4.0 mm diameter, 8 mm high) were produced according to the procedures described in ISO 1559:1995, Alloys for dental amalgam.

After ageing for 7 days, 17 discs (4 mm diameter, 1 mm thick) were cut from the cylindrical specimens for each alloy. One of the two flat surfaces was metallographically polished, except for the GaIn alloy, which was ground using FEPA P1200 grit.

TABLE I Composition of alloys

Name of alloy	Composition of powder (wt %)							Composition of liquid (wt %)				
	Ag	Sn	Cu	Pd	Pt	Zn	Ge	Ga	In	Sn	Bi	Hg
GF	50	25.7	15.0	9.0	–	0.3	–	65	19	16	–	–
Gallaoy	60.1	28.5	11.8	–	0.05	–	–	62	25	13	0.05	–
GaIn*	49	–	51	–	–	–	–	75.5	24.5	–	–	–
LumiAlloy	56	28.8	15.0	–	–	–	0.2	–	–	–	–	–

*Experimental alloy.

One disc of each of the four alloys was mounted in 17 acrylic dentures with the polished or ground surfaces in the buccal surfaces. The technique used was previously reported by Herø *et al.* [9]. Each specimen was identified by digits on the bottom of the disc.

The patients in the study were recruited from among the patient population at the Faculty of Dentistry, University of Oslo, Norway. They were instructed in dental hygiene procedures, i.e. to clean the dentures with a soft brush in water and to avoid using chemicals. Eight of the specimens were removed from the dentures after 2–4 months, and seven specimens were removed after 6–9 months. The specimens from two patients were lost.

The exposed surfaces of the specimens were observed in a light optical microscope before they were cut perpendicular to the exposed surface and embedded in epoxy. The exposed cross-sections were then metallographically ground and polished following standard metallographic procedures. The degree of deterioration from corrosion in the areas near the exposed surface and also on the bottom surface of the specimens was studied in cross-section using a scanning electron microscope (SEM) (Philips XL 30, Eindhoven, The Netherlands) and energy dispersive spectroscopy (EDS) (Philips DX-4, Eindhoven, The Netherlands).

3. Results

There was generally little difference observed with regard to the corrosion of the 2–4 month specimens versus the 6–9 month specimens. However, substantial differences were found among individual patients. An SEM micrograph showing a cross-section of the GF alloy (Fig. 1) displays distinct deterioration of the $CuGa_2$ phase located near the surface after 3 months. The $CuGa_2$ phase appears as a dark reaction layer around the unconsumed alloy particles. It should be noted that this specimen was retrieved from the denture of a patient (A) who was a heavy smoker. Attempts were made to analyse the composition of this phase in the area immediately below the corroded surface, but no reliable indication of the selective dissolution of either Cu or Ga could be detected. Furthermore, no deterioration of the Sn-rich phase or of other phases could be observed. Both the Sn-rich and the Ag_9In_4 phases have a similar, white appearance in the SEM micrographs and cannot be distinguished in the present micrographs. A similar micrograph of the same alloy placed in another patient (B) after 9 months is shown in Fig. 2. Note that in this case, there is less corrosion of the $CuGa_2$ phase, and no detectable corrosion of the other phases is seen.

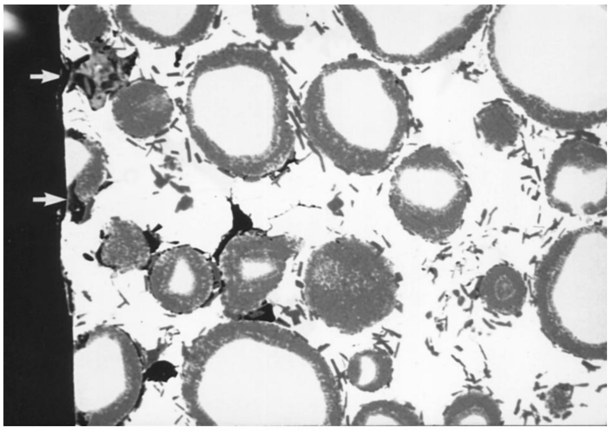

Figure 1 SEM micrograph of a cross-section of the GF alloy after 3 months in the oral cavity (patient A). Substantial corrosion shown of the dark $CuGa_2$ phase (white arrows). Mix of secondary and back-scattered electrons. Magnification 1000×.

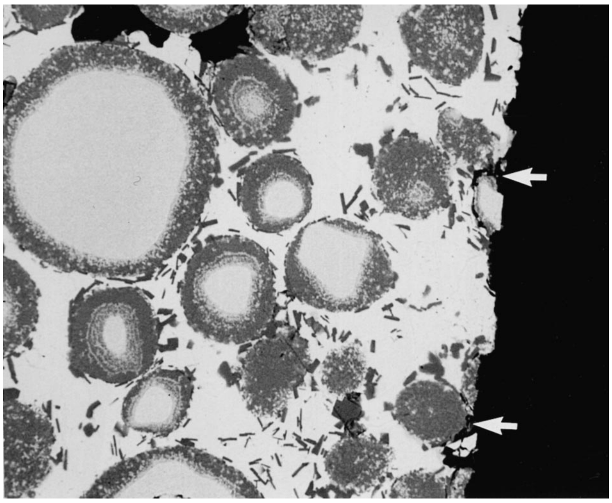

Figure 2 SEM micrograph of a cross-section of the same alloy shown in Fig. 1 after 9 months in oral cavity (patient B). Note the shallower deterioration of the $CuGa_2$ phase for this patient compared with patient A in Fig. 1. Back-scattered electrons. Magnification 1000×.

Similar corrosive attacks on the $CuGa_2$ phase were also found in the experimental GaIn alloy which contained rather large CuGa crystals. Since these crystals were clearly delineated, the deteriorated areas were easily detectable, as can be seen in Fig. 3 (Patient A, 3 months).

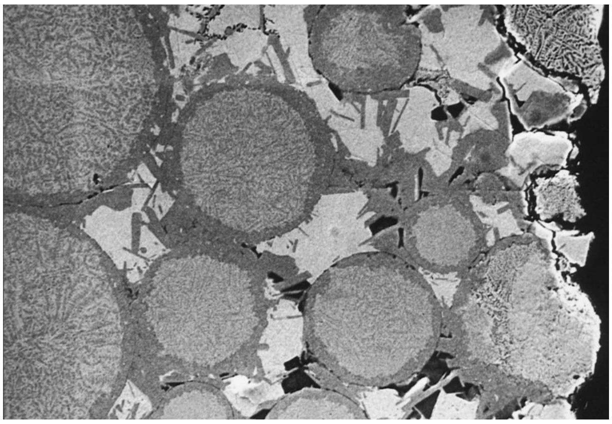

Figure 3 SEM micrograph of a cross-section of the experimental GaIn alloy after 3 months in the oral cavity (patient A). Secondary electrons. Magnification 1000×.

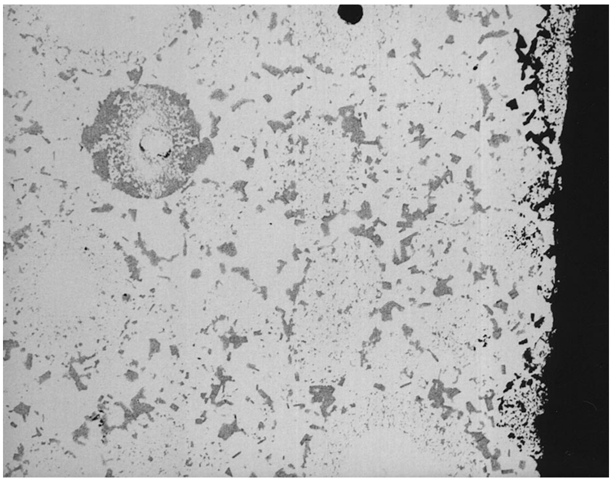

Figure 4 SEM micrograph of a cross-section of Galloy after 3 months in the oral cavity of patient A. Note the many small black holes adjacent to the surface due to the corrosion of the $CuGa_2$ phase. Back-scattered electrons. Magnification 1000×.

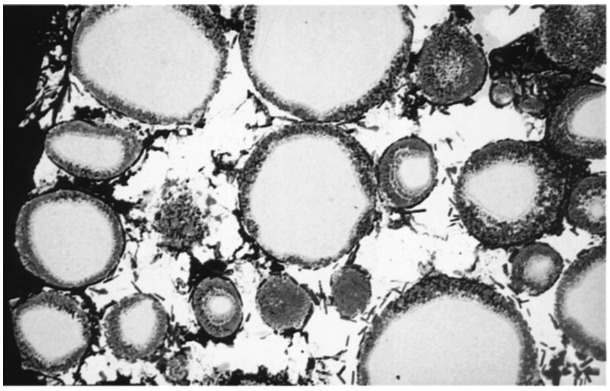

Figure 5 SEM micrograph of a cross-section of the GF alloy from the bottom of the specimen after 9 months in the oral cavity of patient B. Note the severe corrosive attacks compared with those displayed on the surface exposed directly to the oral cavity of the same specimen in Fig. 2. Back-scattered electrons. Magnification 1000×.

In contrast to the two gallium alloys described above, the structure of Galloy was much more fragmented and finely dispersed. The corrosive attacks on this alloy thus appear to be on a finer scale than on the GF or the GaIn alloys (Fig. 4).

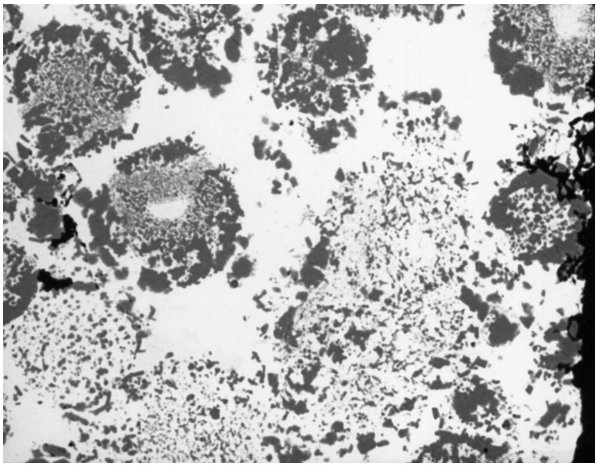

Figure 6 SEM micrograph of a cross-section of the amalgam control after 9 months in the oral cavity of patient B. Some corrosion of the Cu-rich phases in the surface region can be observed. Back-scattered electrons. Magnification 1000×.

In general, for all of the three Ga alloys after either 2–4 months or 6–9 months *in vivo*, it was observed that the $CuGa_2$ phase near the surface was corroded. However, no visible sign of corrosion of the other phases, including the Sn-rich phase, was seen. No substantial difference could be observed between the extent of corrosion after 2–4 months versus 6–9 months. The depth of the corroded area of the *in vivo* exposed surfaces was up to 20 μm.

The $CuGa_2$ phase was observed to corrode more substantially up to a depth of 30 μm on the bottom of the specimens placed in the denture (Fig. 5) compared with the surfaces exposed directly to the oral cavity (Fig. 2).

The amount of corrosion found on the amalgam was generally less than the amount found on the gallium alloys. This is illustrated in Fig. 6 for patient B; some signs of dissolution of the dark Cu-rich phase located near the surface are evident.

4. Discussion

One of the most unexpected observations was the lack of detectable evidence of corrosion of the tin-rich phase in the specimens retrieved from the dentures exposed to saliva in the oral cavity. This is in distinct contrast to the previous findings from immersion tests *in vitro* using saline (0.9% NaCl) [8] or 0.1 mol/l NaCl/lactic acid solutions [7]. In these two previous experiments, the tin-rich phase adjacent to the surface was found to have almost completely dissolved. This illustrates that results from accelerated *in vitro* tests can be substantially different from results gathered under *in vivo* conditions.

While no corrosion could be detected on the tin-rich phase *in vivo*, the $CuGa_2$ phase was found to have deteriorated in all alloys for all patients. The observed *in vivo* corrosion of this phase is thus in agreement with that found *in vitro*. The same applies to the observed corrosion resistance of the other phases of the investigated gallium alloys, except for tin. This element has a higher standard electrode potential

($Sn^{2+} + 2e^{-} = Sn; -0.1375$ V) than gallium ($Ga^{3+} + 3e^{-} = Ga; -0.560$ V) [10]. These data, therefore, indicate higher corrosion resistance for tin than for gallium. However, gallium, unlike tin, is not present as a metal in these alloys, but is found mainly in two intermetallic compounds ($CuGa_2$ and $Ag(Pd)_6Ga$). The corrosive characteristics of a compound can be significantly different from the individual metals of which it is composed. In this case, only the Cu–Ga compound has been found to corrode in the oral cavity.

The components of the structure in Galloy are on a finer scale than for the other two gallium alloys. Thus, the cavities formed by corrosion in the surface region are correspondingly smaller.

In the present study, no determination could be made of a difference in the degradation rate among the gallium alloys investigated, partly due to the scatter in the corrosion found among the various patients. The overall depth of the corroded surface region is approximately the same size after the two trial periods, indicating a decrease in the corrosion rate with time and corrosion depth. The combination of wear and corrosion which frequently occurs in the oral cavity may alter this picture.

It is interesting to note the substantially increased depth of the corrosion on the bottom of the embedded specimens compared with the surfaces exposed directly to the oral cavity. The occurrence of crevice corrosion on the bottom of the specimens is one possible explanation for this observation.

Fewer corrosive attacks were found on the amalgam alloy than on the gallium alloys. This agrees with the overall clinical tendencies that have been reported for GF [11–13].

The present study was performed by embedding specimens on the side wall of the dentures. Therefore, the results may be different if the gallium alloy specimens are placed on the occlusal surfaces where physical surface changes and mechanical deformation of the specimens could occur.

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