Corrosion Sealing of Amalgam Restorations 

In Vitro

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Clinical Relevance
After placement, amalgam restorations exhibit a gap between the restoration and tooth structure, which fills with corrosion products during time in clinical service. To reduce the time necessary to fill this gap, an amalgam that exhibits a small initial gap shortly after setting and an amalgam that contains zinc is recommended.

SUMMARY
Amalgam restorations, when first placed, have been shown to exhibit a gap at the amalgam/tooth interface. With time in service, this gap fills with corrosion products that have the potential to “seal” the restoration. With the advent of high-copper, more corrosion-resistant amalgams, there has been concern that the time required to create this seal would be increased significantly when compared with low-copper traditional amalgams. The current study was designed to address this concern. Amalgam was condensed into a MACOR mold, simulating a Class I cavity form and then immersed into a 1.0% NaCl solution to simulate oral conditions. Using an air pressure test, the sealing was monitored over time. The results showed that the sealing was influenced by the size of the initial gap prior to immersion as well as corrosion resistance of the amalgam and that a corrosion-resistant amalgam with a small initial gap size can seal as quickly as a corrosion-prone amalgam. Therefore, it is not possible to predict sealing behavior based on corrosion resistance, alone. Furthermore, the presence of zinc in the amalgam alloy has been shown to result in the formation of zinc corrosion products in the amalgam/mold margin, which contributes to more rapid sealing. Analysis of a tooth extracted after 16 years of clinical service that had been restored with an amalgam-containing zinc was also shown to contain zinc corrosion products in the occlusal marginal area. This could explain the reported reduction in marginal fracture of clinically placed amalgam restorations made from zinc-containing alloys.

PART 1
INTRODUCTION
Most amalgam restorations contract on setting, which results in the formation of an interfacial gap between the amalgam and tooth structure.1 Pulpal fluid fills this gap as a result of the higher pressure of the pulpal
fluid compared with atmospheric pressure and capillary action induced by the relatively small size of the gap. Physical conditions that create movement of this fluid, or pressure changes in this fluid, have been shown to cause postoperative sensitivity. This fluid-filled gap can also serve as a pathway for the ingress of cariogenic bacteria and its byproducts. With time in clinical service, corrosion products formed by the interaction of metallic ions from amalgam with chlorine and oxygen in the oral environment fill this gap and have the potential to seal the amalgam restoration. However, because the buildup of corrosion products takes time, it would be advantageous if these interfacial gaps could be sealed as quickly as possible.

Recently, an hypothesis was proposed that amalgam restorations seal as a result of internal phase changes, which cause a “creep-expansion” of the amalgam. Evidence from in vitro testing has shown that amalgam expands with time at 37°C, and this expansion is related to the conversion of the Ag-Hg (γ1) phase to the Ag-Hg (β2) phase; furthermore, corrosion appears to enhance this conversion. However, an examination of the extracted teeth that had been restored with amalgam shows that the formation of corrosion products also plays a significant role in the corrosion sealing of amalgam restorations.

For many years, the corrosion of dental amalgam in clinical service was enhanced by the presence of the tin-mercury phase, known metallurgically as γ2. In the 1960s, alloys containing significantly higher copper content were introduced, which resulted in the elimination of this phase, thereby making amalgams more resistant to corrosion. Although these newer high-copper, more corrosion-resistant amalgams showed superior clinical performance, there was concern that the “self-sealing” characteristic of clinical amalgam restorations would be compromised, or at least delayed in action, by use of these more corrosion-resistant amalgams. A number of in vitro studies have been conducted that address this concern by comparing the microleakage behavior of simulated amalgam restorations made from both the high-copper and low-copper alloys when stored for periods of time in liquid solutions similar in action to that of oral fluids; microleakage being a measure of gap size. The parameter used to evaluate sealing characteristics was the time required to reduce or eliminate microleakage. However, the results have not been consistent.

One reason for this inconsistency is that some reported experiments have been designed without considering the size of the marginal gaps present after setting of the amalgam but prior to immersion into the test solution. Obviously, the time to seal the interfacial gap would depend not only on the corrosion behavior of the alloy but also on the initial gap size of the amalgam restorations made from these alloys. Without this pre-testing determination of gap size for the alloys to be selected for study, differences in sealing behavior cannot be attributed to only the difference in corrosion resistance of the amalgams to be tested.

To investigate this problem, methods that employ the penetration of fluids followed by sectioning through the interfacial gap and observing the depth of penetration have significant limitations. First, the same specimen cannot be used to measure both the initial- and after-immersion gap size and, because the gap is not uniform in size, measurements of multiple specimens would be required to satisfy requirements for valid statistical analyses. Furthermore, measurements using penetration and sectioning methods are mostly non-parametric in nature, and the statistical analyses required for non-parametric data are much less powerful than those used for parametric data.

The current study compared the corrosion sealing behavior of corrosion-resistant high-copper amalgams to that of traditional low-copper amalgams using a method that can quantitatively measure the size of the gap present both prior to and subsequent to immersion in the test solution and to allow for parametric statistical evaluation of the data.

**METHODS AND MATERIALS**

The method used in the current study was an air-pressure test similar to one previously reported, which measures the flow of air passing through the margins of a simulated Class I amalgam restoration. A schematic sketch of this test is shown in Figure 1. In the current study, the mold used to simulate a Class I cavity preparation was prepared from a machinable ceramic material (MACOR, Corning Incorporated, Corning, NY, USA) and measured 12.7 mm in diame-

![Figure 1. Schematic sketch of the air pressure device used to measure gap size (microleakage).](http://meridian.allenpress.com/operative-dentistry/article-pdf/34/3/312/1820076/08-94.pdf)
ter by 4.0 mm thick with a 4.0 mm diameter hole drilled and reamed through the center of the mold. The mold was placed into a recessed steel disk that provided a bottom surface. All the amalgams were triturated at speeds and times prescribed by the manufacturer. The amalgam was then condensed into the mold with an amalgam condenser having a 1.5 mm diameter face, using a monitored force of 1.4 kg (3.0 lbs). The mold was overpacked, and two minutes later, the amalgam was trimmed flat with a razor blade, carving from the mold to amalgam to avoid burnishing the amalgam at the margins.

The filled molds were stored in air at 37°C for one week to ensure adequate setting. They were then placed in the air pressure device, where the volume of air that passes through the entire amalgam-mold interface was measured using an air pressure of 600 mm Hg (see Figure 1). This measurement, described as microleakage, was used to indicate both the initial gap size and the gap size after being subjected to corrosion sealing. The molds were then immersed in a 1.0 % NaCl solution at 37°C for eight weeks. The selection of 1.0% NaCl as the test solution was based on the fact that the corrosion products identified in the margins of the simulated restorations used in this study were determined to be essentially the same as those found in the margins of restored teeth after years of clinical service. When compared with oral fluids, the 1.0% NaCl solution has a higher Cl concentration and is therefore more aggressive in its action. This has the advantage of conducting relevant tests in vitro in a shorter period of time than would be the case for clinically derived data. At each weekly time point, the filled molds were removed, washed with distilled water, allowed to dry in air at 37°C for two days, then remeasured for microleakage. The filled molds were then re-immersed in fresh 1.0% NaCl solution for one week until the next measurement time. This drying procedure was necessary, because the air pressure test is not effective when the gap is filled with liquid.

The alloys selected for testing are listed in Table 1. They consist of five high-copper alloys, whose amalgams are free of the corrosion-prone tin-mercury phase ($\gamma_2$), and two low-copper alloys, whose amalgams contain about 13% by volume of the $\gamma_2$ phase. Three specimens were tested for each alloy, and the time to seal was the parameter used to compare differences in sealing ability among the alloys.

### RESULTS

The results are shown in Figure 2, where microleakage for the simulated amalgam restorations of the seven test alloys, after immersion in 1.0 % NaCl, is plotted at weekly intervals for eight weeks. Each plotted point is the average of the three test runs conducted for each alloy at each weekly time point. For all the amalgams except the alloy TYT, the margins of the restorations are virtually sealed at eight weeks of immersion time. However, most of the sealing occurred at early times of immersion. When examining the microleakage at two weeks of immersion time, the two low-copper corrosion-prone amalgams, SHO and NTD, were close to being sealed, as were three of the high-copper corrosion-resistant amalgams DIS, PHD and CON. However, the two high-copper amalgams, VAL and

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*NOTE: Alloys SHO and NTD are low-copper alloys (≤6% Cu), while the remaining alloys are high copper alloys (≥12% Cu).*

![Figure 2. Microleakage of the test amalgams vs time when stored in 1.0% NaCl.](http://meridian.allenpress.com/operative-dentistry/article-pdf/34/3/312/1820076/08-94.pdf)
TYT, exhibited less sealing, while amalgam TYT was not close to being sealed at this time.

It is apparent that the time necessary to achieve sealing is influenced by two factors: 1) the initial gap size prior to immersion in the test solution, as indicated by microleakage at the 0 time point in Figure 2 and 2) the corrosion sealing effect, which is indicated by the slope of the curve between the zero and one week time point after immersion in the test solution. These slopes for the seven test alloys are essentially equal to the decrease in microleakage between the zero and one week time point and are plotted in bar graph form in Figure 3. In this figure, a greater decrease in microleakage represents a rapid filling of the interfacial gap with corrosion products, while a lesser decrease in microleakage represents a prolonged filling of the interfacial gap with corrosion products. These results also show primarily two groupings of the alloys. The first group consists of the four high-copper amalgams, TYT, VAL, PHD and CON, which seal more slowly, while the second group consists of the two low-copper amalgams, NTD and SHO and the one high-copper amalgam, DIS, which seals more rapidly. Alloy DIS represents a distinct anomaly in that it is a high-copper alloy, yet its sizeable decrease in microleakage falls in the second group, with the low-copper alloys. A two-factor ANOVA followed by Scheffe’s contrasts at α = 0.05 was conducted on the data and showed no significant difference among the alloys within each of the two groups but it did show a significant difference between the two groups.

**DISCUSSION**

Figure 2 shows that the two high-copper corrosion-resistant alloys, TYT and VAL, seal less rapidly than the two low-copper corrosion-prone alloys, SHO and NTD. However, a further examination reveals that the two high-copper alloys, PHD and CON, seal just as quickly as these same two low-copper alloys, SHO and NTD. The contributing factor to this incongruity is initial gap size, as indicated by the microleakage values on the zero time axis of Figure 2. The PHD and CON alloys have relatively low initial gap sizes and, although these alloys are high-copper corrosion-resistant alloys, even a small amount of corrosion can cause them to seal as quickly as the low-copper alloys. Because virtually all commercial alloys on the market today are of the high-copper type, selecting alloys on the basis of a low initial gap size can result in sealing characteristics similar to that of traditional low-copper alloys. The initial gap size or microleakage of 33 high-copper alloys has been published\(^a\) and could serve as a reference for selection.

![Figure 3. Decrease in microleakage due to corrosion of the test amalgams between 0 and 1 week of storage in 1.0 % NaCl. Vertical lines indicate the Standard Deviation of the data.](image)

The corrosion-sealing characteristic demonstrated in Figure 3 clearly shows that the corrosion-resistant behavior of the four high-copper alloys, TYT, VAL, PHD and CON, have smaller reductions in microleakage when compared to the higher reductions in microleakage shown by the two low-copper alloys, SHO and NTD. The sealing effectiveness, based on corrosion alone between the low- and high-copper alloys, is approximately a factor of three. However, the anomaly of the faster corrosion rate of the high-copper alloy DIS being similar to that of the two low-copper alloys but dissimilar to the other high-copper alloys suggests examining any basic difference between alloy DIS and the other four high-copper alloys. One such difference is the presence of 1.3% zinc in the formulation of alloy DIS,\(^b\) while each of the other four tested high-copper alloys is virtually zinc-free. A determination of whether the presence of zinc is the reason for this anomaly is presented in Part II of this study.

**CONCLUSIONS**

Within the limitations of this in vitro study, the sealing of amalgam restorations by corrosion products with time in clinical service can be predicted by both the corrosion resistance of the amalgam and the initial size of the interfacial gap between the amalgam and tooth structure. Thus, a high-copper corrosion-resistant amalgam with a small initial gap can seal as rapidly as a traditional low-copper corrosion-prone amalgam with a high initial gap. The corrosion sealing of the alloy DIS, a high-copper alloy, behaved comparably to that of low-copper alloys. It was hypothesized that the presence of 1.3% zinc in the alloy DIS could be the cause of this anomaly.
PART 2
INTRODUCTION

The second part of the current study addresses the anomaly found in Part I, wherein the corrosion-sealing behavior of an amalgam made from alloy DIS, a high-copper corrosion-resistant alloy, showed more rapid corrosion sealing similar to that of traditional low-copper corrosion-prone alloys. It was hypothesized that the reason for this anomaly is the presence of 1.3% zinc in alloy DIS,2 while the other high-copper alloys examined in this study are essentially zinc-free, as stated by the manufacturer. To test this hypothesis, three alloys in addition to alloy DIS, which were available in both zinc-containing and non-zinc formulations, were tested for their corrosion sealing effect.

If this hypothesis proved correct, it would be important to determine the mechanism of how the presence of zinc promotes more rapid corrosion sealing. A possible mechanism could be the formation of a zinc-containing corrosion product in the margin between the amalgam restoration and the mold in which it is placed. In two previous studies, using X-ray diffraction analysis, zinc corrosion products were found on the surfaces of amalgam specimens made from zinc-containing alloys that had been subjected to storage in a 1.0% NaCl solution.30-31 However, neither of these studies evaluated simulated amalgam restorations where margins are present between the amalgam and a mold in which it is placed. This can produce a very strong corrosion environment, known as crevice corrosion, where the pH is significantly low. Therefore, a determination of the presence and location of zinc-containing corrosion products in the margin of an amalgam made from alloy DIS placed in a Class I cavity would be a more relevant approach for determining the mechanism for the increased sealing behavior of this alloy.

In addition, there was the question of whether the results of this in vitro study could be applicable to a clinically placed amalgam restoration after some period of time in the oral environment. Fortunately, a tooth that had been restored with alloy DIS, which had been extracted after 16 years of clinical service, was available for examination. In this case, the corrosion products at the amalgam/tooth margin were examined for the presence of zinc.

METHODS AND MATERIALS

In Part I of the current study, it was found that sealing was influenced by the initial gap size of the margin between the mold and the amalgam after setting, as well as the corrosion behavior of the amalgam after immersion in a 1.0% NaCl solution. Therefore, in order to examine only the corrosion sealing effect, as it relates to the presence of zinc, the influence of the initial gap size was eliminated by making the gap size the same for all test specimens. This was accomplished using the following method:

The centered holes in the MACOR molds used to simulate the Class I preparation were tapered using a No 1 taper pin reamer. This produced a 1/48 taper of the cylindrical amalgam specimens, which allowed them to be unseated after setting by the application of a moderate force. After condensing the amalgam, the specimens were allowed to set for one week at 37°C and were then unseated from the mold. They were then reseated and tested for microleakage. The size of the hole was adjusted using the taper pin reamer, and the process was repeated until each specimen exhibited the same initial gap size as indicated by a measured microleakage of approximately 3.0 mL/minute.

Four dental amalgam alloys, which were available in both non-zinc and with-zinc formulations totaling eight alloys, were selected for measurement of their corrosion sealing behavior. They are listed in Table 2 and consisted of alloy DIS, the alloy whose anomalous behavior was responsible for conducting Part II of this study; two other high-copper alloys, UDP and TYT; and one other low-copper alloy, NTD. In the case of alloy TYT, only the non-zinc formulation was available commercially. However, an experimental version of alloy TYT was made available by the manufacturer in which 1.0% Zn had been added to its formulation. Three test runs were conducted for each alloy.

In order to determine the mechanism involved as to how the presence of zinc could reduce microleakage, an amalgam specimen of alloy DIS in a MACOR mold that
had been subjected to the 1.0% NaCl solution was sectioned in half longitudinally and mounted in a ring with epoxy resin. Electron microprobe analysis of the amalgam/MACOR margin area at the outside edge of the specimen was conducted using colored X-ray dot maps for Zn and Sn superimposed on a secondary electron image. Sn in the form of oxides and hydroxy chlorides are the more commonly measured corrosion products in the amalgam/tooth margins of both in vivo clinical restorations and in vitro laboratory specimens. However, studies showing the presence of zinc corrosion products, specifically in the margins of amalgam restorations, are notably absent.

To determine whether this in vitro representation is applicable to an amalgam restoration in a clinical environment, the same analytical procedures described above were also conducted on an extracted premolar that had been restored in a Class I configuration with alloy DIS and which had been subjected to 16 years of clinical experience. The restored tooth was embedded in a ring with epoxy resin, and one proximal surface of the tooth was ground down through the marginal ridge to expose the restoration. Electron microprobe analysis was then conducted, as previously described for the laboratory prepared section of the amalgam/MACOR specimen.

RESULTS

In Figure 4, the microleakage of the four zinc-containing and the four non-zinc alloys are plotted versus time in 1.0% NaCl. Each point represents the average of three test runs conducted for each alloy. The sealing effect represented in this figure is indicated by the decrease in microleakage with time, where greater decreases in microleakage indicate a more rapid rate of sealing, while smaller decreases in microleakage indicate prolonged sealing. It appears that the zinc-containing alloys show a faster rate of sealing than the zinc-free alloys. This difference in sealing rate can be quantified by measuring the actual decrease in microleakage between the zero- and one-week time points of immersion in the 1.0% NaCl solution where most of the sealing occurs. The decrease in microleakage for the eight alloys for this one week period are shown in bar graph form in Figure 5, where the zinc-containing alloys clearly show greater decreases in microleakage compared with the non-zinc alloys. A two-factor ANOVA, followed by Tukey’s contrasts at a confidence level of α<0.001, showed a highly significant difference between microleakage reductions in the non-Zn and the-Zn formulations for each alloy tested.
Figure 6 shows an electron microprobe image in the back-scattered mode of a section of the occlusal margin of amalgam DIS and the MACOR mold after storage in 1.0% NaCl solution. Colored X-ray dot images for zinc, shown in yellow, and tin, shown in green, have been superimposed on this image. Using energy dispersive spectroscopic analysis (EDS), in the area where zinc appears to be concentrated labeled (Zn corrosion) the presence of zinc and oxygen, indicates the formation of ZnO₂.

In Figure 7, a section of the occlusal margin of the 16-year old extracted tooth is shown, which had been restored with alloy DIS. The same microprobe analysis used for the in vitro restoration, shown in Figure 6, was applied to this clinical restoration. The corrosion product layer that lies between the amalgam and tooth structure is more than 20 µm in width, which confirms that the sealing of amalgam restorations with time-in-service includes the buildup of corrosion products in the amalgam/tooth interface. The gap between the corrosion layer and the tooth is an artifact due to shrinkage of the tooth caused by the high-vacuum environment of the electron microprobe. The presence of gaps is a common occurrence when examining clinically-restored teeth in the microprobe. Using EDS, the area marked Sn Corrosion on Figure 7 shows predominantly Sn corrosion products, while the area marked Zn + Sn Corrosion, which extends 60 µm or 70 µm from the occlusal amalgam/tooth margin, points to a layer of corrosion products containing both tin and zinc. However, zinc is virtually absent further down the margin to the pulpal wall.

**DISCUSSION**

The results shown in Figures 4 and 5 validate the hypothesis that zinc in the amalgam alloy is responsible for the more rapid corrosion-sealing of amalgams made from zinc-containing alloys and could result in a reduction of the postoperative sensitivity commonly associated with placement of amalgam restorations. The anomaly of corrosion-sealing behavior of the zinc-containing alloy DIS being similar to that of low-copper alloys can then be explained on the basis of the presence of zinc in alloy DIS.

Examination of the micrograph in Figure 6 shows that the mechanism for the more rapid sealing of amalgams made from the zinc-containing alloys is the relatively early formation of ZnO₂, which fills the gap at the amalgam/mold interface.

The question—whether zinc corrosion products are present in the margins of clinical restorations and whether these products remain after years of clinical service—can be answered by examination of the micrograph in Figure 7. In this figure, the presence of zinc can be observed in the two narrow bands of the upper part of the corrosion product layer close to the occlusal margin. Another observation based on this micrograph is the width of the corrosion product area, which measures approximately 30-40 µm. This observation supports the concept that corrosion product buildup in the amalgam/tooth interface of amalgam restorations with time in clinical service is a significant factor in the sealing of amalgam restorations.

Previous reports have shown that the improved clinical performance of amalgam restorations, as measured by a reduction in marginal fracture, is also related to the presence of zinc in the amalgam alloy. The presence and location of zinc at the margins of the 16-year old clinical amalgam restoration shown in Figure 7 could be related to this improved clinical performance. Thus, there appears to be multiple benefits from the presence of zinc in amalgam alloys.
In the past, the selection of non-zinc alloys over zinc-containing alloys has been based on avoiding delayed expansion resulting from the formation of hydrogen gas when oral fluids, such as saliva or moisture, are incorporated into amalgams made from zinc-containing alloys. Apparantly, pressure from the formation of hydrogen gas exerts an internal force that causes a creep-induced expansion of the amalgam. This was a problem with traditional low-copper alloys, because their values for creep were relatively high. However, currently available alloys are of the high-copper type, which have very low creep values and therefore do not exhibit a significant degree of delayed expansion.

CONCLUSIONS

Simulated amalgam restorations made from alloys containing zinc exhibit more rapid corrosion-sealing of their margins, similar to that shown by traditional low-copper alloys. The mechanism for this improved sealing behavior is the formation of a zinc-corrosion product at the amalgam/mold interface. The margins of a clinical restoration made from a zinc-containing alloy in an extracted tooth that had been in service for 16 years show the presence of zinc-containing corrosion products in the occlusal-marginal area.

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References


