

1992

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### Recommended Citation

Marshall, Grayson W. Jr.; McCoy, D. D.; Kinney, John H.; Letzel, Hugo; and Marshall, Sally J. (1992) "Microstructural Changes in Retrieved Amalgam Restorations," *Cells and Materials*: Vol. 2 : No. 1 , Article 4.

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## MICROSTRUCTURAL CHANGES IN RETRIEVED AMALGAM RESTORATIONS

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(Received for publication October 21, 1991, and in revised form March 13, 1992)

### Abstract

Many blended or dispersed phase high Cu amalgams show excellent clinical performance in long term clinical trials. However, little is known concerning the microstructural changes that occur during clinical use of these systems. This investigation sought to characterize some of the changes that occur in the Ag-Cu particles and their surrounding reaction zones based on a study by backscattered scanning electron microscopy (BSEM), energy dispersive spectroscopy and a new microprobe technique called Colorad which assigns various colors to elements and element combinations and indicates changes in elemental concentration by changes in color value (brightness). Restorations were retrieved from clinical trials and compared to control restorations prepared and retrieved in the same way. The clinical restorations showed marked changes in the composition of the Ag-Cu particles with the composition approaching that of the surrounding matrix phase so that they appear as pale particles in BSEM. These particles were often surrounded by a ring of Sn-rich corrosion product which replaced the normal reaction zone. The reaction zones appeared to be complex and have a number of subzones of varying composition. Many of the reaction zones also underwent coarsening of their structure. Corrosion is thought to play a prominent role in the conversion of the Ag-Cu particles to a Ag-Hg composition similar to the surrounding matrix. There appeared to be more transformation in the L system, a dispersed phase system without Zn, which has poorer clinical survival, than in the D system, a dispersed phase system with 1% Zn, which shows superior clinical performance.

**Key Words:** Amalgam, microstructure, backscattered scanning electron microscopy, microprobe, elemental mapping.

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### Introduction

It is well known that many high copper dental amalgam alloys yield restorations with enhanced marginal integrity (Mahler *et al.*, 1973b; Osborne *et al.*, 1980), corrosion resistance (Sarkar and Greener, 1972; Greener, 1976; Marshall and Marshall, 1986) and creep properties (Mahler *et al.*, 1970) as compared to traditional amalgams based mainly on Ag-Sn alloys. In blended or dispersed phase high Cu amalgams, reaction zones are formed around the Ag-Cu particles which predominantly contain Cu<sub>6</sub>Sn<sub>5</sub> and the  $\gamma_1$  Ag-Hg phase (Mahler *et al.*, 1975; Okabe *et al.*, 1977).

The Ag-Cu particles and their reaction zones are of substantial importance since they are associated with reduction or elimination of the corrosion prone  $\gamma_2$  Sn-Hg reaction product and may play a crucial role in the enhanced performance of these amalgam systems. However, the reaction zone contains very finely divided phases which are difficult to resolve by scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). Results suggest that the phase contents may vary considerably from system to system (Marshall and Marshall, 1982). Bryant (1984; 1985) conducted microprobe analysis of the Ag-Cu particles and reaction zones of freshly prepared laboratory samples. His analysis suggested that the reaction zone is subdivided into at least two regions, a dark outer zone containing a high concentration of Cu-Sn and a lighter inner zone with less Cu-Sn and more Hg. He also suggested that Cu-Hg phases may be contained in these regions in addition to the widely accepted presence of the  $\gamma_1$  Ag-Hg phase. Sarkar *et al.* (1991) presented supporting evidence based on differential scanning calorimetry for the presence of a Cu-Hg phase in this zone, but the complexity of the reaction zone and difficulties of its analysis have so far precluded a definitive characterization of the zone. Furthermore, little is known of the changes induced in the particles or zones by intraoral exposure. *In vitro* corrosion studies (Lin *et al.*, 1983) showed corrosion of the reaction zones that was similar to reactions occurring in retrieved restorations (Marshall *et al.*, 1987).



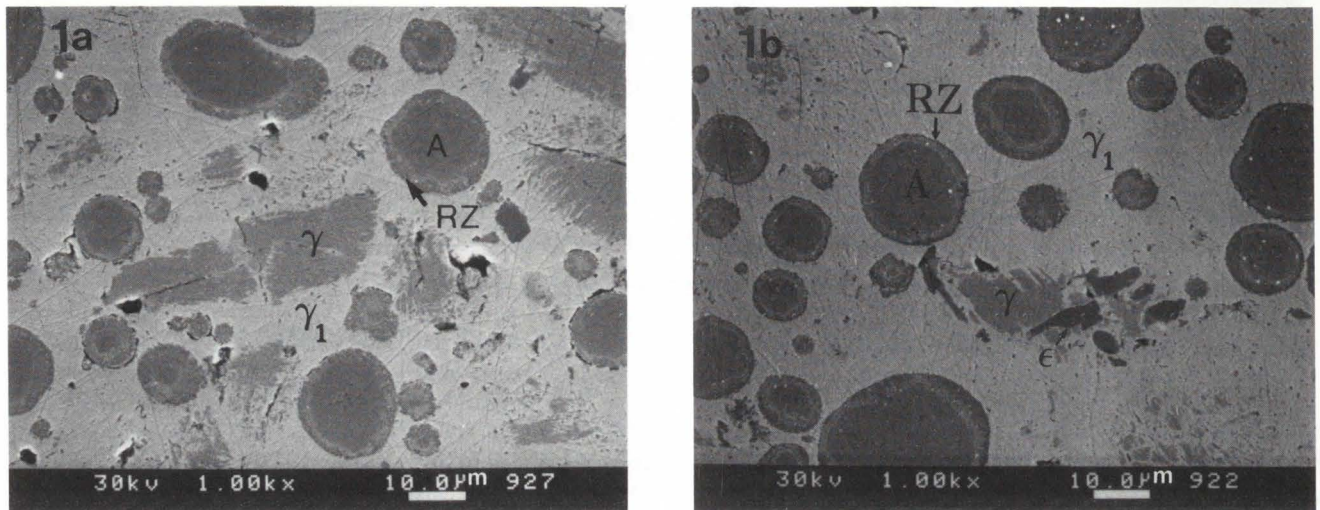


Figure 1. BSEM micrographs of control specimens (a - D control; b - L control) showing the similarity of structure and presence of common phases:  $\gamma$  - Ag-Sn alloy particles; A - Ag-Cu alloy particles; RZ - reaction zones;  $\epsilon$  - Cu-Sn particles; and  $\gamma_1$  - Ag-Hg matrix phase.

Table 1. Sample Characteristics

Sample No.	Code <sup>1</sup>	Grade <sup>2</sup>	Age/(Yrs.) <sup>3</sup>	Reason for Removal
17	D	3.0	7.9	Bulk Fracture
18	D	3.0	8.0	Outline crevice
25	D	3.0	6.7	Unrelated Caries
36	D	3.0	5.8	Esthetics
26	L	3.0	7.0	Bulk Fracture
33	L	3.0	5.5	Bulk Fracture
82	L	3.0	6.1	Enamel Fracture
94	L	3.0	5.8	Bulk Fracture
130	L	3.0	6.7	Bulk Fracture
165	L	3.0	8.9	Marginal fracture
<b>Controls</b>				
M52	D	NA	NA	NA
M59	L	NA	NA	NA

<sup>1</sup>D = Dispersalloy, Johnson & Johnson, USA, 1% Zn; L = Luxalloy, Degussa, Germany, 0.0% Zn.

<sup>2</sup>Grade = marginal deterioration photographic grade on a scale of 1 (good) to 6 (poor); see Marshall *et al.* (1987).

<sup>3</sup>Age = clinical age in years at removal; all controls were stored for a minimum of 5 years prior to analysis at ambient temperature.



## Microstructural changes in amalgams

In clinical trials, restorations made from similar blended systems appear to have substantially different survival rates (Letzel *et al.*, 1989; 1990), although there is little comparative microstructural information on these systems after clinical use. Therefore, the purpose of this work was to compare the microstructures of the Ag-Cu particles and the reaction zones from two similar amalgam types retrieved from clinical trials to determine if similar microstructural changes occurred in both systems.

### Materials and Methods

Amalgam restorations were retrieved from ongoing clinical trials after clinical failure as previously described (Marshall *et al.*, 1987). Two systems representing similar blended high Cu systems were selected for study based on substantial differences in overall survival rate. System D is a dispersed phase amalgam system with two alloy particles, Ag-Sn irregular particles with 1% Zn and Ag-Cu eutectic particles. System L is Zn free and is also a dispersed phase amalgam with irregular Ag-Sn particles and spherical Ag-Cu particles. The 12.5 year survival rate for restorations from system D was approximately 85%, while the rate for system L was approximately 60% (Letzel *et al.*, 1990). The restorations were selected for this study on the basis of similar marginal deterioration indices (midway on a 6 point scale) during the clinical trials. In addition, control restorations were prepared in typodont teeth using the same alloys. These control restorations were never exposed to *in vivo* or *in vitro* corrosion or other testing and were retrieved using the same methods as used in the clinical trials. They were stored for a minimum of 5 years at room temperatures prior to analysis.

The retrieved restorations and control restorations were embedded in slow curing epoxy and metallographically polished through 0.01  $\mu\text{m}$  alumina. Most restorations were scored to provide a fiducial mark which facilitated examination of the same areas in the scanning electron microscope (SEM) and microprobe. Three types of studies were conducted on the samples. First was a generalized microstructural study of the bulk of the samples and characteristics of corroded areas of the restorations near surfaces which had been exposed to the intraoral environment. The microstructures were studied at 15-30 keV by backscattered SEM (BSEM) (ISI SX-40A SEM, Milpitas, CA, equipped with a Robinson backscatter detector) and energy dispersive spectroscopy (EDS) elemental mapping (Kevex Delta Class IV Quantum EDS Detector with fast X-ray mapping, San Carlos, CA). Secondly, detailed composition analyses of the center of the Ag-Cu particles and their surrounding reaction rings were conducted from spot or high magnification area analysis by collecting a minimum of 5 EDS

spectra at 15 keV from each sample. The spectra were analyzed using a no standards atomic number-absorption-fluorescence (ZAF) correction computer program (Kevex Quantex program with Magic V ZAF corrections).

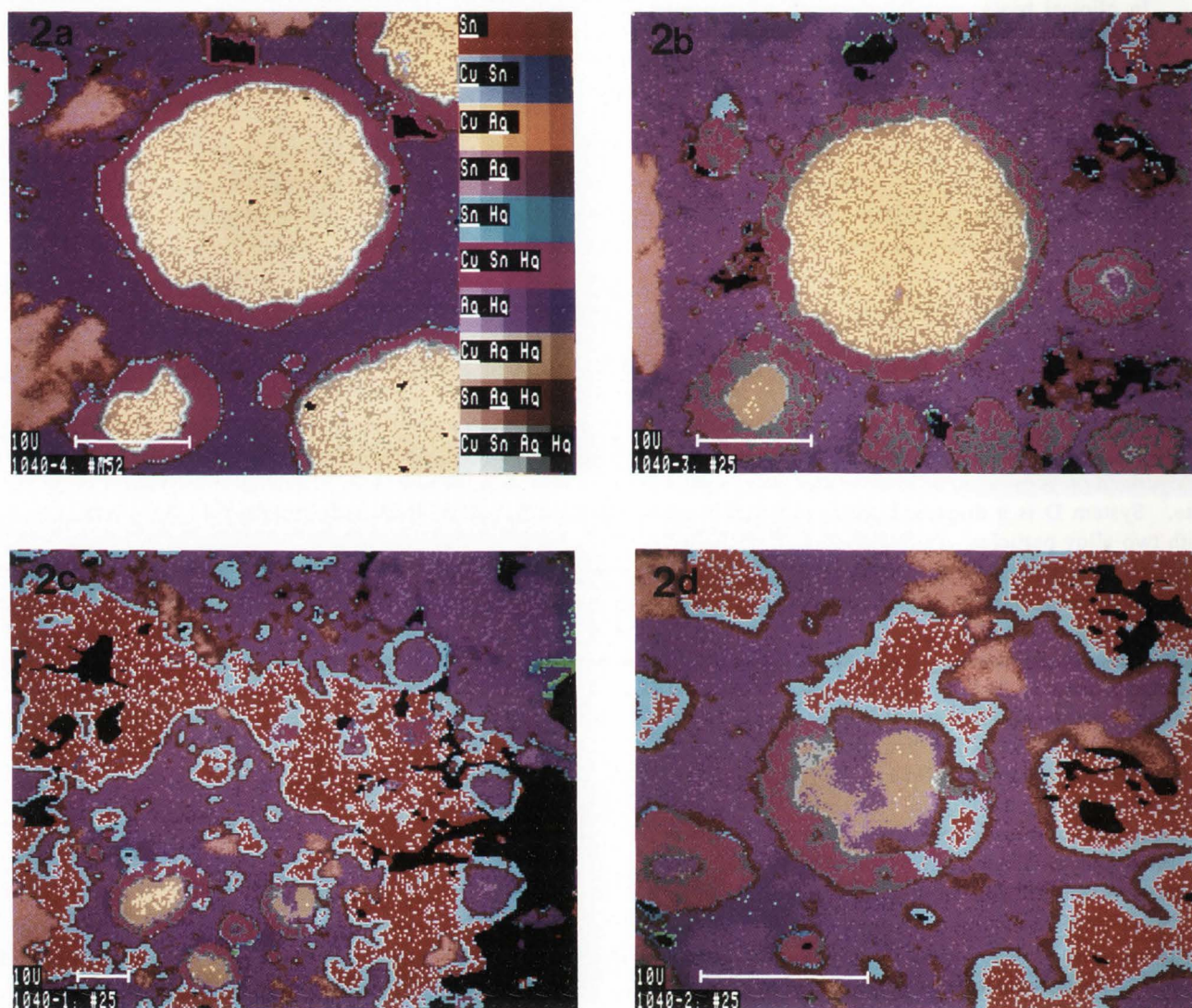
Thirdly, the microstructures were studied using a microprobe (JEOL Superprobe 733, JEOL, Tokyo, Japan) operated at 15 keV and 100 nA beam current monitored by a Faraday cup. The microprobe was equipped with the Colorad X-ray mapping system (McCoy, 1987). X-rays from 4 element lines at a time were collected using 3 wave length dispersive spectrometers (WDS) and an EDS system. Normally the Cu  $L\alpha_1$  (TAP crystal), Sn  $L\alpha_1$  (PET crystal), Ag  $L\alpha_1$  (PET crystal) were collected using the WDS spectrometers and Hg  $M\alpha_1$  was collected with the EDS system (Kevex EDS System 7000, San Carlos, CA). The Colorad system assigns a specific color (hue and chroma) to an element or combination of elements. Variations in elemental composition are displayed in a 256 by 256 pixel array by means of different brightness (luminosity or value) of the selected color. The resolution is limited by beam spreading, not pixel size. For various element combinations, a single element of the combination is followed by the change in lightness. This system has not been previously used for analyses of dental amalgam microstructures.

### Results

Table 1 lists the samples, brands and histories for the D and L restorations and their controls. Figures 1a and 1b show low magnification BSEM photomicrographs of the D and L control restorations. The similarity of microstructure is obvious and consists of residual irregularly shaped  $\gamma$  Ag-Sn particles with  $\epsilon$  Cu-Sn inclusions, the round Ag-Cu particles surrounded by a reaction zone, and the Ag-Hg  $\gamma_1$  matrix phase common to all amalgams. Occasional porosity also can be seen.

Figure 2 is a color composite of microprobe images collected using the Colorad system for system D. Figure 2a shows the appearance of a control with the color assignments for each element combination. It also shows the remnants of the two alloy particle types,  $\gamma$  Ag-Sn (brown) and A particles. The A particles consist of Ag-Cu eutectic (yellow-tan) with complex reaction zones which are relatively uniform, circumscribe the particle (dark pink) and contain mostly Cu-Sn with small amounts of Ag-Hg. The interface between the unreacted particle and the reaction zone contains several well demarcated regions which reflect changes in the silver content. The regions also contain Cu, Hg, and Sn. A similar region often occurs with less completeness at the interface between the reaction zone and the



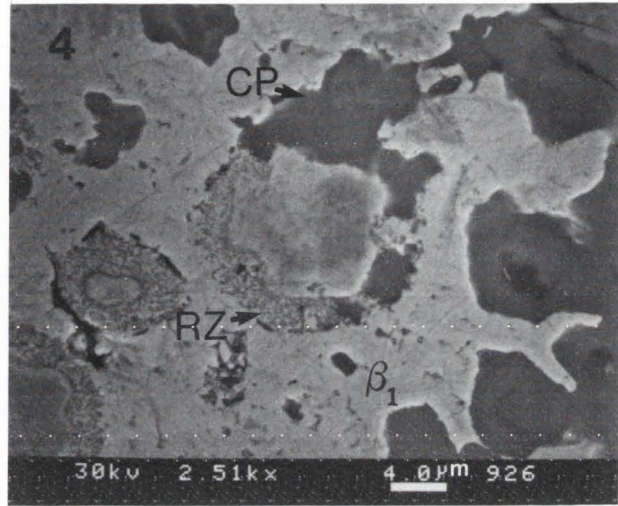
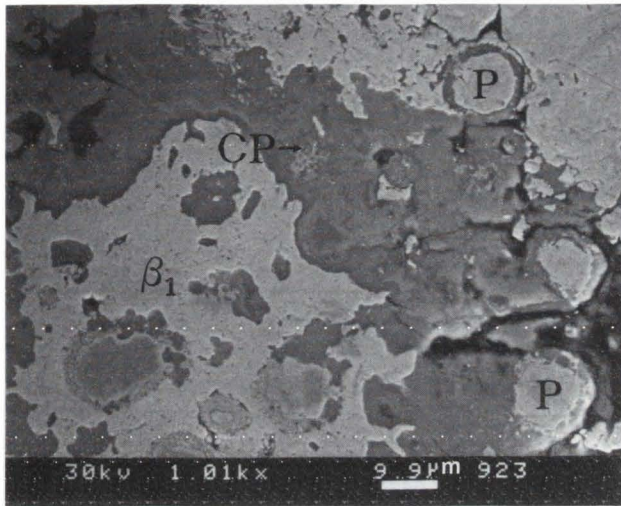


**Figure 2.** Colorad X-ray images of amalgams from system D. **a.** Control amalgam with color scales used for all samples shown. Gamma particles are brownish-purple, the matrix is purple, Ag-Cu particles are yellow-tan, the reaction zone contains several thin subzones at the interface but is largely dark pink. **b.** Retrieved restoration interior showing similar particle. Changes are seen in the matrix, which is mostly a lighter purple, presence of corrosion products (aqua) in pores (black); reaction zone is coarsened (gray and dark pink), the Ag-Cu particle is less yellow and more tan. **c.** Retrieved restoration near occlusal surface (exposed occlusal surface at right edge). Sn rich corrosion products penetrate the restoration (aqua and red); composition of the matrix is largely light purple and the same shade as the three converted particles at right on the exposed surface; particle at center is partially changed in its composition, while particle at lower left has even less change. **d.** Image of partially transformed particle at lower center of **c**, showing details of the composition transformation. Corrosion products penetrate partially around the reaction zone space.

matrix. In Figure 2b, the typical appearance of changes occurring in the interior of the restoration can be seen. These include an apparent composition change in the matrix as seen by a change in color of the matrix to a lighter shade of purple indicating a higher Ag concentration, the appearance of well known Sn containing corro-

sion products (aqua, red) (Marshall and Marshall, 1980), coarsening of the reaction zone, in which the normally featureless zone is divided into distinct regions (pink and gray), and slight changes in composition of the Ag-Cu particles. In Figure 2b, the  $\gamma_1$  (dark purple) and  $\beta_1$  (light purple) Ag-Hg phases can be easily distinguished.





**Figure 3 (at left).** BSEM of the sample area shown in Figure 2c (CP - corrosion product). The particles at the periphery (P) appear pale as they change composition to that of the Ag-Hg matrix ( $\beta_1$ ). Partially pale particle at center shows various gray shades indicating its transformation.

**Figure 4 (at right).** Higher magnification BSEM of the partially pale particle of Figure 3 which also corresponds to the Colorad image of Figure 2d (CP - corrosion product, RZ - reaction zone, and  $\beta_1$  - Ag-Hg matrix phase).

The A particle has a relatively uniform internal structure containing Cu and Ag, with limited areas of varying composition containing small amounts of Sn and Hg. Corrosion products were sometimes found throughout a sample, while in other samples, much of the interior had little or no corrosion product.

In areas near the external or occlusal surface, the changes were much more pronounced. Figure 2c shows the Colorad image of this area. At the right of the micrograph, the A particles at the occlusal surface appear to take on the same color as the matrix, which is largely the Ag-rich shade associated with the  $\beta_1$  composition. The reaction zone for these particles is filled with Sn-rich (aqua) corrosion products which have been identified in these systems many times. This was confirmed by EDS. Significant quantities of corrosion product (red) penetrate porous spaces near the exposed surface. Other Ag-Cu particles, near the left of the image show composition changes indicative of various degrees of Cu loss and partial conversion of the interior to Ag-Hg  $\beta_1$  phase (light purple). Figure 3 shows the same area as seen by BSEM. The particles that have been largely converted to the matrix-like composition appear pale, matching the shade of the matrix, while the partly converted particles show partially pale characteristics. Figure 4 is a higher magnification of one of the partially pale particles. Corrosion product penetrates the reaction zone space at the top and right of the particle, while the remaining reaction zone appears to have a coarsened

structure divided in various substructures as noted previously. Figure 2d shows the corresponding Colorad image of the same area showing conversion of a portion of the center to the matrix composition (light purple), the loss of Cu indicated by the less yellow and more brown regions, the penetration of the zone by the red and aqua corrosion products, and the coarsening of the reaction zones. The apparent differences in the composition of the Ag-Cu particles and their reaction zones were investigated by EDS analysis. The results are shown in Table 2 for the Ag-Cu particles, classified as pale or normal, based on appearance. It can be seen that the composition changed substantially as compared to the controls. Zn was not found in the analyses of D Ag-Cu particles. These particles do not contain Zn and the transformation does not lead to Zn accumulation in these areas. Efforts were made to separate the overall composition of the pale particles into constituent phases based on composition of the corresponding controls. However, since the particles are mainly an eutectic mixture of phases based on Ag and Cu, it was not possible to determine the amounts of each phase which had reacted.

### Discussion

Dental amalgam is a dynamic material. After placement and clinical set it continues to undergo a variety of reactions and changes. Eventually, many restora-



tions undergo sufficient changes that failure results and the restoration must be replaced. The changes that are most important and eventually lead to clinical failure are incompletely understood. Many of the changes in structure are associated with corrosion and it is well established that the Sn containing phases are highly susceptible to this process. However, little previous work has been directed at analysis of changes in the Ag-Cu particles of blended amalgams. In this work we found that these particles change. They appear to contain more Hg than in freshly prepared amalgams, and a variety of particles can be found in retrieved clinical restorations which have undergone considerable composition change. These changes appear to be related to a process in which the particles which are originally Ag-Cu are slowly altered so that they are converted to a structure containing mostly Ag and Hg, essentially indistinguishable from the matrix of the amalgam in both BSEM and Colorad. Thus the particles become pale. EDS analysis of the particles demonstrated a major increase in Hg and significant decreases in Cu and Ag. The change appeared to be most pronounced in areas of highest corrosion activity and may occur to different extents in the two amalgam brands. Evidence for this change was found in nearly all samples studied, at least to some extent. Our observations suggested that it occurs more readily in L than in D restorations, but there is insufficient quantitative data to establish this firmly at this time. However, if this observation proves to be correct, it could be related to differences seen in the long term clinical survival of the two similar brands of blended high Cu amalgams (Letzel *et al.*, 1989; 1990), which may be dependent upon the differences in Zn content.

The mechanism of conversion of the Ag-Cu or A particles to pale particles appears strongly linked to the corrosion process. During the setting process, Cu from the Ag-Cu particles reacts with Sn to form Cu-Sn phases in the reaction zone and Ag reacts to form matrix. These reactions might allow Hg diffusion to form additional Ag-Hg matrix phase. Corrosion processes ensue and Sn and Cu form a variety of corrosion species and products. Some of the released Sn may also react with the Cu in the A particle to further deplete the A particle of Cu and promote its conversion to a more matrix-like composition. Hg would be available for reaction with the Ag of the particle since the solid state transformation of the matrix from  $\gamma_1$  to  $\beta_1$  would also be proceeding and the transformation has been shown to be accelerated by corrosion (Lin *et al.*, 1983). Thus, the reaction proceeds from the inner edge of the reaction zone inward until eventually the A particle is largely converted into more matrix and is surrounded by a zone which is often invaded by corrosion product.

Many of the details concerning the continuing re-

actions at the inner periphery of the reaction zone in these blended amalgams are still not well understood. A common observation is the formation of Ag-Hg globules along this interface following metallographic preparation. These globules have been attributed to polishing artifacts (Mahler *et al.*, 1973a), but their consistent observation and relationship to the interface between the A particle and its reaction zone raises questions about this interpretation. Furthermore, other authors (Sarkar *et al.*, 1991; Bryant, 1985) suggested that it is related to the ongoing reactions associated with setting of the amalgam and some evidence has been presented that formation of Cu-Hg and the Sn-Hg  $\gamma_2$  phase may be short lived intermediates in the reactions at this interface. These contentions would be consistent with our observations in the clinically retrieved restorations, since the formation of Cu-Hg intermediates would contribute to the ongoing loss of Cu from the A particle and its transformation to Ag-Hg by subsequent reaction with the Hg. Furthermore the presence of  $\gamma_2$  would accelerate corrosion attack in the area resulting in more corrosion products and the release of more Hg to continue the transformation of the A particle. Bryant (1985) suggested that several distinct subzones occur in the reaction zones of these amalgams. The work shown here suggests that the reaction zones may be even more complex than he has suggested with 4 or more zones present and changes induced by clinical use resulting in coarsening. Our EDS analyses could not be used to indicate the presence of discrete zones because beam spreading makes it difficult to determine the excited volume for X-ray generation. Thus we found indications of zones of different composition but could not precisely define the composition of the various subzones. There is no evidence to suggest that any phases not previously identified occurred in these complex zones. The coarsening of the zones is also an interesting phenomenon and its relationship with the corrosion process needs additional clarification. We noted that in the interior coarsening was often present without the presence of corrosion products. This suggests that the process leading to this coarsening in structure may be related more to grain growth at elevated body temperature for long periods of time than it is to the corrosion processes. Such coarsening did not occur in the controls held at ambient temperatures.

## Conclusions

1. The Ag-Cu particles of two brands of dispersed phase amalgam changed composition as a result of intra-oral exposure for prolonged periods. The particles became pale in appearance in BSEM and probably contain substantial amounts of the  $\beta_1$  phase.



Microstructural changes in amalgams

Table 2. EDS Spherical Particle Compositions

Sample	Code	Particle Type*	n	Composition (wt %)			
				Cu	Ag	Sn	Hg
18	D	P	4	13.5 (7.3)	40.6 (6.3)	8.2 (2.3)	37.6 (14.4)
25	D	N	7	26.4 (2.0)	71.5 (1.6)	0.2 (0.4)	1.8 (1.8)
		P	4	12.6 (5.0)	47.5 (5.6)	2.5 (2.6)	37.4 (7.2)
26	L	N	10	20.0 (7.0)	78.0 (6.0)	1.9 (1.2)	0.2 (0.4)
33	L	P	16	5.1 (2.2)	45.2 (4.8)	5.7 (1.6)	44.0 (5.2)
130	L	N	9	36.2 (1.8)	63.6 (1.8)	0.0 (0.0)	0.2 (0.2)
		P	3	7.9 (0.9)	44.0 (3.2)	1.8 (1.2)	46.2 (2.1)
165	L	N	5	37.5 (1.5)	62.5 (1.5)	0.0 (0.0)	0.0 (0.0)
		P	5	14.9 (3.6)	37.2 (3.2)	10.0 (1.3)	37.8 (3.4)
Control							
M52	D	N	5	27.2 (1.6)	70.8 (2.3)	0.2 (0.4)	1.9 (1.8)
M59	L	N	27	33.3 (1.3)	64.9 (1.7)	1.8 (1.3)	0.0 (0.0)

\*P = pale particle; N = normal; ( ) = standard deviation; n = number of particles analyzed in each sample

2. The phenomenon of altered composition leading to pale particles appeared to be most pronounced in areas of high corrosion, especially near exposed surfaces. A mechanism for this change in composition probably involves a combination of corrosion induced changes effecting the Cu-Sn phase and reaction of the residual particle with Hg released during the  $\gamma_1$  to  $\beta_1$  transformation.

3. Some changes were also seen in many reaction zones surrounding the Ag-Cu particles in both the pale or more normal states. These changes appeared to be in the form of coarsening of the structure of the reaction zone.

4. A new technique, Colorad microprobe X-ray imaging, was utilized and provided valuable information on the phase relationships in the dental amalgams.

5. Ag-Cu particles in both systems D and L underwent transformations, but additional work is needed to determine if such changes occur in all high Cu amalgam types. Our observation of a limited number of samples suggested that the process might be more extensive in system L, which has poorer clinical survival.

Thus, the quantitative relationships between corrosion and pale particle development need additional study since any differences may be related to differences in performance.

#### Acknowledgment

This work was supported by NIH Grant DE 06563.

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Editor's Note: All of the reviewer's concerns were appropriately addressed by text changes, hence there is no Discussion with Reviewers.