Mercury release from dental amalgams into continuously replenished liquids

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Abstract

Objective: Studies have been performed using high- and low-copper amalgams to measure the amounts of mercury dissolution from dental amalgam in liquids such as artificial saliva; however, in most cases, mercury dissolution has been measured under static conditions and as such, may be self-limiting. This study measured the mercury release from low- and high-copper amalgams into flowing aqueous solutions to determine whether the total amounts of dissolution vary under these conditions when tested at neutral and acidic pH.

Methods: High- and low-copper amalgam specimens were prepared and kept for 3 days. They were then longitudinally suspended in dissolution cells with an outlet at the bottom. Deionized water or acidic solution (pH1) was pumped through the cell. Test solutions were collected at several time periods up to 6 days or 1 month and then analyzed with a cold vapor atomic absorption spectrophotometer. After dissolution testing, the specimens were examined using SEM/XEDA for any selective degradation of the phases in the amalgam.

Results: Except for the high-copper amalgam in the pH1 solution, the dissolution rates were found to decrease exponentially with time. The rate for the high-copper amalgam in pH1 solution slowly increased for 1 month. The total amounts ($\mu g/cm^2$) of mercury released over 6 days or 1 month from both types of amalgam in deionized water were not significantly different ($p \geq 0.05$). The high-copper amalgam released significantly more mercury than the low-copper amalgam in the pH1 solution at both time periods. For both amalgams, the dissolution in pH1 was significantly higher than in deionized water.

Significance: Mercury dissolution from amalgam under dynamic conditions is enhanced in an acidic media, and most prominently for a high-copper formulation.
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1. Introduction

Recent advances in chemical analysis and detection technology have permitted scientists to detect a minimal amount of mercury released from dental amalgams. This technological development has attracted considerable attention because of increased public concern about possible health hazards and environmental contamination by mercury. A review of the literature on in vivo and in vitro corrosion of dental amalgams, however, indicated that no major corrosion product in which the main constituent is mercury has been found [1]. Therefore, independent of amalgam composition, mercury liberated in aqueous media is usually freed into solution or re-amalgamated with residual alloy.

A number of investigators have examined the extent to which both mercury in dental amalgams and pure mercury droplets dissolve into water, NaCl solution, and artificial saliva. In vitro studies in human saliva were carried out by investigators such as Frykholm [2], Mayer and Diehl [3], Brune [4] and Brune and Evje [5]. An in vivo study by Ott et al. [6] claims to have detected dissolved mercury. A number of reports have been published on in vitro studies using simulated oral liquids [4,5,7–25]; however, the reported rate of mercury dissolution exhibited a high degree of variability. For instance, the cumulative amount of mercury dissolved from amalgams into artificial salivas ranged from 0.3 to 74 $\mu g/cm^2/day$. There were also conflicting reports as to which type of amalgam (high- or low-copper) released more mercury [3,14,17,18,26–28]. Okabe et al. [24] reported that the amount of mercury dissolved from a single-composition, high-copper amalgam was

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Table 1
Chemical compositions (wt%) of alloys employed in the present study

Alloy[a]	Ag	Sn	Cu	Zn
Dispersalloy	69.6	17.7	11.8	0.67
Velvalloy	70.3	25.9	2.75	0.93

[a] Alloy compositions obtained from de Frietas [39].

greater than from an admixed high- or a low-copper amalgam. The measurement of mercury dissolution from pure mercury also fell within a wide range [24].

Despite differences in the cumulative amounts of mercury released or in which type of amalgam produces greater mercury release, the consensus among investigators seems to be that the dissolution rate decreases sharply with an increase in immersion time [3]. Recent information provided by Marek [29] indicated that the degree of acidity in the artificial saliva used for testing can affect mercury dissolution; pH-independent dissolution occurred in the range of pH 3–8 (0.12–0.16 $\mu g/cm^2$/day for Velvalloy and 0.08–0.17 $\mu g/cm^2$/day for Tytin), and much faster dissolution took place at pH1 (2.29 $\mu g/cm^2$/day for Velvalloy and 2.10 $\mu g/cm^2$/day for Tytin).

Most of the studies carried out so far have been performed under static conditions by immersing amalgam specimens in solutions kept in vials. However, unchanged solutions may self-limit the amount of mercury dissolved. In the actual oral situation or in waste water systems, elemental dissolution rarely occurs under static conditions, since amalgam restorations or waste amalgam particles are, in many cases, covered by constantly moving aqueous media. Thus, the purpose of the present study was to determine how much mercury in dental amalgams dissolves into flowing aqueous solutions. The hypotheses to be tested were that (1) more mercury is released in flowing solutions with a lower pH value; and (2) more mercury will dissolve from a high-copper amalgam than a low-copper amalgam. Although the study was designed to eliminate a build-up in concentration of dissolved species and its effect on the dissolution rate, the objective was to determine the effect of amalgam type and pH of the medium on mercury release and not to compare the release under static and flowing conditions.

2. Materials and methods

2.1. Alloys used

Two types of alloys, a high-copper admixed alloy, Dispersalloy (Johnson and Johnson Inc., Montreal, Canada) and a low-copper alloy, Velvalloy (S.S. White Dental Products International, Philadelphia, PA), were employed (Table 1). The nominal chemical compositions (wt%) of the main constituents of each alloy powder are listed in Table 1. Although low-copper amalgams are no longer routinely used in American dental practices, there is a large amount of data accumulated over the years from various areas of research including the dissolution of mercury. Velvalloy is a good representative of the low-copper alloys. Dispersalloy was chosen because it is a frequently used high-copper amalgam.

2.2. Specimen preparation

Two tablets from each of the alloys tested were used to prepare amalgam specimens with approximately 47% residual mercury for both amalgams. The triturated amalgam was condensed in a steel die at 14 MPa pressure, as required in ANSI/ADA Specification No. 1, to produce specimens measuring 3 mm × 3 mm × 25 mm. Each specimen was stored in air at room temperature for 3 days before dissolution testing.

2.3. Dissolution test

Dynamic dissolution tests were performed in deionized water with a resistivity of 18.2 $M\Omega$·cm (pH, 6.54 ± 0.02) or in a pH 1.0 acidic solution buffered with HNO_3 and KNO_3. The pH1 solution was added to the study because Marek [29] found that the rate of dissolution of mercury from amalgams statically soaked in a synthetic saliva increased three to four times at pH1 compared with neutral pH. The solutions were chosen to determine the effect of pH instead of simulating the chemistry of the oral environment.

Dissolution testing was carried out in a device created exclusively for this purpose (Fig. 1). A peristaltic pump (cassette pump, Monostat, division of Barnant Co., USA) pumped the test solutions into plastic test tubes (95 mm long, 12 mm diameter) containing the amalgam specimens. A hole (2 mm diameter) was bored into a rubber stopper fitted into the open end of each test tube. Fishing line was attached to one end of the specimen and then fixed with glue through the hole in the stopper so that the specimen was suspended in the test tube without touching the walls. Plastic tubing (1/16 in. i.d.) was connected to the hole in the stopper; the other end of the tubing was attached to the peristaltic pump. A 1 gal tank contained the liquid used in the experiment; it was connected to the other end of the pump. Four dissolution cells were hooked up to the pump so that data could be gathered simultaneously from each of the four cells for a particular experimental condition.

Before filling the cell (leaching tube) with solution, the bottom outlet of the tube was closed with laboratory film (Parafilm M; American National Can, Chicago, IL). Each cell was then filled with the test solution to 70% capacity and closed with the rubber stopper containing the plastic tubing. The specimen was suspended in the cell, as described earlier, and the stopper tightly sealed using inlay casting wax (Blue Inlay Casting Wax; Kerr Corp., Romulus, MI). The pressure of the air column maintained a constant airspace above the solution in the cell, which
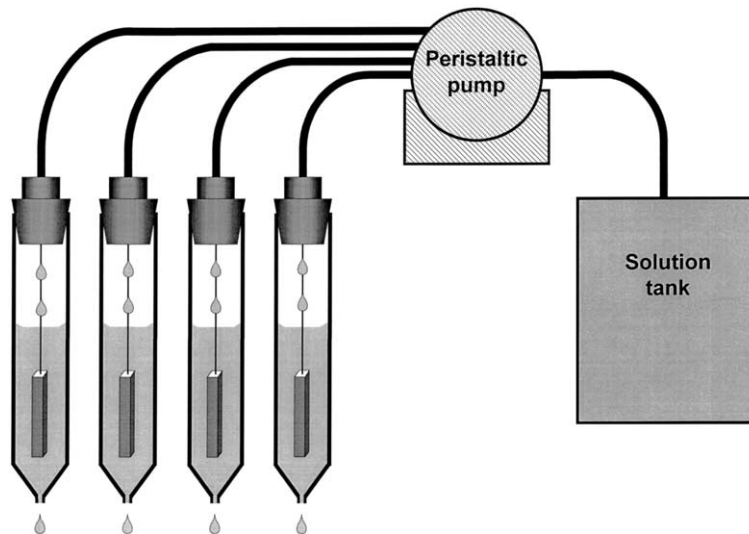
Fig. 1. Diagram of set-up testing dynamic dissolution of mercury from dental amalgam.

resulted in a continuous fluid flow out of the cell throughout the experiment.

The parafilm at the bottom of the cell was then removed, and the pump was turned on to initiate the flow of solution at a rate of 0.3 ml/min. The first sample collection was made 90 min later. The solution dripped into a glass container holding 1.5 ml HNO$_3$ in order to prevent the adsorption of mercury ions onto the vial wall while storing the test solution before chemical analysis. Over a 50 min period, 15 ml of solution was collected in the container. The container with a total volume of 16.5 ml of acidified sample solution was then tightly sealed until the mercury in the solution was measured.

Each experiment was first performed at room temperature (22 ± 0.5 °C) over a 6 day period and then repeated for a 1 month period. The 1 month experiment was performed in order to observe any changes occurring during a longer immersion period that might be overlooked in a short immersion period. The test solution was sampled at 90 min, 3, 4.5 h, and then once a day up to 6 days. For the 1 month experiment, the test solution was sampled first at 1 day (24 h) from the initiation of the experimental conditions and then at 3 (72 h), 7 (168 h), 14 (336 h), 21 (504 h), and 30 (720 h) days. The concentration of mercury in each sampled solution was determined with the cold vapor atomic absorption technique (Varian AA20 Atomic Absorption Spectrometer with VGA-76 Vapor Generator, Australia). These analytical techniques using the atomic absorption spectrophotometer were established earlier in our laboratory [19,24]. The experiment was repeated three to four times for each experimental condition.

The results for the test and wash solutions were combined to reflect the total metal ion release for each condition. The mean of the dissolution rate of mercury ions (μg/cm^2/h) for each sampling period was calculated and plotted in terms of the time period. For each experimental condition, the best

fitting method with SigmaPlot software was employed to establish a satisfactory curve. The total amount of mercury dissolved (μg/cm^2) during each experimental condition for each alloy was calculated with the integration of each curve. Three-way analysis of variance (ANOVA) was performed to compare the total amount of Hg released from the amalgams evaluated according to the alloy, time period, and solution type. There were significant differences ($p < 0.001$) among amalgams tested, as well as significant differences among time periods and solution types ($p < 0.001$). In addition, there was a significant difference among the amalgams according to the time and solution used (interaction) ($p < 0.001$). To further investigate this three-way interaction, one-way analysis of variance (ANOVA) was performed to evaluate the relationship between Hg released from each amalgam type (Dispersalloy and Velvalloy) and pH1 and DI solution at each time period (6 days and 1 month). In addition, Student–Newman–Keuls tests of multiple comparisons were conducted at $a = 0.05$ to compare the amalgams.

After the dissolution test, the exterior surfaces and the cross-sections of the specimens ($n = 2$) for each experimental condition were examined with scanning electron microscopy.

3. Results

Sets of the plots for the mean dissolution rate vs. time for the two amalgams, Dispersalloy and Velvalloy, are shown in Figs. 2–5: the results found in deionized water for 6 days (Fig. 2) and 1 month (Fig. 3); and the results found in pH1 solution for 6 days (Fig. 4) and 1 month (Fig. 5). For each amalgam, the total amounts of mercury dissolved for different time periods in different test mediums are shown in Fig. 6. These values were obtained by
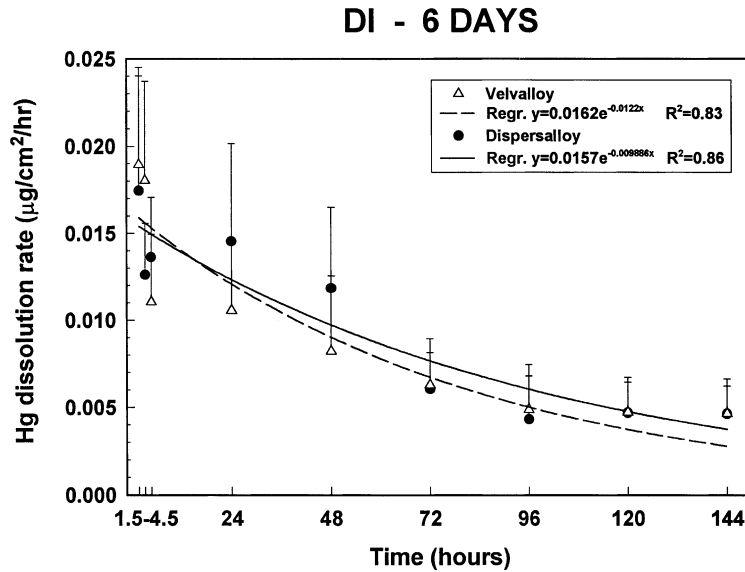
DI - 6 DAYS

Fig. 2. Mercury dissolution rate vs. time in deionized water over 6 days.

integrating the most probable curve estimated from the dissolution rate vs. time plots for each experiment. As shown in Figs. 2 and 3, there was no significant difference ($a > 0.05$) in mercury dissolved in the deionized water for both time periods, regardless of the type of amalgam. On the other hand, in the pH1 solution, a significantly ($a < 0.05$) greater amount of mercury was dissolved from the high-copper amalgam for the longer time period. This was expected from the linear dissolution change with time (Figs. 4 and 5) for Dispersalloy. In each amalgam, significantly ($a < 0.05$) more mercury was dissolved in the pH1 solution for each corresponding experimental condition.

SEM examination after the dissolution tests revealed appreciable microstructural changes near the surfaces, parti-

cularly in Velvalloy specimens tested for 1 month in the pH1 solution. Fig. 7(a) and (b) show typical microstructures of polished cross-sections of Velvalloy and Dispersalloy specimens after the dissolution test in pH1 solution for 1 month. Both figures show the area perpendicular to the specimen surfaces facing the test solution. In both amalgams, the structure deteriorated considerably because of the corrosion in the acidic pH1 solution. In the Velvalloy specimen (Fig. 7(a)), areas (arrow A) where gamma-two Sn–Hg grains presumably existed appeared to be corroded. In many of these areas, tin and oxygen were detected, indicating that corrosion products remained. Also seen are the corroded grain boundary areas (arrow B) of the gamma-one Ag–Hg grains. Macro-examination of the Velvalloy
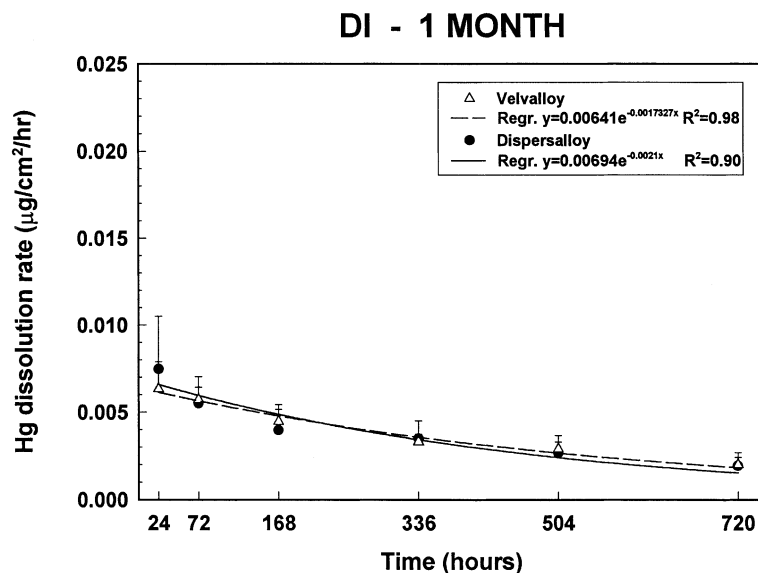
DI - 1 MONTH

Fig. 3. Mercury dissolution rate vs. time in deionized water over 1 month.
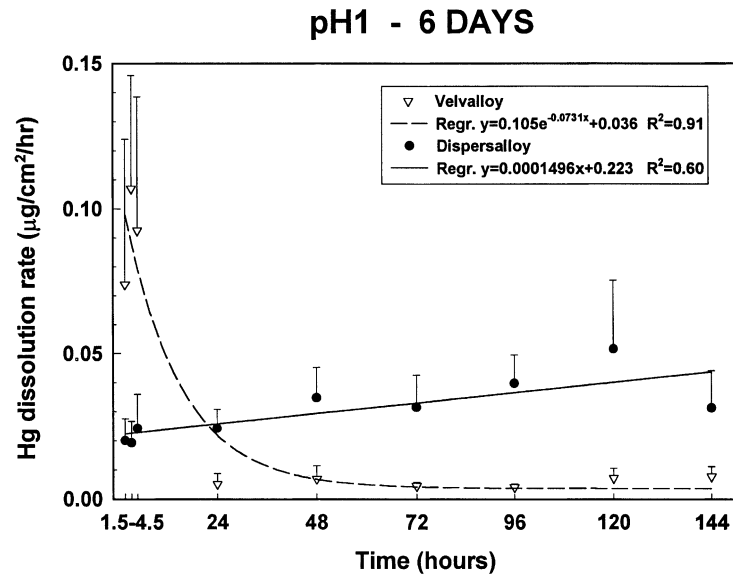
pH1 - 6 DAYS

Fig. 4. Mercury dissolution rate vs. time in pH1 solution over 6 days.

cross-sections showed that the corrosion process in the pH1 solution for 1 month had penetrated to a depth of more than 0.5 mm from the surface. In the Dispersalloy specimen (Fig. 7(b)), the corrosion penetrated along the surfaces of the unconsumed alloy particles (both Ag–Sn (C) and Ag–Cu (D) particles) and created a gap between each particle and the gamma-one matrix. The deteriorated gamma-one grain boundaries (E) seen in Velvalloy are also observed in Dispersalloy.

4. Discussion

The dissolution rate for both amalgams over 144 h (6 days) (Fig. 2), which started near 0.016 $\mu g/cm^2/h$, exponen-

tially decreased with time. For both amalgams, the exponential decrease in the dissolution rate with time in deionized water continued up to 1 month (Fig. 3). In the deionized water, it is expected that only minimal corrosion will take place for both amalgams. This is the main reason why the changes in the mercury dissolution rate from the low- and the high-copper amalgams were similar. When an amalgam specimen is placed in the solution, mercury dissolves from Hg-containing phases through a tin oxide layer produced in air [30]. When the amalgam contains zinc, the oxide is more complex, containing zinc oxides and hydroxides in addition to tin oxide [31]. In each type of amalgam, the main source of dissolving mercury is the mercury-rich gamma-one phase [32], which is the matrix of the structure. The gamma-two phase in low-copper
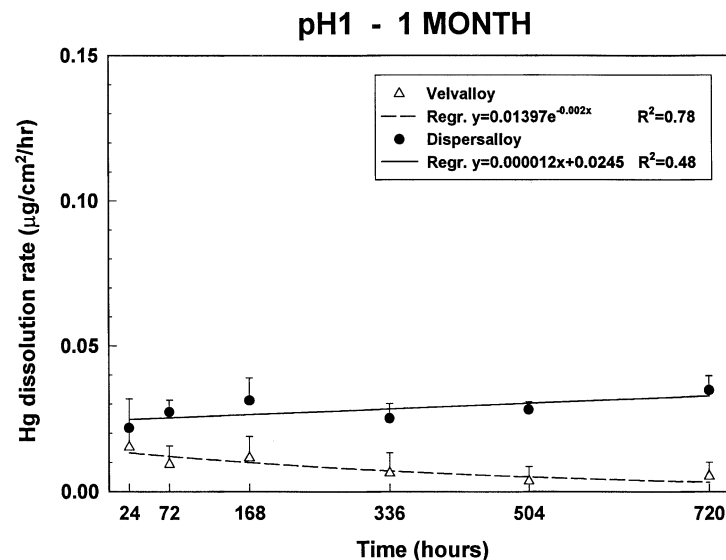
pH1 - 1 MONTH

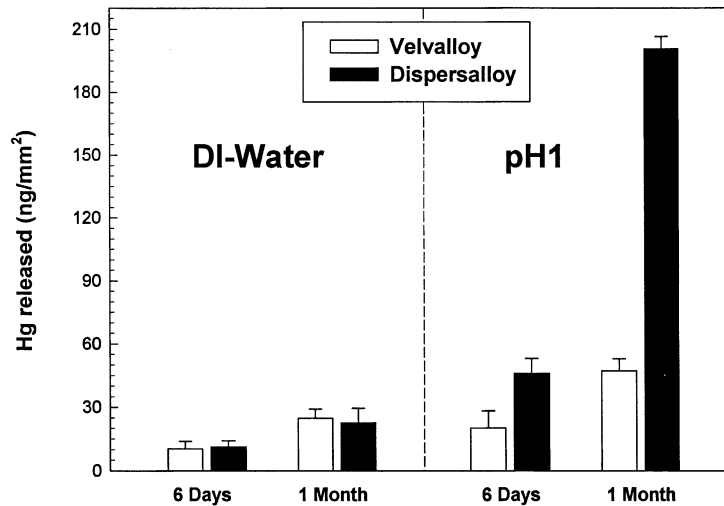Fig. 5. Mercury dissolution rate vs. time in pH1 solution over 1 month.

Fig. 6. Estimated total amount of released mercury into the deionized water and the pH1 solution.

amalgams contains less mercury and more tin than gamma-one and thus can be expected to form a thicker tin oxide and release little mercury when in a passive state [32]. The other phases either contain little mercury or are present in insignificant amounts when compared with gamma-one. As the tin oxide film grows and thickens in the water with time, the mercury dissolution rate presumably diminishes, since the whole process is controlled by the solid-state diffusion of mercury in the gamma-one grains and through the growing oxide layer on the gamma-one grains. Because both amalgams in this study contained a small amount of zinc, it is not possible to attribute any specific influence on mercury dissolution to zinc. However, one may conjecture that due to the additional oxide, dissolution might be lower from these amalgams under similar conditions than from ones without zinc.

In contrast to the similar dissolution behavior for both amalgams in deionized water, the results found in the pH1 solution (Fig. 4) revealed a drastic difference between the two amalgams. In the dissolution from Velvalloy, the rate determined as approximately 0.1 $\mu g/cm^2/h$ during the first several hours exponentially decreased with time, reaching an almost constant value after 24 h. This tendency was almost the same as that found for Velvalloy in deionized water except that the initial dissolution rate was much higher in the pH1 solution. On the other hand, the dissolution rate for Dispersalloy linearly increased. The mercury dissolution behavior in the pH1 solution differs from that in the deionized water because corrosion takes place for both Velvalloy and Dispersalloy due to the instability of tin oxide at this level of acidity [29]. In Velvalloy, mercury initially dissolves at a relatively high rate not only from the gamma-one phase, on which the tin oxide film is being thinned by dissolution, but also due to corrosion of gamma-two grains at or near the surface, which liberates mercury. When corrosion of the gamma-two phase penetrates deeper into the structure, the liberated mercury is more likely to be absorbed in the surrounding phases than released through the corrosion products to the outside, and the mercury dissolution rate decreases. The surface of the amalgam is gradually covered with insoluble corrosion products of tin from both the gamma-one and gamma-two phases, which impedes mercury release from the gamma-one grains [33]. Such products were found on the specimens immersed for 1 month (Fig. 7(a)). The result is a dissolution rate decreasing with time, as shown by the results of the 1 month dissolution test for Velvalloy in the pH1 solution (Fig. 5).

The initial high mercury dissolution rate observed for Velvalloy in the first several hours was not observed for Dispersalloy in the pH1 solution (Fig. 4). Instead, the dissolution rate for mercury from Dispersalloy monotonically increased with time up to 1 month (Fig. 5). The initial difference appears to be due to the absence of substantial amounts of mercury-containing, highly corrosion-prone phases, such as gamma-two, in Dispersalloy. The continuing higher mercury release rate from Dispersalloy than from Velvalloy may be due to the lower tin content in the gamma-one phase in Dispersalloy than in low-copper amalgams [34]. The effect may be related to stabilization of the gamma-one phase by tin [35], or a thicker layer of tin corrosion products on the amalgam with higher tin content in the gamma-one phase and from corrosion of the surface grains of gamma-two.

As found earlier [36–38], copper from the η' Cu–Sn compound in Dispersalloy is expected to be the element that dissolves first. When the copper-containing compound/phase in the gamma-one matrix corrodes, new surfaces of the gamma-one grains are opened up, which in turn become a new source for mercury dissolution. The increase in the surface area of the gamma-one grains may account for the slight increase in the mercury dissolution rate with time (Fig. 5). A polished cross-section of a typical Dispersalloy specimen after a 1 month dissolution test (Fig. 7(b)) clearly
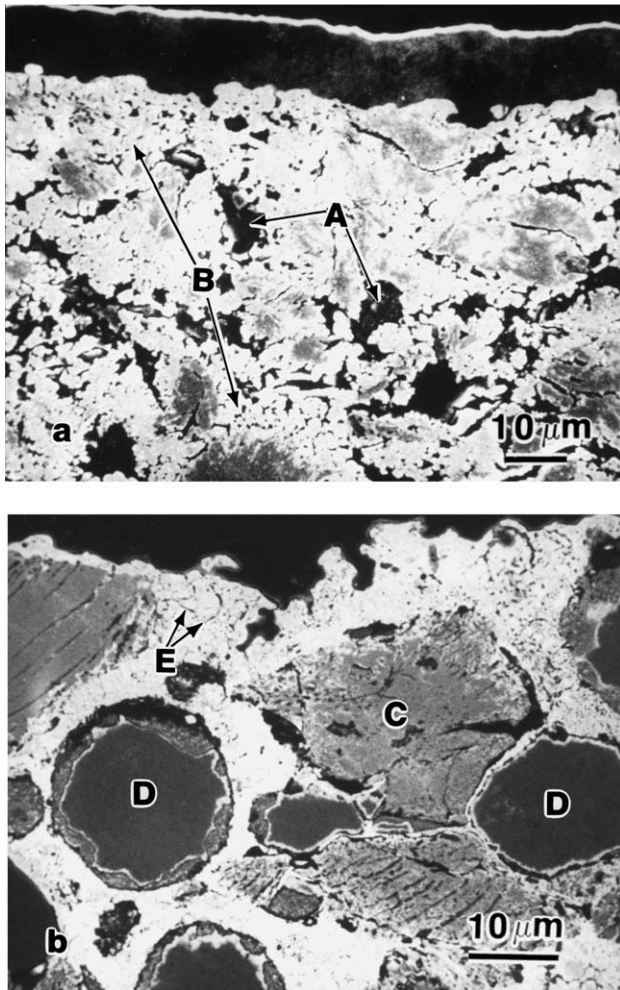
Fig. 7. (a) Typical cross-sectional view near the surface of a Velvalloy specimen after immersion in the pH1 solution for 1 month. (b) Typical cross-sectional view near the surface of a Dispersalloy specimen after immersion in the pH1 solution for 1 month.

revealed evidence of widened interphase boundaries between the Cu-containing phases and gamma-one grains.

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