

Reconfirmation of the existence of δ_2 in dental amalgams

N. K. SARKAR, K. LIAN

Division of Biomaterials LSU School of Dentistry, New Orleans, LA 70119, USA

The $\sim 90^\circ\text{C}$ endotherm peak in the thermogram of a conventional dental amalgam is due to two overlapping peritectic transitions involving SnHg- δ_2 and HgAgSn- γ_1 , respectively. The aim of the present study is to separate these two events and thus confirm that the δ_2 phase is indeed a part of an amalgam microstructure. The materials used in this study were: sample 1, $\gamma_1 + 1\text{ wt \% Sn}$; sample 2, $\gamma_1 + 2\text{ wt \% Sn}$; sample 3, $\gamma_1 + 3\text{ wt \% Sn}$; and sample 4, a commercial conventional amalgam with 48 wt % Hg. In powder form, they were exposed to 1 wt % NaCl solution at 37°C for up to 45 days. At 15 day intervals, samples were withdrawn from the solution, washed, dried and then characterized by the differential scanning calorimetry (DSC) technique. Corrosion of Sn from ternary γ_1 matrix and intergranular δ_2 in respective materials during their exposure to the NaCl solution led to the following: (a) a progressive increase in $\gamma_1 \rightarrow \beta_1$ transition temperature in samples 1 and 2; (b) a gradual decrease in δ_2 peak and its disappearance in sample 2; and (c) in samples 3 and 4, initial splitting of the $\sim 90^\circ\text{C}$ peak into two distinct endotherms associated with δ_2 and γ_1 , respectively. Continued corrosion of the last two materials produced further changes in δ_2 and γ_1 in a manner similar to that seen in samples 1 and 2. On the basis of these observations, we have concluded that the $\sim 90^\circ\text{C}$ endotherm is a valid indicator of the existence of the δ_2 phase in dental amalgams.

1. Introduction

The primary product of reaction between a dental amalgam alloy and mercury is the silver–mercury γ_1 phase [1]. This phase is more complex than a simple binary intermetallic represented by the formula Ag_2Hg_3 , as it may contain small amounts of Sn, Zn and Cu. It has been shown in our previous studies [2–4] that the maximum solid solubility of Sn in γ_1 is about 1.0 wt % and Sn dissolved in γ_1 lowers the $\gamma_1 \rightarrow \beta_1$ transition temperature. The addition of more than 1.0 wt % Sn to γ_1 leads to intergranular segregation of SnHg- δ_2 . The existence of this phase in conventional dental amalgams has been demonstrated. It has been shown further that some high copper amalgams may contain this phase under certain conditions.

We have stressed that the δ_2 phase provides a structural basis of many formerly inexplicable phenomena in dental amalgams; including creep, internal and intergranular corrosion, and brittle fracture. In addition, the δ_2 phase offers a satisfactory explanation for the “creep jump” and inferior marginal fracture characteristics of some γ_2 -free amalgams.

Such conventional metallurgical techniques as optical and electron microscopy and X-ray diffraction are not suitable for characterizing the presence of δ_2 in dental amalgams. The identification of this phase in our studies has been accomplished with the DSC technique. Unlike conventional techniques, this tech-

nique does not allow visualization of structural entities; nor does it provide any direct information related to their compositions and structures. In essence, the technique measures energy change associated with physical and chemical changes in a material as a function of its temperature. The temperature, T , at which such changes take place and the resultant energy change, ΔH , are thermodynamic constants for a specific material or its constituents. These parameters, therefore, can be used as “finger prints” of a material or its constituent phases. Though indirect, the DSC technique has proved to be an elegant and powerful tool for characterizing microstructures of metallic systems [5].

In our studies, the specific parameter used in identifying the δ_2 phase is the $\sim 90^\circ\text{C}$ endotherm. We have shown that this endotherm in a dental amalgam results from two closely spaced overlapping peritectic transitions involving δ_2 and γ_1 , respectively [2–4]. However, others attribute this endotherm to a single event, namely, the $\gamma_1 \rightarrow \beta_1$ transformation [6–8]. The purpose of this study is to clarify this interpretational discord.

2. Experimental procedure

The materials used in this study were: sample 1, $\gamma_1 + 1\text{ wt \% Sn}$; sample 2, $\gamma_1 + 2\text{ wt \% Sn}$; sample 3, $\gamma_1 + 3\text{ wt \% Sn}$; and sample 4, a Zn-free conventional

amalgam (New True Dentalloy) with 48 wt % Hg. The nominal chemical compositions (wt %) of the above materials were as follows: sample 1, Hg-71, Ag-28, Sn-1; sample 2, Hg-70, Ag-28, Sn-2; sample 3, Hg-69, Ag-28, Sn-3; and sample 4, Ag-36.4, Sn-13.5, Cu-2.1, Hg-48. In fabricating the $\gamma_1 + \text{Sn}$ specimens, the following raw materials were used:

1. Ag powder (2.0–3.5 μm);
2. Sn, as SnHg amalgam powder containing 75% Sn; and
3. ADA certified Hg.

They were mixed in the following proportions (parts by mass) for respective materials: sample 1, 28:1.33:70.67; sample 2, 28:2.7:69.32; and sample 3, 28:4.0:69.0. Thereafter, they were triturated in a mechanical amalgamator at 4500 r.p.m. for 15 s. Following amalgamation, they were first stored at 60 °C for two days and then at 37 °C for one week. Amalgam specimens of New True Dentalloy were made according to the manufacturer's (S. S. White) recommendation. No Hg was condensed after trituration and the specimens were stored at 37 °C for one day prior to any further study.

All materials thus prepared were pulverized in a porcelain mortar. It was the intention to use fine powders (–170 mesh) of these materials for this study. It was noted, however, that the grinding procedure caused partial oxidation of Sn in samples of this dimension (confirmed by DSC). Accordingly, coarser particles (+170 mesh) of each material were utilized.

Each material (2 g) in powder form was exposed to 1 wt % NaCl solution (40 ml) in a sealed glass container at 37 °C for up to 45 days. Once a week, the powder was gently rubbed with a glass rod of 1 cm diameter, the solution was discarded and the container was filled with fresh NaCl solution. Samples were removed from the solution at 15 day intervals, rinsed thoroughly with water and acetone, dried in air, and then characterized by the DSC technique. The materials exposed to the NaCl solution will be referred to as treated samples. Untreated samples served as controls.

The rationale for the NaCl treatment was as follows. The element Sn is known to corrode in an NaCl solution. Exposure of the four materials to the NaCl solution was expected to remove Sn from both the $\gamma_1 + \text{Sn}$ matrix and the δ_2 phase of the respective specimens. From our previous study [2], it was anticipated that the removal of Sn through corrosion would produce the following effects:

1. a reduction in the amount of δ_2 or its complete elimination, and
2. an increase in the $\gamma_1 \rightarrow \beta_1$ transition temperature.

In specimens showing overlapping $\gamma_1 + \delta_2$ transitions and treated with the NaCl solution, these effects, it was reasoned, would lead to separation and resolution of the two individual transitions.

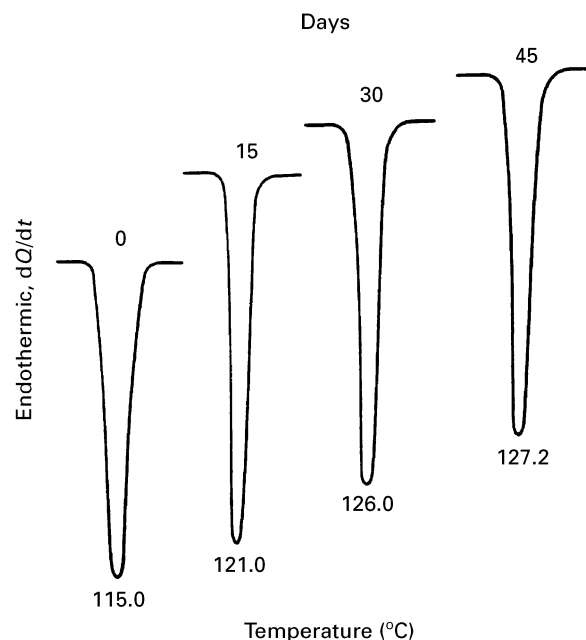


Figure 1 Thermograms of $\gamma_1 + 1 \text{ wt } \% \text{ Sn}$ specimens as a function of 1 wt % NaCl solution treatment time.

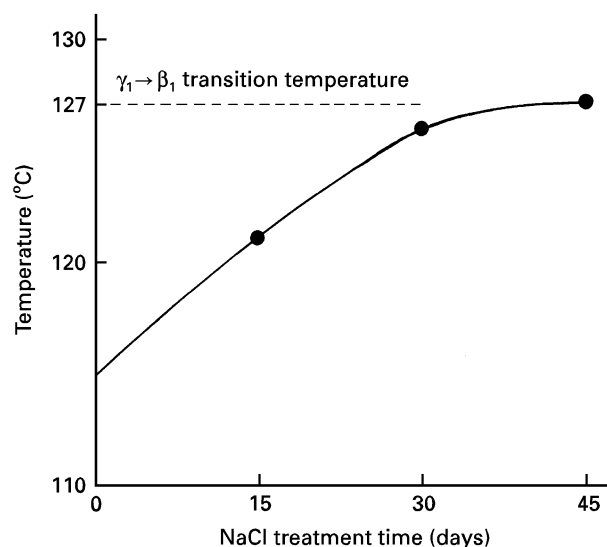


Figure 2 Transition temperatures of $\gamma_1 + 1 \text{ wt } \% \text{ Sn}$ specimens as a function of 1 wt % NaCl solution treatment time.

3. Results

The thermograms of the treated and untreated $\gamma_1 + 1 \text{ wt } \% \text{ Sn}$ specimens are shown in Fig. 1. The term dQ/dt in Fig. 1 and other thermograms represents the rate of heat flow ($Q = \text{heat}$, and $t = \text{time}$). The endotherm associated with the untreated control (day 0) is characteristic of its single phase nature and is the result of the $\gamma_1 \rightarrow \beta_1$ transition. It is apparent from Fig. 1 that the temperature of this transition shifts upwards with an increase in treatment time. This was expected and is due to the loss of Sn from this material. As noted before, solid solution of Sn in γ_1 lowers the $\gamma_1 \rightarrow \beta_1$ transition temperature.

The transition temperatures of the $\gamma_1 + 1 \text{ wt } \% \text{ Sn}$ specimens obtained from Fig. 1 are plotted as a function of their respective treatment times in Fig. 2. The rate of temperature rise, i.e. loss of Sn, is relatively fast

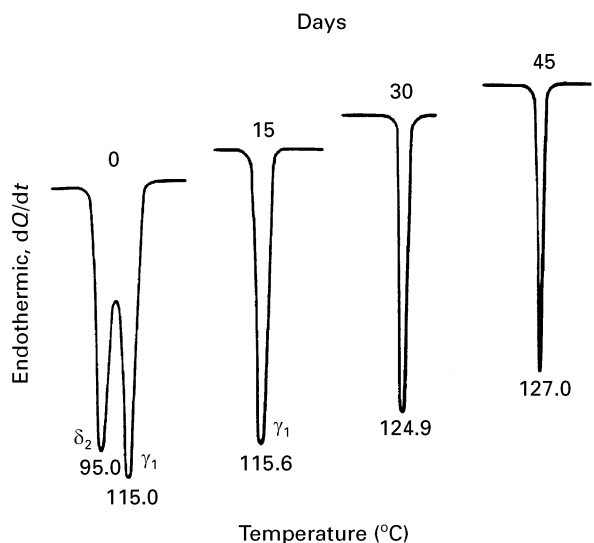


Figure 3 Thermograms of $\gamma_1 + 2$ wt % Sn specimens as a function of 1 wt % NaCl solution treatment time.

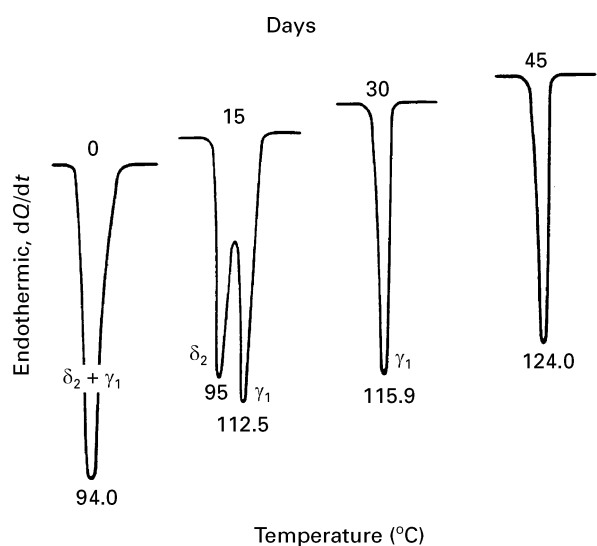


Figure 4 Thermograms of $\gamma_1 + 3$ wt % Sn specimens as a function of 1 wt % NaCl solution treatment time.

initially; then it levels off in 30 days. The final transition temperature after 45 days is 127.2°C. This temperature of transition is the same as that reported [9] for pure binary AgHg- γ_1 indicating that the $\gamma_1 + 1$ wt % Sn specimen by this time (after 45 days) has lost all of its Sn.

Fig. 3 shows the thermograms of the $\gamma_1 + 2$ wt % Sn specimen treated with the NaCl solution for various lengths of time. The control sample (day 0), consistent with its duplex structure, shows two transitions indicating the presence of δ_2 and γ_1 , respectively. The NaCl solution treatment and the attendant Sn loss led to (a) the disappearance of the δ_2 peak in 15 days, and (b) a gradual shift in the $\gamma_1 \rightarrow \beta_1$ transition temperature from 115 to 127°C.

The thermograms of the $\gamma_1 + 3$ wt % Sn and the conventional amalgam specimens, treated and untreated, are shown in Figs 4 and 5, respectively. The untreated samples (day 0) for both materials are associated with the “controversial” single endotherm peak. The following sequential events are seen in the ther-

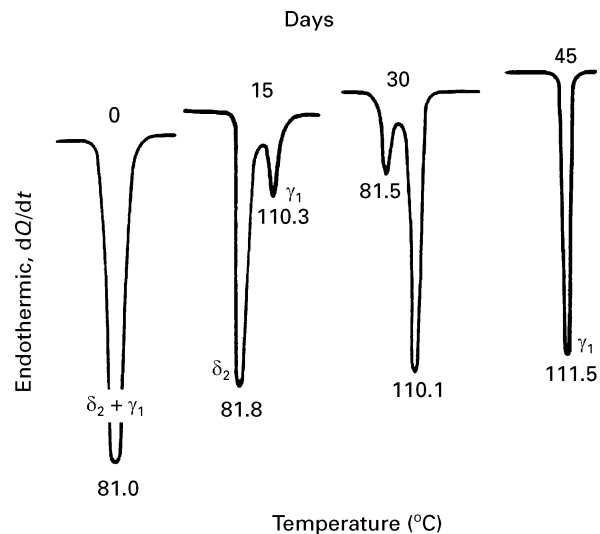


Figure 5 Thermograms of conventional amalgam (New True Dentalloy) specimens as a function of 1 wt % NaCl solution treatment time.

mograms of the two amalgams as a function of their treatment time in the NaCl solution:

1. the emergence of an endotherm associated with the $\gamma_1 \rightarrow \beta_1$ transition (15 days);
2. the disappearance of the δ_2 endotherm; and
3. a rise in the $\gamma_1 \rightarrow \beta_1$ transition temperature with time.

The most noteworthy event is the appearance of the γ_1 endotherm, which in effect splits the single endotherm into two well defined endotherms representing the peritectic transitions of δ_2 and γ_1 , respectively.

It is of interest to note that the rate of progression of the events listed above is slower in the conventional amalgam (Fig. 5) than in the $\gamma_1 + 3$ wt % Sn specimen (Fig. 4). While the presence of a small amount of δ_2 is still evident in the conventional amalgam after 30 days, the $\gamma_1 + 3$ wt % Sn specimen treated for the same time period shows no δ_2 . There is a significant rise in the $\gamma_1 \rightarrow \beta_1$ transition temperature with treatment time in the $\gamma_1 + 3$ wt % Sn specimen. In contrast, this transition temperature remains low ($\sim 112^\circ\text{C}$) in the conventional amalgam even after 45 days, suggesting that a significant amount of Sn is still retained in its matrix γ_1 .

4. Discussion

The 90°C endotherm in a conventional dental amalgam has been generally accepted to be due to a single transition, $\gamma_1 \rightarrow \beta_1$. On the basis of our extensive study [2] on $\gamma_1 + \text{Sn}$ specimens containing up to 4 wt % Sn, we have shown that this is not so. Rather this endotherm represents two overlapping events; namely, the peritectic transformations of δ_2 and γ_1 , respectively. The endotherm associated with the first (δ_2) predominates masking the effect of the second (γ_1) transition. Compared to the enthalpy, ΔH , of the second transition ($\sim 7 \text{ J g}^{-1}$), the larger ΔH ($\sim 10 \text{ J g}^{-1}$) of the overlapping transitions is consistent with our interpretation [2]. The results presented above have

reconfirmed the overlapping nature of the two transitions. By removing Sn from δ_2 and $\gamma_1 + \text{Sn}$, the two endotherms have been separated and resolved.

In addition to clarifying the structural origins of the 90 °C endotherm in conventional amalgams, the data obtained in this study contribute further to a better understanding of a number of phenomena observed in dental amalgams [10–13]. They are:

1. the presence of Sn oxidation products in grain boundaries and pores,
2. intergranular corrosion;
3. corrosion enhanced β_1 formation; and
4. reduction in creep with corrosion.

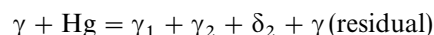
The following discussion is in order to clarify the relationship between these phenomena and the corrosion of solid solution and intergranular Sn in γ_1 .

The corrosion of Sn in dental amalgams is known to form various oxides and oxychlorides of Sn [14]. When exposed to the NaCl solution, the initial tarnishing of all powders was an indication of the formation of these oxidation products. However, these products were somewhat non-adherent and were easily removed during grinding and washing (with the exception of the dental amalgam, all other materials became progressively shiny with continued corrosion). It is conceivable that in a solid amalgam the corrosion products thus formed internally will deposit at grain boundaries and pores. The corrosion of δ_2 , in addition to contributing to these corrosion products, will lead to intergranular separation. The loss of δ_2 , the primary factor in grain boundary sliding, will make the amalgam more resistant to creep. The Hg released from δ_2 due to corrosion of Sn will react with Ag_3Sn forming β_1 and γ_2 . This proposed mechanism, the subject of another study [15], is consistent with the observation that in the presence of a limited amount of Hg (such as that present in δ_2), the reaction between γ and Hg yields β_1 and γ_2 [16, 17].

5. Conclusions

The results obtained in this study have demonstrated unequivocally that the δ_2 phase is an integral part of a conventional amalgam microstructure. Its presence in the Sn–Hg alloy system is no longer an uncertainty [18]. In view of the above observations and considering the profound influence this phase

exercises in the properties and performance of dental amalgams, we propose that the setting reaction of conventional amalgams be revised in accordance with the following equation:



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