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Intergranular structure in dental amalgams

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The existence of an intergranular precipitate that provides a structural basis of creep, intergranular corrosion and thermal instability in dental amalgams has been in dispute. Also in dispute is a related matter concerning the solid solubility of Sn in γ_1. Both these aspects have been examined in this differential scanning calorimetry (DSC) study using the following materials: (a) a conventional γ_2-containing amalgam, (b) six γ_2-free amalgams, and (c) a series of γ_1 specimens with up to 4 wt% Sn. It has been observed that the solid solubility of Sn in γ_1 is about 1.0 wt%. Above this Sn concentration, an intergranular precipitate, identified as the δ_2 phase of the SnHg system, appears in γ_1. This phase is characterized by a low melting temperature ($\sim$ 90 °C). The existence of this phase in the conventional dental amalgam has been confirmed. It has been observed further that the γ_2-free dental amalgams, depending on their nature and Hg contents, may contain δ_2 either as a transient or a permanent phase.

1. Introduction

In 1985, we presented evidence in support of the existence of a previously unknown structure in dental amalgams [1–2]. This structure was identified as the δ_2 phase of the SnHg system. Its crystalline structure is orthorhombic [3] in contrast to the hexagonal nature of the known γ_2 phase. Its melting temperature is around 90 °C which is significantly lower than that of γ_2 (214 °C) and γ_1 (127 °C), respectively. Being SnHg, it has corrosion characteristics identical to that of γ_2. Most importantly, its intergranular location contrasts sharply with the island-like distribution of γ_2 in γ_1 matrix.

This intergranular phase provides a reasonable structural basis of many important phenomena in dental amalgams including creep [4–6], internal and intergranular corrosion [7–11], and intercrystalline fracture [12–13]. None of the previously known phases have been directly linked to these phenomena. In addition, the low melting temperature of δ_2 offers a satisfactory explanation for the thermal instability in dental amalgams around 80 °C that leads to a precipitous decrease in strength, sudden increase in mechanical damping, discontinuous dimensional change, and incipient fusion and Hg release [14–17].

We suggested that the formation of δ_2 is inherent in the setting reaction of conventional dental amalgams [1]. During amalgamation and soon thereafter, the plastic amalgam mass can well be considered a liquid melt of Ag, Sn and Hg, if one excludes the unconsumed remains of the original AgSn alloy. As amalgamation proceeds, supersaturation of Hg with Ag and Sn leads to the nucleation and growth of γ_1 and γ_2. At the same time, the remaining liquid becomes concentrated in Ag and Sn. As this liquid becomes progressively saturated with Ag and Sn, further nucleation and growth of γ_1 and γ_2 take place. During the final stage of setting, it is likely that the last liquid, largely a solution of Sn and Hg with small amounts of Ag will freeze at grain boundaries giving rise to the segregated Hg-rich δ_2 phase. In high copper amalgams Cu, with its strong affinity for Sn, scavenges Sn away from grain boundaries and thus can prevent the formation of δ_2 [2]. However, to be effective in suppressing δ_2 formation, an optimum amount of Cu must be available in the last liquid to combine with all Sn released during amalgamation.

In two other related studies [18, 19], we showed that the solid solubility of Sn in the γ_1 phase of dental amalgam is virtually nil. Consequently, the addition of Sn to γ_1 leads to the precipitation of a SnHg intergranular structure which was found to influence strongly the creep in γ_1. In addition, the presence of a SnZnHg intergranular precipitate in a Zn-containing dental amalgam was reported [20].

Mahler and Adey [21] found no evidence of any such intergranular precipitate in a spherical traditional composition dental amalgam. Moreover, they presented data showing (a) significant (1.0–3.0%) solubility of Sn in γ_1, and (b) slight or no difference in Sn content of γ_1 grain and grain boundaries. Marek's recent electrochemical data [22], contrary to their previous observation [23], established the solubility of Sn in γ_1 at around 1.25 wt%. No intergranular structure was identified in this study [22].

The concept of an intergranular structure in dental amalgams provides a unique opportunity to reconcile many conflicting theories about the mechanism of marginal fracture, the major deficiency in an amalgam restoration. Fundamental to this reconciliation is the observation that at one time or another, attempts have been made to relate marginal fracture to creep [24, 25], internal corrosion [7, 26–28] and thermal instability [29]. It is quite resonable to assume that the

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intergranular structure identified in our study is a common link to all these phenomena. In consideration of this importance of the intergranular structure and in view of the information presented by Mahler and Adey [21] and Marek [23] which is in conflict with our observation, it was felt necessary to re-examine our previous studies. The data obtained during this re-examination are presented here.

2. Materials and methods

The materials studied are listed in Table I. They include: six commercial alloys, one experimental gold-containing silver–tin alloy, and a series of γ_1 specimens containing varying concentrations of Ag and Sn.

Of the commercial alloys, New True Dentalloy is a traditional low copper (~ 4.0%) amalgam alloy and the others contain high (> 9.0%) copper. In general, amalgams prepared from the latter group are γ_2-free and resist creep and marginal fracture better than the traditional amalgams which contain γ_2 [24, 25]. Exceptions to this behaviour have been found in Optaloy II and Micro II. Although these two amalgams are γ_2-free, their resistance to creep and marginal fracture is similar to that of γ_2-containing amalgams [30]. The gold containing amalgam which is also γ_2-free exhibited high creep and high incidence of marginal fracture [31].

Amalgam specimens of New True Dentalloy, Optaloy II, Micro II and the gold amalgam were prepared according to the respective manufacturer's direction and the ADA specification 1. They were stored at 37 °C for 1 day. Amalgam specimens of Dispersalloy, Tytin and Sybraloy were prepared in a mechanical amalgamator and were studied as a function of Hg content and aging at 37 °C for up to 1 month.

In fabricating the Sn-containing γ_1 specimens, the following raw materials were used: (1) Ag powder (2.0–3.57 μ); (2) Sn as SnHg (83/17) amalgam powder; and (3) triple distilled Hg. Considering the criticism [21] of our previous sample preparation technique, these specimens were prepared using a standard trituration procedure in a mechanical amalgamator at 4500 rpm for 15 s. The specimens were stored at 37 °C for at least 1 month after amalgamation.

TABLE I Commercial and experimental materials studied

Commercial	
Alloy	Manufacturer
New True Dentalloy (Zn-free)	S. S. White Co., Philadelphia, PA
Optaloy II	L. D. Caulk Co., Milford, DE
Micro II	L. D. Caulk Co., Milford, DE
Dispersalloy	J & J. Dental Products Co., East Windsor, NJ
Tytin	S. S. White Co., Philadelphia, PA
Sybraloy	Kerr Manufacturing Co., Romulus, MI
Experimental	
Gold-containing silver-tin alloy; supplier, Dr. L. B. Johnson University of Virginia, VA	
Sn-containing AgHg (γ_1) specimens:	18 different compositions Hg = 70% Ag = 30–26% Sn = 0–4%

Differential scanning calorimetry (DSC) was used to characterize the microstructure of all materials. The specimens were heated in air between 35 ° and 250 °C at a scan rate of 10 °C min^{-1}.

3. Results

The thermograms of γ_1 as a function of its Sn content are shown in Figs 1–3. The number at the base line of each thermogram represents the Sn content of the respective specimen. Up to 1% Sn, all specimens exhibit a single endotherm peak (Fig. 1). This peak is the result of $\gamma_1 \rightarrow \beta_1$ transition. There is a gradual lowering of this transition temperature from 125.6 °C to 115.3 °C as Sn content increases from 0 to 1%. The thermogram of the specimen containing 1.25% Sn shows an additional endotherm peak at around 95 °C. In accordance with our previous study [1], this peak is attributed to the presence of δ_2 in this specimen.

With further increase in Sn concentration (Fig. 2), there is a progressive increase in δ_2 content. Note that in spite of the increase in δ_2 content, the transition temperature of δ_2 remains essentially unchanged at

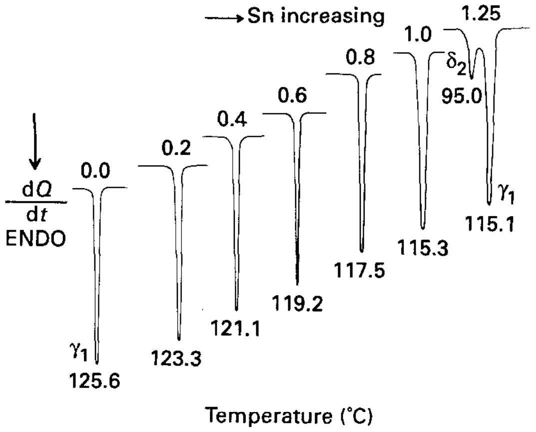

Figure 1 Thermograms of γ_1 as a function of its Sn content (0.0–1.25 wt %).

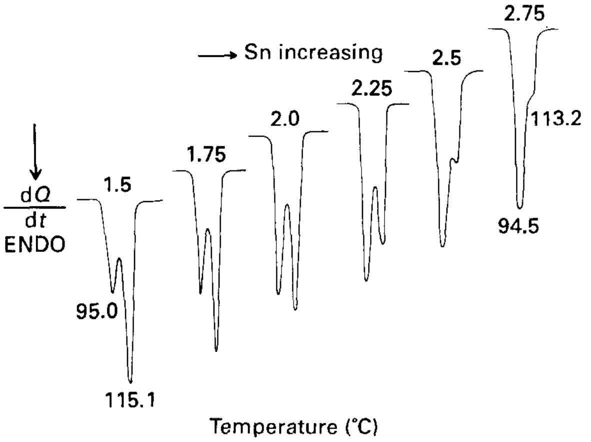

Figure 2 Thermograms of γ_1 as a function of its Sn content (1.5–2.75 wt %).

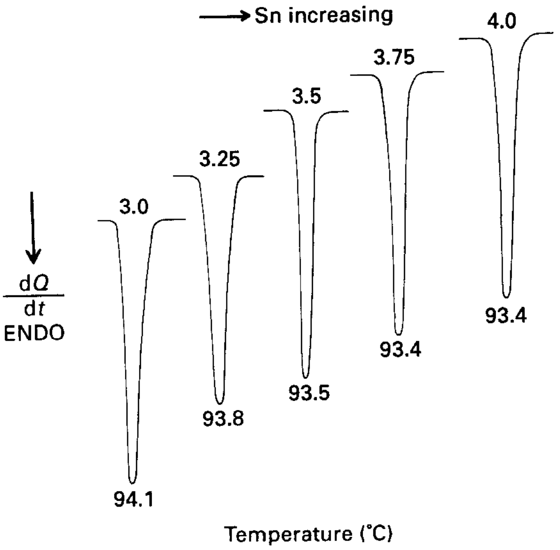

Figure 3 Thermograms of γ_1 as a function of its Sn content (3.0–4.0 wt %).

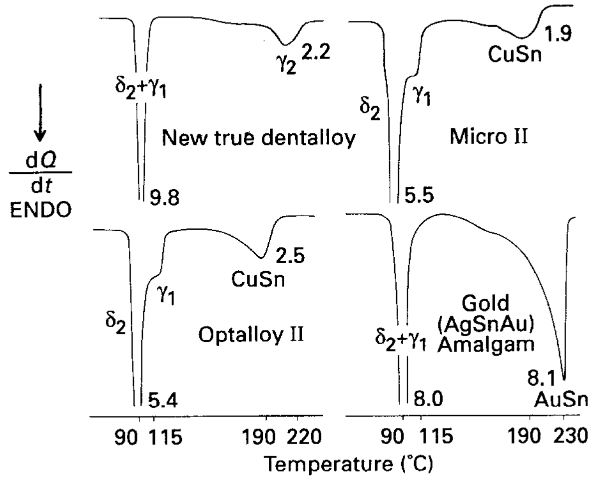

Figure 4 Thermograms of New True Dentalloy, Optaloy II, Micro-II and the gold-containing amalgam.

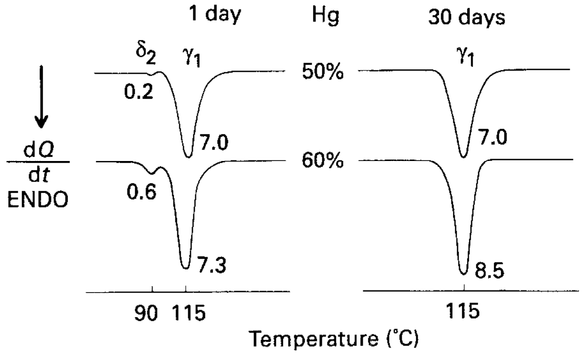

Figure 5 Thermograms of Dispersalloy amalgam as a function of Hg content and ageing at 37 °C.

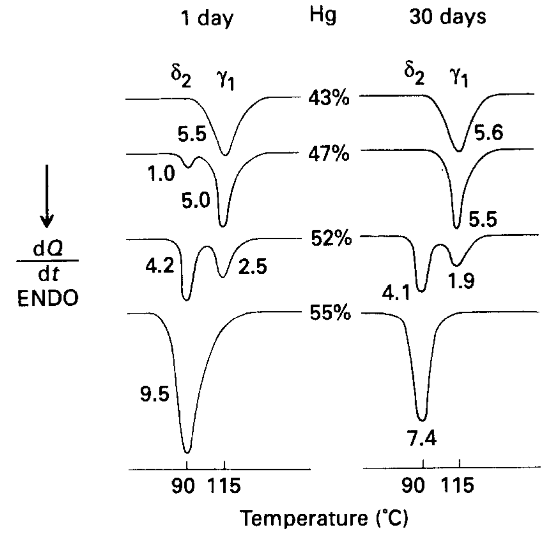

Figure 6 Thermograms of Tytin amalgam as a function of Hg content and ageing at 37 °C.

around 95 °C. Similarly, an increase in Sn content above 1% does not significantly ($\Delta T = 2\,°\mathrm{C}$) alter the β_1 transition temperature (~ 115 °C). At 3% Sn and above (Fig. 3), the two transitions overlap giving rise to a single endotherm.

The thermograms of New True Dentalloy, Optaloy-II, Micro II and the gold amalgam are shown in Fig. 4. The number adjacent to each peak represents energy change (J/gm) associated with the endotherm and is proportional to the amount of the corresponding structure responsible for the endotherm. The endotherm in New True Dentalloy at around 90 °C has been attributed to overlapping of δ_2 and γ_1 transitions on the basis of data shown in Figs 2 and 3. The other endotherm at around 220 °C is due to the transition of γ_2. The thermograms of Optaloy II and Micro II indicate the presence of (1) no γ_2, and (2) a significant amount of δ_2 (~ 90 °C) and CuSn (~ 190 °C). The shoulder adjacent to the δ_2 peak is due to γ_1 transition. The energy change associated with this transition has not been determined. The thermogram of the gold amalgam indicates the presence of AuSn (~ 230 °C), overlapping δ_2 and γ_1 (~ 90 °C) but no γ_2. Ageing of these amalgams up to a week at 37 °C did not produce any significant change in their thermograms from that shown in Fig. 4.

The thermograms of Dispersalloy amalgam as a function of Hg content (50 and 60%) and ageing (1 day and 30 days) at 37 °C are shown in Fig. 5. The presence of a small amount of δ_2 and a significant amount of γ_1 is indicated in the thermogram of the 1-day amalgam at all Hg concentrations. The amount of δ_2 is seen to increase with an increase in Hg content. However, the amount of γ_1 was not largely influenced by an increase in mercury concentration. Ageing at 37 °C for 1 month led to the disappearance of δ_2. It should be noted that the thermogram of this amalgam indicated the presence of CuHg and CuSn but no γ_2 at any of the Hg concentrations and time period studied (not shown).

The thermograms of Tytin as a function of mercury content and ageing at 37 °C are shown in Fig. 6. The 1-day-old amalgam with 47% Hg shows the presence of a small amount of δ_2 although it is absent in the specimen containing 43% Hg at 1 day. The amount of δ_2 increases with an increase in Hg concentration leading to the overlapping of δ_2 and γ_1 transitions at 55% Hg. The small amount of δ_2 that is present in the 1-day-old Tytin amalgam containing 47% Hg disappears with ageing. However, ageing for 1 month does

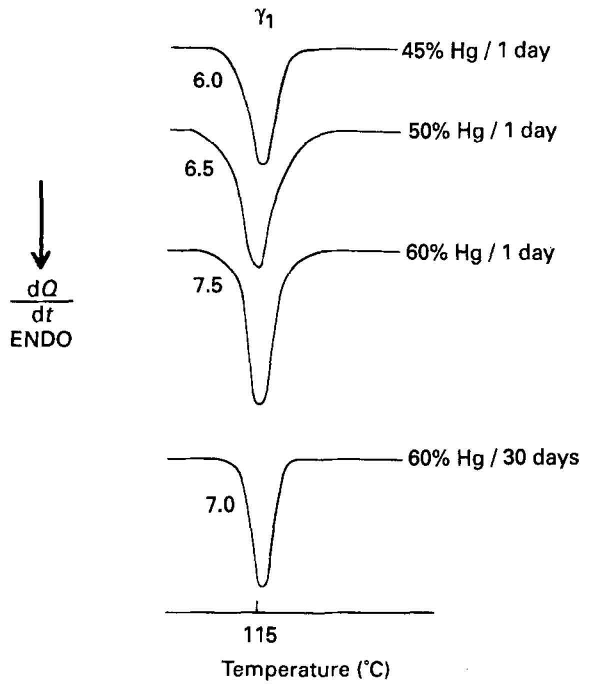

Figure 7 Thermograms of Sybraloy amalgam as a function of Hg content and ageing at 37 °C.

not lead to the elimination of δ_2 in amalgams containing higher amounts of Hg.

The thermograms of Sybraloy amalgam as a function of Hg content and ageing are shown in Fig. 7. Regardless of the mercury content and ageing, no evidence of δ_2 is seen in this amalgam. It showed the presence of only γ_1 and CuSn (not shown).

4. Discussion

The presence of a single endotherm peak and the gradual decrease in transition temperature in γ_1 specimens containing up to 1% Sn, and the first appearance of δ_2 in the specimen containing 1.25% Sn strongly suggest that the solubility of Sn in γ_1 is below 1.25%. This observation is at variance with our previous study [18] but is in close agreement with that recently reported by Marek [22]. It appears that the virtual insolubility of Sn in γ_1 as determined previously [18] may have been influenced by the oxidation of Sn resulting from the complex sample preparation technique. Based on the data presented here, our previous study thus stands corrected. However, the solubility of Sn in γ_1 in excess of 1% as reported by Mahler and Adey [21] is not confirmed in the present study.

The overlapping of δ_2 and γ_1 transitions seen in γ_1 specimens containing 3% or more Sn (Fig. 3) and in Tytin with 55% Hg (Fig. 6) provides an explanation as to why a separate $\gamma_1 \rightarrow \beta_1$ transition peak is not seen in the thermogram of a conventional amalgam (Fig. 4). The athermal dissolution of γ_1 in Hg released from melting of δ_2 was suggested as an explanation [1, 2]. That this is not so is apparent from Figs 2 and 3 which indicate that when the amount of δ_2 in γ_1 matrix exceeds a certain critical amount, δ_2 transition can overlap and mask the γ_1 transition. In the presence of a smaller amount of δ_2, both endotherms can coexist. It should be stressed that regardless of the Sn content, the transition temperatures of δ_2 and γ_1 (Figs 1 and 2) remain essentially unchanged at around 95 ° and 115 °C, respectively. Thus the first endotherm seen in conventional dental amalgams at around 90 °C should not be attributed to $\gamma_1 \rightarrow \beta_1$ transition alone as has been done in the past [32, 33]. The presence of soluble Sn in γ_1 can lower its transition temperature to a minimum of 113 °C (Figs 1 and 2).

The critical role Cu (or Au) plays in influencing the formation of δ_2 is illustrated in the thermal behaviour of the dental amalgams studied (Figs 4–7). As noted before, to prevent δ_2 formation, an optimum amount of Cu (or Au) must be available to combine with all Sn released during amalgamation. The amount of Cu (or Au) available in the amalgamated mass is controlled by a number of factors including the nature and composition of the alloy and the Hg content [34]. The existence of δ_2 in Optaloy II, Micro II and the gold amalgam (Fig. 4) suggests that not enough Cu (or Au) is available to scavenge Sn away from the grain boundary area. It should be noted that the first two amalgams contain about 9.0% Cu and the amount of Au in the last amalgam is about 10% [30, 31].

The presence of a significant amount of δ_2 in the three γ_2-free amalgams (Fig. 4) not only explain their high creep values but also aid in elucidating the complex relationship between creep, corrosion and marginal fracture. All three amalgams, it should be noted, are associated with high incidence of marginal fracture. While creep has been found to be a valid predictor of marginal fracture in these amalgams, a cause and effect relationship between the two has never been established [24]. On the other hand, there is strong evidence to directly implicate internal corrosion and the attendant undermining of the amalgam at the tooth interface in marginal fracture [1, 7–11]. Examination of the gold amalgam following clinical service has revealed extensive internal corrosion damage [31]. Both creep and internal corrosion have their origin in the intergranular structure. Thus a direct link between this structure and the marginal fracture of dental amalgams can be envisioned.

The formation of δ_2 as a transient phase in Dispersalloy (Fig. 5) can be attributed to the localized nature of Cu in the microstructure of this amalgam. When mixed with Hg, Cu amalgamates within the periphery of the AgCu eutectic particles and mostly remains in this place because of diffusion limitations [35, 36]. It appears that in areas away from the AgCu eutectic, insufficient Cu is available to combine with Sn released during amalgamation of Ag_3Sn. As a result, δ_2 forms. However, with time Sn from δ_2 diffuses into the CuHg area and combines with Cu forming CuSn. In the process, δ_2 is eliminated as is seen in the 1-month-old amalgam. The presence of δ_2 in Dispersalloy provides a reasonable explanation for grain boundary sliding [5, 6] and intergranular corrosion [8] in this amalgam. That there is more sliding of γ_1 grains in areas away from the periphery of the AgCu eutectic [6] is consistent with the mechanism of δ_2 formation suggested above.

The importance of the amount of Cu available during amalgamation in controlling δ_2 formation is further evident in the thermal behaviour of Tytin (Fig. 6) and Sybraloy (Fig. 7). In amalgams containing low concentrations of Cu (12–13%) such as Tytin, the potential for segregation of Sn 'in some form in γ_1 and/or the γ_1 grain boundaries' exists when the Hg content exceeds a critical value [37]. There is reason to believe that this Sn 'in some form' and the δ_2 reported in Tytin containing 47% or more Hg (Fig. 6) are one and the same. Considering the intergranular nature of δ_2, the characteristic 'creep jump' observed in Tytin at 47% Hg can be attributed to δ_2 and not to γ_2 as has been previously suggested [38]. The absence of δ_2 in Sybraloy even at 60% Hg can be explained by its high Cu content (30%). As the amount of Cu increases, the chances for the formation of δ_2 are minimized.

5. Conclusions

In view of the data presented above, our previous observation regarding the solubility of Sn in γ_1 needs revision. According to the present study on Sn-containing γ_1 specimens prepared following standard trituration procedure, the solubility of Sn in γ_1 has been found to be about 1%. This value is in agreement with that reported by Marek [22].

The addition of more than 1% Sn to γ_1 leads to the precipitation of a SnHg phase at γ_1 grain boundaries. This intergranular structure with a characteristic low transition temperature (~ 95 °C) has been identified as δ_2, the orthorhombic phase of the SnHg system. The existence of this structure in a conventional dental amalgam has been reconfirmed. Depending on the nature of the alloy and Hg content, γ_2-free dental amalgams may contain δ_2 either as a transient or permanent phase.

At present, little or no attention has been paid to this structue in dental research. Considering that a low melting intergranular structure provides a reasonable basis of many previously inexplicable phenomena in dental amalgams, discussion of properties and performance of dental amalgams in the future should take into consideration the existence of δ_2 in a particular amalgam.

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