The matrix phase of a ductile dental amalgam

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In this study, the ternary HgAgSn-γ_1 matrix of a ductile dental amalgam has been characterized and compared with that of a brittle amalgam. Specimens of both amalgams were prepared from commercial alloy powders according to the ADA specification 1, stored at 37 °C and studied by differential scanning calorimetry technique at timed intervals up to 1 year. Experimental amalgams of AgCu eutectic admixed with varying concentrations of Sn were used as standards. The matrix of the ductile amalgam was found to contain two substructures initially. One was saturated with Sn and the other contained lesser amounts of Sn. These substructures disappeared with time leading to a matrix in which Sn was well below its saturation limit but uniformly distributed. The matrix of the brittle amalgam, on the other hand, was saturated with Sn during the entire period of this study.

1. Introduction

There has been a trend towards a reduction in the Ag content of amalgam alloys in recent times. The introduction of Artalloy (Degussa AG, Germany) with about 80% Ag is a significant departure from that trend [1]. Artalloy is a mechanical mixture of two alloys, one spherical and the other lathecut, in the ratio of 80:20. The spherical alloy contains 83% Ag, 15% Cu and 2% Sn, and thus consists of two solid solutions, α-Ag (CuSn) and β-Cu (AgSn). This duplex structure is similar to that of the Ag–Cu eutectic component of Dispersalloy (Johnson & Johnson, USA), a well-known brand [2]. The lathecut alloy is of conventional composition (Ag = 71.0, Sn = 25.7 and Cu = 3.3) and consists mainly of Ag_3Sn.

Other than its high Ag content, another unique characteristic of Artalloy amalgam is its ductility, which has been claimed to be comparable to that of noble metal casting alloys [3]. In contrast, all other amalgams are considered to be brittle—a major deficiency of this type of material [4–6].

The ductility of Artalloy amalgam has been attributed to its high Ag content [1]. Considering that this is a structure-sensitive property, such a compositional explanation is not satisfactory. The available structural information on this amalgam was also found to be not satisfactory to explain its ductile behaviour. To clarify, microstructurally Artalloy amalgam is similar to some other amalgams such as Dispersalloy in that they all contain γ_1, Cu_6Sn_5 and unreacted remnants of original alloy particles [1, 2]. The phase Cu_6Sn_5 is confined to the periphery of the Cu-rich alloy particles. Although there is variation in the relative amounts of these phases in different amalgams, such variation cannot account for the vast difference in their ductility.

The search for the structural origin of the ductility of Artalloy amalgam led to the present study—the purpose of which was to obtain as yet unknown information on its microstructure. In conducting this study, emphasis was placed on the ternary HgAgSn-γ_1 matrix. As the major structural component of all amalgams including Artalloy, this phase has a significant influence on their mechanical behaviour [4–6].

2. Materials and methods

In addition to Artalloy, the other commercial material examined in this study was Dispersalloy. This alloy is a mechanical mixture (2:1) of Ag_3Sn (CuZn) and a AgCu eutectic. It has been noted before that amalgams prepared from this alloy are considered to be brittle. Specimens of both amalgams were prepared according to the ADA Specification 1.

During the course of this study, for structural identification and confirmation, it was necessary to prepare amalgams of AgCu eutectic admixed with varying concentrations of Sn. Tin was introduced in the form of Ag_3Sn. For the sake of brevity, only data pertaining to the following two amalgams will be reported here.

Experimental Amalgam 1 — AgCu:Ag_3Sn:Hg = 27.5:22.5:50.0

Experimental Amalgam 2 — AgCu:Ag_3Sn:Hg = 30:20:50

The two amalgams were prepared in a mechanical amalgamator at 4500 rpm for 15 s. All amalgams were stored at 37 °C after preparation and studied at timed intervals up to 1 year.

A thermoanalytical technique, differential scanning calorimetry (DSC), was used to characterize the microstructure of all amalgams. This technique has been successfully used in revealing many complex ultrastructural details of amalgams that are otherwise

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difficult to resolve by traditional techniques such as light microscopy, Scanning electron microscopy (SEM) and X-ray diffraction (XRD) [7–10]. 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 "fingerprints" of a material or its constituent phases. In this study, the temperature (T) of transitions has been used as the main guide for structural characterization. DSC measurements were carried out in ambient air with a heating rate of 10 °C/min within the temperature range 35° to 250 °C.

3. Results and discussion

For the sake of completeness, we note that in the thermograms presented below, data in the temperature range 150° to 250 °C are not included. This range deals with transitions of CuHg and Cu_6Sn_5, phases that are not the subject of the present study. The presence of both of these was seen in Dispersalloy [9, 10]. Artalloy and the experimental amalgams contained Cu_6Sn_5 but no CuHg. The amount of Cu_6Sn_5 in Artalloy was significantly less than that observed in Dispersalloy.

The thermograms of 1-day-old Artalloy and Dispersalloy are shown in Fig. 1. The two endotherms seen in Dispersalloy are indications of the presence of δ_2 and γ_1 in this amalgam. The phase δ_2 is a SnHg intergranular precipitate which undergoes a peritectic transition at around 90 °C [10]. The γ_1 phase represents the ternary HgAgSn matrix. The endotherm at 112 °C is associated with its transition to β_1. Note that this transition temperature is lower than that ($\sim$ 127 °C) of Sn-free binary HgAg-γ_1 phase. This observation is consistent with our previous study [10] in which it has been shown that Sn dissolved in γ_1 lowers its transition temperature. In Artalloy, two closely spaced endotherms are seen. Similar overlapping peaks in this region were not seen in any amalgams in the past [7–10]. The temperature of the first endotherm (111 °C) is too high to be due to δ_2 transition ($\sim$ 90 °C) [10]. The temperature (117 °C) of the second endotherm is too low to be due to non-equilibrium CuHg phase (150 °C) [9].

To facilitate identification of the structures responsible for the above two endotherms, thermograms of the experimental amalgams are presented in Fig. 2. On it is superimposed the thermogram of 1-day-old Artalloy. The experimental amalgams are associated with a single endotherm resulting from the $\gamma_1 \rightarrow \beta_1$ transition. However, there is a significant (6 °C) difference between the transition temperatures of the two amalgams. On the basis of our previous observation that the transition temperature of the ternary γ_1 is a function of its Sn content [10], this difference is attributed to differences in their matrix Sn content. The matrix in amalgam 1 with a transition temperature of 111 °C is expected to contain more Sn than that in the matrix of amalgam 2 with a higher transition temperature (117 °C). It is of interest to note that the transition temperature of amalgam 1 with high Sn corresponds to the low-temperature transition of Artalloy and the second transition in Artalloy takes place at a temperature identical to the transition temperature of amalgam 2 containing low Sn.

The above observation and analysis leads us to suggest that the two endotherms in Artalloy signify the presence of two different matrix substructures in this amalgam—one with high Sn and the other with low Sn. Considering further that the major source of this Sn is that dissolved from the lathecut Ag_3Sn alloy during amalgamation and that Sn in the vicinity of spherical AgCuSn particles forms Cu_6Sn_5, it is further suggested that the matrix adjacent to the Ag_3Sn particle should contain high concentrations of Sn. On the other hand, low Sn would be the characteristic of the

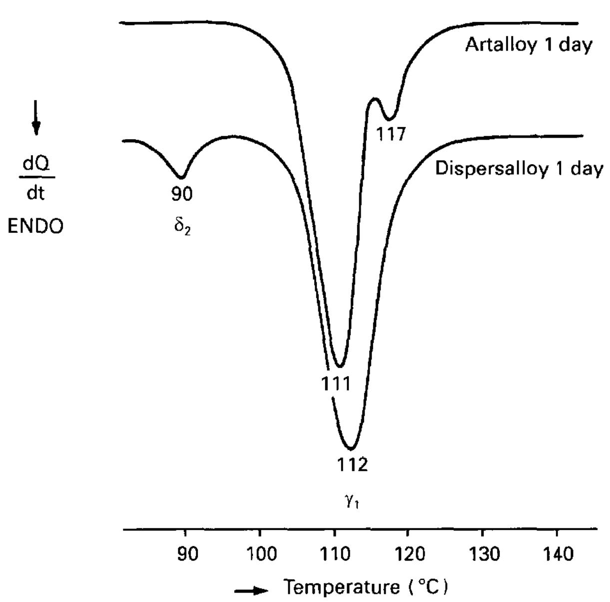

Figure 1 DSC thermograms of Artalloy and Dispersalloy amalgams (1 day).

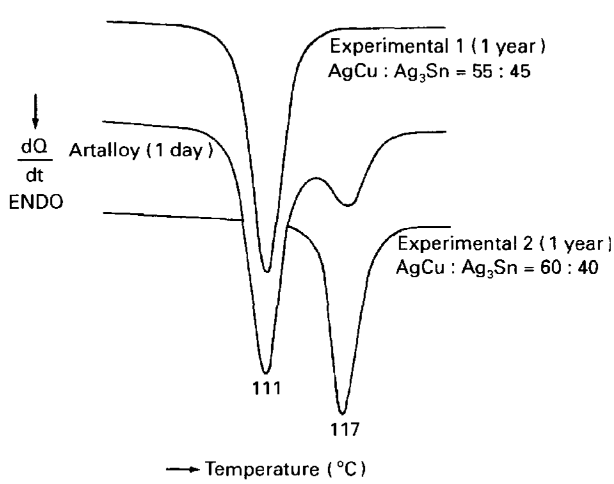

Figure 2 DSC thermograms of Artalloy (1 day) and two experimental amalgams (1 year).

matrix away from Ag_3Sn and adjacent to the AgCuSn particles. In contrast, the single endotherm (112 °C) in Dispersalloy is an indication of a matrix in which Sn is homogeneously distributed. Furthermore, the presence of δ_2 suggests that the matrix is saturated with Sn [10].

The transition temperature of Dispersalloy matrix is 1 °C higher than the first transition in Artalloy. This may seem to indicate that the amount of Sn in Dispersalloy matrix is lower than that in the high Sn submatrix of Artalloy. Because of the preponderance of Ag_3Sn in Dispersalloy and the presence of δ_2, an index of solute saturation, we rule this possibility out. Dispersalloy contains Zn and its relatively high transition temperature of 112 °C results from the presence of Zn in its matrix. The transition temperature of γ_1 is raised by the presence of Zn [11].

In characterizing the Sn content of the two matrices, we have used the terms "high-Sn" and "low-Sn" without any clear definition. The present data do not allow determination of the exact amount of Sn in various matrices. However, some approximations can be made and tentative Sn content can be assigned to "high-Sn" and "low-Sn" matrices on the basis of the following observations: (1) the maximum solubility of Sn in γ_1 is 1% [10]; (2) the lowest temperature of the matrix transition has been recorded to be 111 °C (Fig. 2); and (3) the transition temperature of Sn-free pure γ_1 is 127 °C.

Assuming that the lowest transition temperature of 111 °C represents a matrix saturated with Sn, it is calculated that 1% Sn leads to a depression in the transition temperature of γ_1 by 16 °C. Assuming further a linear relationship between Sn content and the transition temperature, it can be deduced that the "high Sn" and "low Sn" matrices in Artalloy contain 1.0 and 0.625% Sn, respectively. The matrix in Dispersalloy saturated with Sn should contain 1% Sn. It should be stressed that these calculations are approximate and must be verified in future studies.

The existence of a Sn concentration gradient in 1-day-old Artalloy matrix led us to speculate that with time Sn will diffuse from "high Sn" to "low Sn" areas. The thermal data on Artalloy (Fig. 3) studied as a function of time confirm our speculation. Between 1 day and 1 month minor changes were noted in the thermograms of this amalgam (not shown). These changes included a slight decrease (~ 0.3 °C) in the two transition temperatures and a slight reduction (~ 10%) in the low-temperature endotherm peak area. With continued ageing to 2 months there was a complete reversal in the relative ratio of the peak areas associated with the two transitions. At 1 year, the low temperature endotherm disappeared. The transition temperature of the single endotherm that remained was 1 °C higher than that of the original high temperature transition (117 °C). The gradual disappearance of the low-temperature endotherm is consistent with the time-dependent diffusion of Sn and the elimination of its concentration gradient. This diffusion by enriching the "low Sn" matrix with Sn should have lowered the transition temperature of the entire matrix to a value between 111° and 117 °C. This is not the case, however. We attribute this to the effect of Cu in AgCuSn which, because of its affinity for Sn, scavenges part of the Sn away from the matrix area. The 118 °C transition temperature of the 1-year-old Artalloy matrix represents an estimated Sn content of 0.563%.

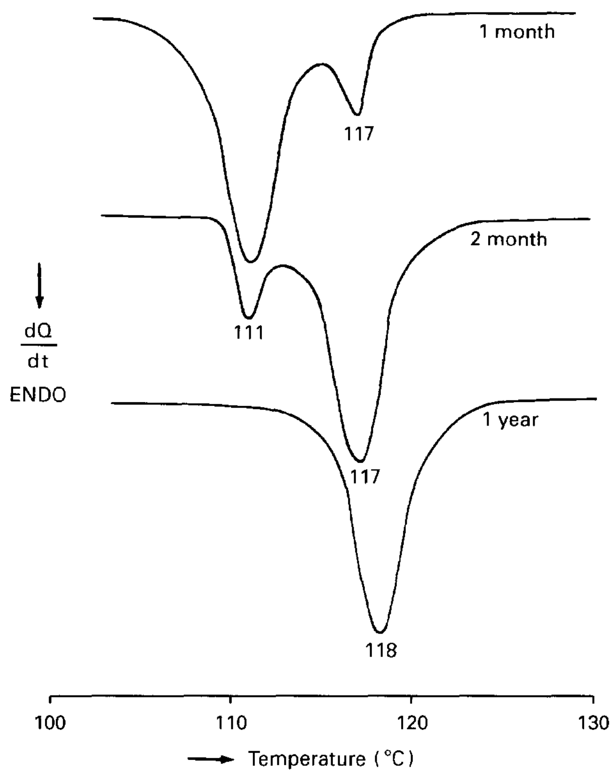

Figure 3 DSC thermograms of Artalloy amalgams as a function of ageing at 37 °C.

The diffusion of Sn was also indicated in the disappearance of δ_2 in aged Dispersalloy through a reaction between δ_2 and CuHg [9]. However, the matrix transition temperature remained the same (112 °C) up to 1 year suggesting that the Sn content of the matrix was essentially unchanged during this time.

4. Summary and conclusions

Compared to other amalgam alloys, the amount of Sn in Artalloy is low (6.7%) and most of this Sn is contained in the minor component—the Ag_3Sn alloy. Only a part of this Sn is released in Hg during amalgamation. The conditions of amalgamation used in this study (4500 rpm, 10 s mixing time) do not allow uniform distribution of Sn in the matrix initially. The ternary HgAgSn-γ_1 matrix in the early stage consists of at least two different sub-matrices. One of these appears to be saturated with Sn and is presumed to be adjacent to the Ag_3Sn particles. The other, which is away from the Ag_3Sn area and closer to the AgCuSn particles, shows lesser amounts of Sn. With time, Sn has been found to diffuse across its concentration gradient leading to a uniform low matrix Sn concentration. In contrast, the matrix in Dispersalloy is saturated with Sn all the time.

It appears that the amount of Sn in Artalloy is too low to saturate its matrix. It is plausible that the ductility of Artalloy is indirectly attributable to this unique Sn unsaturated matrix which precludes intergranular segregation—the direct cause of brittleness in dental amalgams.

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