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Mechanism of β_1 formation in conventional dental amalgams

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This study reexamined the mechanism of β_1 formation in conventional dental amalgams in the light of a previously unrecognized intergranular structure, the SnHg-δ_2 phase. Two amalgams, A (45.5% Hg) and B (65.0% Hg), were made from a Zn-free alloy of the following composition (wt%): Ag-70, Sn-26, Cu-4. After storage at 37 °C for 1 day, both amalgams were heat treated at 70 °C for up to 16 days. The structural changes in the two amalgams as a function of their heat treatment were characterized by differential scanning calorimetry and X-ray diffraction techniques. On the basis of the experimental data, we have proposed a new mechanism on β_1 formation. This mechanism involves a series of interrelated reactions. The primary one is a reaction between AgSn-γ and δ_2 that leads to the nucleation of β_1 at γ boundaries. Simultaneous operation of several secondary and tertiary reactions result in (1) further growth of β_1 and its continuing change in composition, (2) loss of Sn from the γ_1 matrix, (3) conversion of CuHg into η', and (4) a possible transformation of γ_2 into Sn-rich β_2 or α_2.

1. Introduction

The time-dependent appearance of AgHg(Sn)-β_1 in dental amalgams has been reported [1–6]. The amount of β_1 formed in an amalgam during service may be an indicator of its stability as it has been shown that amalgams with more extensive β_1 formation exhibit poorer clinical performance [7–9]. The elemental composition of β_1, as reported by different authors [6, 8, 10–11], shows a large variation and is within the following range: 36–45% Ag, 47–63% Hg and 0.4–8% Sn. It contains less Hg than AgHg(Sn)-γ_1, the initially formed major matrix phase. The composition of γ_1 is rather well defined in a narrow range and is as follows: 28–32% Ag, 68–72% Hg and 1–2% Sn.

Regarding the origin of β_1, it is thought to be the product of a diffusion-controlled reaction between Ag_3Sn-γ and Ag_2Hg_3(Sn)-γ_1 in which γ_1 readily loses Hg and is transformed into β_1 [1–5]. The driving force for this reaction is postulated to be (1) the thermal and structural instability of γ_1, and (2) the existence of a Hg concentration gradient between γ and γ_1. Until recently, γ_1 was considered to be the lowest melting ($\sim$110 °C) of all constituent phases in dental amalgams.

There is a need to re-examine the above mechanism in view of the detection of a previously unknown phase in conventional dental amalgams [12–15]. This phase, identified as the δ_2 phase of the SnHg system, is located at γ_1 grain boundaries and various interphase boundaries. It is characterized by a low melting temperature ($\sim$90 °C) and appears to be stable only in a Hg-rich environment [12, 16, 17]. Considering that δ_2 is the least stable of all phases in dental amalgams, we have proposed an alternative mechanism of β_1 formation [15]. According to this mechanism, β_1 is primarily the product of a reaction between γ and δ_2. The purpose of the present study was to verify experimentally whether such a relationship between β_1 and δ_2 does indeed exist.

2. Materials and methods

Two amalgams, A and B, were prepared from a Zn-free conventional alloy (New True Dentalloy, S.S. White) which had the following composition (wt %) : Ag-70, Sn-26, Cu-4. The final Hg-contents of the two amalgams were 45.5% and 65.0%, respectively. Amalgam A was prepared in accordance with the manufacturer's recommendation and the American Dental Association Specification 1. Amalgam B was prepared with the requisite amount of Hg but no subsequent condensation was carried out. All amalgam specimens were stored at 37 °C for 1 day following preparation. Thereafter, they were heat treated at 70 °C for up to 16 days. Portions of heat treated specimens were withdrawn periodically and stored at 37 °C for at least 1 day prior to their structural characterization by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques. Specimens stored at 37 °C for 1 day and receiving no heat treatment served as controls.

The DSC technique was used to monitor quantitatively changes in the relative amounts of mainly γ_1, γ_2 and δ_2 as a function of heat treatment. All measurements were carried out in air in the temperature range 35° to 275 °C with a heating rate of 10 °C/min. The furnace temperature was calibrated from time to time using standards of pure tin, indium and lead. The

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XRD technique was used to qualitatively monitor progress in β_1 formation and changes in γ, γ_1, and γ_2. It should be noted that the phases γ and β_1 are isomorphous [1–4]. As a result, their diffraction lines overlap. The decrease in γ is shadowed by an increase in β_1 line intensity. The diffraction pattern of γ_2 is almost identical to that of δ_2 [16, 17]. Therefore, it is difficult to demonstrate the difference between the two by the conventional XRD technique. The XRD analysis was carried out at ambient temperature using CuK_α radiation at 35 KV and 15 mA and within the 2θ range 25 to 45 °. Specimens used for XRD analysis were in powder form (– 325 mesh).

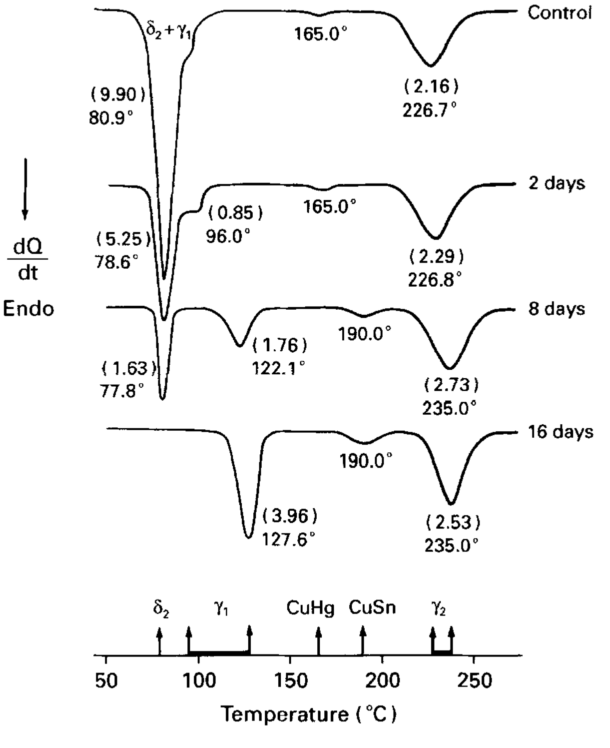

Figure 1 Thermograms of New True Dentalloy (45.5% Hg) amalgam as a function of heat treatment at 70 °C.

3. Results

The thermograms of control and heat treated specimens of amalgam A are shown in Fig. 1. All thermograms exhibit several endotherm peaks. Barring secondary reactions, each peak signals the presence of a certain phase which undergoes structural transformation at the peak temperature. The area under each peak represents the resultant energy change (ΔH = J/gm) which is proportional to the amount of the phase responsible for the endotherm.

The specific phases contributing to various endotherms are indicated at the bottom in the temperature axis of Fig. 1. The two numbers adjacent to each peak describe the following: the top number in parenthesis represents the ΔH value and the bottom the corresponding transformation temperature. The ΔH values for the minor endotherms have not been determined. They include endotherms at 165 ° and 190 °C which are associated with the presence of CuHg and CuSn(η'), respectively [14, 18]. Cu is a constituent of the alloy used in this study.

It is apparent from Fig. 1 that the control specimen contains δ_2, γ_1, CuHg and γ_2. Note that the first endotherm at 80.9 °C is due to two overlapping transformations and is indicative of the presence of both δ_2 and γ_1 [14, 15]. Several gradual changes were seen in these thermograms as a function of heat treatment. They were the following: (1) splitting of the first endotherm into its two components, δ_2 and γ_1; (2) disappearance of δ_2; (3) a significant increase in γ_1 and its transformation temperature; (4) disappearance of CuHg and formation of η'; and (5) an overall increase in γ_2 and an upward shift in its transformation temperature.

The XRD profiles of control and selected heat treated specimens of A are shown in Fig. 2. The

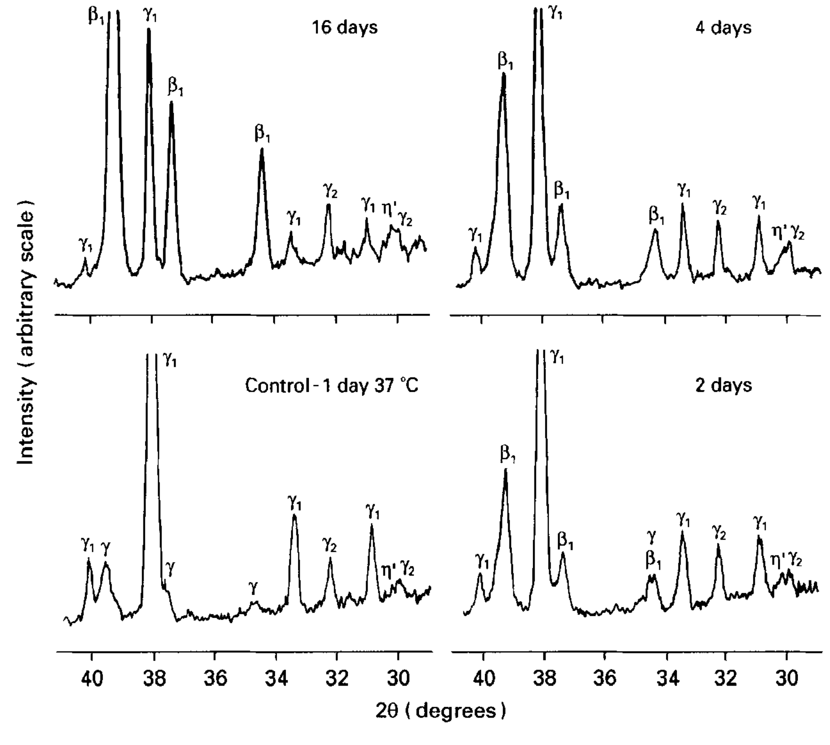

Figure 2 X-ray diffraction patterns of New True Dentalloy (45.5% Hg) amalgam as a function of heat treatment at 70 °C.

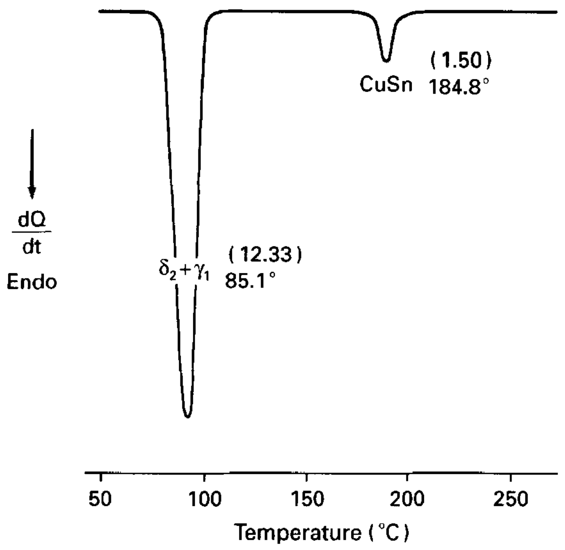

Figure 3 Thermogram of New True Dentalloy (65.0% Hg) amalgam after 1 day at 37 °C.

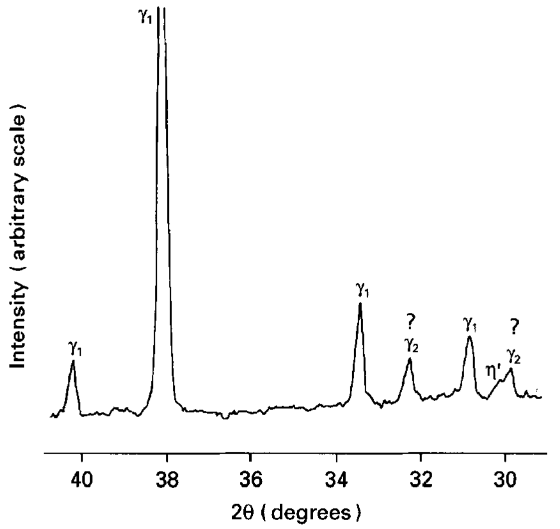

Figure 4 X-ray diffraction pattern of New True Dentalloy (65.0% Hg) amalgam after 1 day at 37 °C.

diffraction pattern of the control specimen is typical of that of a conventional amalgam in that it shows the presence of $\gamma, \gamma_1, \gamma_2$ and η'. It has previously been noted that it is difficult to distinguish between γ_2 and δ_2 using the conventional XRD technique [16, 17]. Thus the lines attributed to γ_2 belong to δ_2 as well. Heat treatment led to the appearance of β_1 and its progressive increase with time. A reduction in γ and γ_1 occurred simultaneously. No attempt was made to evaluate minor changes in γ_2 (or δ_2) and η' lines that occurred during heat treatment.

The thermogram of amalgam B control, shown in Fig. 3, indicates the presence of δ_2, γ_1, and a significant amount of η' in this amalgam. It is of interest to note that this amalgam is γ_2-free. The ΔH value of the first endotherm is about 24% larger than that oberved in amalgam A control. This is consistent with its higher Hg content, which results in the formation of a larger amount of γ_1 and δ_2. With the exception of the following changes, the thermal profile of amalgam B remained essentially unaffected by heat treatment. The changes (not shown) due to heat treatment for 16 days included (1) a 20 % decrease in the ΔH value of the first endotherm, (2) a 7% increase in the ΔH value of the second endotherm (η'), and (3) a 6 °C rise in the transformation temperature of the second endotherm. The lower transition temperature of this endotherm in control B (184.8 °C) is an indication that it is associated with a non-stoichiometric η' phase. Since this phase forms from CuHg [18], we believe it to be deficient in Sn and may contain some Hg [19]. The XRD pattern of amalgam B (Fig. 4) remained the same before and after heat treatment and indicated the presence of γ_1, $\gamma_2(\delta_2)$ and η' but no γ.

4. Discussion

The alternative mechanism [15] we proposed regarding the origin of β_1 is embodied in the following two reactions:

$$\gamma + \text{Hg} \rightarrow \gamma_1 + \gamma_2 + \delta_2 + \gamma\ (\text{R}) \tag{1}$$

$$\gamma\ (\text{R}) + \delta_2 \rightarrow \beta_1 + \gamma_2 \tag{2}$$

The first of these represents the setting reaction of conventional dental amalgams revised in consideration of the δ_2 phase. The second one deals with β_1 formation. In this reaction, Hg from δ_2 diffuses into residual alloy particles, γ (R), forming β_1 and γ_2. In the process, δ_2 itself is transformed yielding additional γ_2. Of the two amalgams studied, control A contained both γ and δ_2 (Figs 1 and 2). Control B was γ-free (Fig. 4) but showed the presence of δ_2 (Fig. 3). According to reaction (2), β_1 formation requires the presence of both γ and δ_2 in the initially set amalgam. The evidence of β_1 in heat treated specimens of A but not in B is thus in agreement with the proposed mechanism. Also in agreement is the observation that β_1 formation is accompanied by a decrease in γ and δ_2 and an increase in γ_2 (Figs 1 and 2).

The above reaction scheme fails to explain the changes in γ_1 seen in amalgam A during heat treatment. Regarding these changes, the results obtained by the two techniques seem to be conflicting in nature. Whereas a significant reduction in γ_1 with heat treatment has been revealed by the XRD data (Fig. 2), the DSC results appear to indicate otherwise (Fig. 1). To clarify that this is not so, we point out that due to overlapping of γ_1 and δ_2 transitions [14], the ΔH value of γ_1 transition (i.e. its amount) in control A cannot be determined. However, it can be estimated and has been calculated on the basis of the following: (1) the ΔH of $\gamma_1 \rightarrow \beta_1$ transition associated with 100% single phase ternary Ag_2Hg_3Sn-γ_1 is 10 J/gm [20], and (2) the volume per cent of γ_1 in a conventional amalgam containing 45.5% Hg is about 60% [21]. The ΔH-equivalent of this volume fraction is 6 J/gm – a value close to that reported for a δ_2-free dispersed-phase amalgam containing 70% Ag [14]. The ΔH value of the γ_1 endotherm in amalgam A following 16 days heat treatment is about 4 J/gm (Fig. 1) suggesting that there is a 33% decrease in its γ_1 content during heat treatment.

In the past, the reduction in γ_1 with β_1 formation has been explained on the basis of a direct $\gamma_1 \rightarrow \beta_1$

transformation theory [1–5]. We question the validity of such an explanation in consideration of the following. The δ_2 phase is structurally and thermally more unstable than γ_1. Moreover, it permeates all grain boundaries and interphase boundaries and is in closer proximity to γ than γ_1. To lower the Hg concentration gradient that exists at γ boundaries, a reaction between γ and δ_2 is more favourable thermodynamically than a reaction between γ and γ_1. To account for the reduction in γ_1 with β_1 formation, we therefore, proposed the following secondary reaction [15] :

$$\gamma_1 + \beta_1 \rightarrow \beta_1' \qquad (3)$$

The above reaction between γ_1 and initially formed β_1 leads to an outward growth of β_1 in the matrix area and a progressive change in its composition (new β_1 is designated as β'_1) with time. The continuing change in the composition of β_1 is rationalized on the diffusion-controlled nature of the above reaction. The driving force for this reaction is the Hg concentration gradient that develops between γ_1 and newly formed β_1 at any instant. As Hg diffuses across β'_1 to lower this concentration gradient, a possible consequence would be the inward growth of β_1' in the interior of residual γ particles. Since the amount of γ_1 in a conventional amalgam far exceeds the amount of γ, it is likely that all γ particles will be consumed with time and some γ_1 will remain untransformed.

This discussion would be incomplete without an analysis of a number of other microstructural changes observed during heat treatment. These changes underscore the microstructural complexity and the structural instability of the as set amalgam and are relevant to the understanding of the mechanism of β_1 formation. One of these changes is the gradual increase in the γ_1 transition temperature signifying loss of Sn from this phase (Fig. 1). The final γ_1 transition temperature (127.6 °C) is close to the reported peritectic transition temperature (127.2 °C) of Sn-free γ_1 [14]. Thus it appears that virtually all Sn is removed from ternary γ_1 in 16 days. This observation is in disagreement with a previous study [22] in which the Sn-content of γ_1 was found to increase with β_1 formation. The upward shift in the transition temperature of the peak identified as γ_2 (Fig. 1) is suggestive of its enrichment with Sn and possible transformation into β_2 and α_2 [17]. The stable transition temperature of this endotherm (235 °C) is close to the melting temperature of pure Sn (231.9 °C). A progressive transformation of γ_2 into higher melting Sn-rich β_2 and α_2 may result from loss of Hg from γ_2. The Hg released in the process may contribute to the formation of β_1. Another interesting observation is the conversion of initially formed CuHg into CuSn-η' (Fig. 1). A possible reaction between CuHg and Sn available from γ_1 and decomposing δ_2 is suggested as an explanation. The upward shift in the η' transition temperature seen in amalgam B due to heat treatment can be attributed to a similar reaction between non-stoichiometric CuSn that forms initially and Sn from δ_2. A reduction in δ_2 and an increase in η' with heat treatment of amalgam B support such an explanation.

The most remarkable observation of the present study is that amalgam B contains δ_2 but no γ_2 (Fig. 3). The unreliability of the XRD technique in characterizing this microstructure is to be noted (Fig. 4). The absence of γ_2 in amalgam B is contrary to the well-accepted mechanism of amalgamation reaction. However, it is consistent with recent studies [12–16] which suggest that in a Hg-rich environment δ_2 rather than γ_2 forms.

5. Conclusions

We have presented experimental data in support of an alternative mechanism to explain the origin of β_1 in conventional amalgams at 70 °C. The mechanism involves a series of interrelated reactions. The first and foremost of these is a reaction between δ_2 and γ that leads to the nucleation of β_1 at γ boundaries. The growth of β_1 and its continuing change in composition follows as a result of a secondary reaction involving Hg diffusion between β_1, γ_1, and γ. Several tertiary reactions involving redistribution of Hg and Sn occur simultaneously leading to (1) loss of Sn from γ_1, (2) conversion of CuHg into η', and (3) a possible transformation of γ_2 into Sn-rich β_2 or α_2. The inadequacy of the XRD technique in characterizing fully these complex microstructural changes has been demonstrated. Further evidence has been gathered (Fig. 3) in support of the existence of δ_2 in conventional amalgams.

As to the origin of β_1, our proposed mechanism is in disagreement with the direct $\gamma_1 \rightarrow \beta_1$ transformation theory. We have pointed out [15], however, that it is consistent with all phenomenological observations on β_1 formation reported previously. They include (1) diffusion controlled nature of this reaction [1–4], (2) nucleation of β_1 at γ boundaries [1–4], (3) gradual disappearance of γ [1–4], (4) partial transformation of γ_1 [1–4], (5) increase in γ_2 [23], (6) corrosion enhanced β_1 formation [7, 8, 24], (7) the variable composition of β_1 phase [6, 8, 10, 11], and (8) reduction in creep and disappearance of grain boundaries [11, 22, 25].

The last phenomenon, in particular, has been perplexing [22] and is inexplicable on the basis of the currently accepted microstructural information on dental amalgams. However, an association between β_1 formation and creep reduction can be readily explained on the consumption of intergranular δ_2 – the phase primarily responsible for creep [14]. In evoking new meaning from these past observations and confirming their validity, the δ_2 phase – the catalyst for β_1 formation has added a new dimension to our understanding of the structural instability in dental amalgams.

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