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Note

CAN DSC BE USED TO IDENTIFY MERCURY-CONTAINING PHASES IN DENTAL AMALGAMS?

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In a recent paper by El-Hadary et al. [1], the microstructure of dental amalgams has been characterized by differential scanning calorimetry. The authors have concluded that, depending on the nature of the microstructure, the presence of either γ_1 or γ_2 or both in dental amalgams can be identified by this technique. The information available in the literature and our own work reported here strongly indicate that some of the above conclusions are based on insufficient evidence and improper interpretation of data. Therefore, to avoid future confusion it is appropriate that they be discussed, clarified and corrected accordingly.

To illustrate our point, DSC curves of three materials: (a) a γ_2-containing dental amalgam (Cresilver, Cresent Dent. Mfg. Co., Lyons, Illinois; 75% Ag content; Hg: Alloy = 1 : 1), (b) $\gamma_1 - Ag_2Hg_3$, and (c) $\gamma_2 - Sn_8Hg$ are shown in Fig. 1. Thermal analysis of these materials and some others reported later was performed in air using a Mettler TA 3000 system. The heating rate was 10 deg/min.

The amalgam used in our study represents a typical lathecut dental amalgam, although the brand is different from that used by the above authors. Since its DSC curve (Fig. 1a) bears a close resemblance to Fig. 1 in the aforementioned paper, this amalgam forms a valid basis for discussion and comparison. It is apparent from Fig. 1b that γ_2 is characterized by a single endotherm peak at around 210°. This temperature is close to the decomposition temperature (213.9°) of γ_2 as indicated in the Sn–Hg phase diagram [2]. The decomposition temperature (120°) of γ_1, shown in Fig. 1c, is also close to that (127°) reported for the peritectic transition of γ_1 [3]. A comparison of the three curves makes it obvious that the 80° endotherm present in conventional dental amalgams can be attributed to neither γ_1 nor γ_2.

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To determine the structural origin of this endotherm, the microstructure of dental amalgams has been studied at great length in our laboratory. The details of this study will be reported in a future paper. The major findings are presented here to address only those questions raised by our observation that the 80° endotherm is not an evidence of the presence of γ_2 in dental amalgams as has been suggested by El-Hadary et al.

On the other hand, it has been determined by us that this endotherm has its origin in a structure not previously identified (evidence follows). This structure occurs at grain boundaries and interphase boundaries in all conventional dental amalgams. A fractional liquefaction technique was used to extract these segregations. The technique involved compressing (180 MPa) the dental amalgam in a stainless steel mold at 80° for 15 mins. The resultant liquid flowing out of the mold was collected and was allowed to cool to ambient temperature (22°). The DSC curve of the extract is shown in Fig. 1d. A comparison of Fig. 1d with Fig. 1a clearly establishes that the 80° endotherm is an effect of fusion of the segregated structure and not due to γ_2.

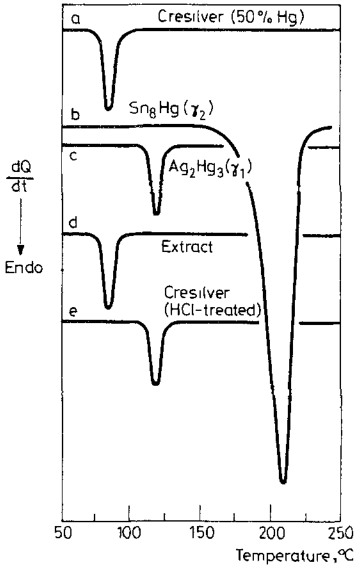

Fig. 1 DSC curves of a conventional dental amalgam and related materials

While the phases present in this segregation remain to be identified, it is of interest to note that the extract at room temperature is a mixture of both liquid and solid phases. The Hg-rich liquid, the predominant phase is likely to be a solution of Ag, Sn and Hg [4]. The solid containing Sn and Hg can very well be a mixture of ε and δ phases present in the Sn–Hg system [2]. Note that the peritectic decomposition temperatures of the two phases are 58° and 91.4°, respectively. It is also noteworthy that the 80° endotherm lies between these two temperatures.

With reference to Fig. 1a, the absence of any endotherm characteristics of γ_1 and γ_2, the major mercury-containing phases in conventional dental amalgams is puzzling, and requires an explanation. Since both γ_1 and γ_2 are surrounded by segregation which contain liquid Hg, it is reasonable to assume that both these phases are in equilibrium with Hg. During heating, the melting of the solid component of this segregation, it is conceivable, releases Hg. This Hg together with the Hg already present will diffuse into adjacent γ_1 and can certainly dissolve it. Such dissolution of γ_1, can occur athermally i.e. without any external energy. No separate endotherm related to γ_1 decomposition has, therefore, been observed. The dissolution of γ_1, which contains about 73.0% Hg and is the predominant phase in dental amalgams, on the other hand, releases a considerable amount of Hg. This in turn can catalyze the destabilization of γ_2. The non-existence of a separate γ_2 endotherm peak can thus be explained. The above mechanism is, in principle, very similar to the one proposed by El-Hadary et al. However, it should be stressed that the source of Hg, the initial catalyst for this chain of transformations, is the newly identified segregated structure and not γ_2 as has been suggested by these authors.

It follows from above that the athermal decomposition of γ_1 can be prevented if amalgams are freed from segregations prior to their thermal analysis. To confirm this speculation segregations were removed from amalgam (a) by short term treatment in a 5% HCl solution. Prior to the acid treatment, the amalgam was pulverized. The thermogram of such a sample (−325 mesh) is shown in Fig. 1e. Note the virtual absence of the 80° endotherm and the appearance of the γ_1 peritectic endotherm. This observation is consistent with the mechanism proposed in the previous paragraph on the non-existence of γ_1 and γ_2 endotherms in Fig. 1a.

These results can be extrapolated to explain the thermal behavior of high copper dental amalgams as well. The absence of the 80° endotherm in Sybraloy and Hg-lean Dispersalloy, as reported by El-Hadary et al., is an indication that these amalgams are virtually free from segregations that give rise to this endotherm. It is known that in high copper amalgams, Cu, because of its strong affinity for Sn, forms Cu_6Sn_5 and prevents the formation of γ_2 [5]. It appears that the elimination of segregations is affected by essentially the same mechanism and occurs concurrently in which Cu scavenges Sn, one of the elements of segregation, away from grain boundaries and interphase boundaries. The coincidence of the two phenomena, absence of γ_2 and elimination of segregations, is to be noted.

However, to be effective in preventing segregations, an optimum amount of Cu must be present to combine with all Sn released during amalgamation. The amount of Cu available in the amalgamated mass is controlled by a number of factors including the composition of the alloy and the residual Hg-content [6]. In amalgams fabricated from alloys containing relatively low concentrations of Cu (12–13%), the potential for the formation of segregation exists when the Hg-content exceeds a certain critical value, characteristic of the specific amalgam [7, 8]. DSC work in our laboratory has indeed confirmed the presence of segregations in a number of Hg-rich high copper amalgams. The thermal behavior of one such amalgam as a function of its Hg-content is shown in Fig. 2 as an evidence. The amalgam is made from a single composition ternary alloy (Aristaloy CR, Engelhard Industries, Carteret, N.J.) containing about 13% Cu.

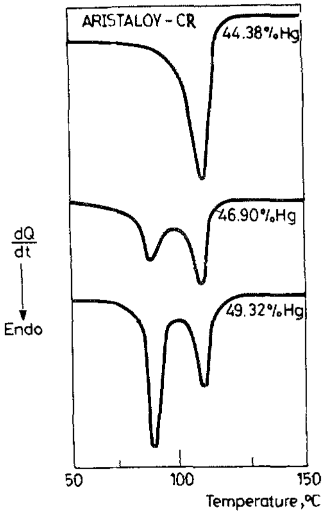

Fig. 2 DSC curves of a high-copper dental amalgam as a function of its Hg-content

Segregations extracted from a number of Hg-rich high copper amalgams have been found to be very similar to those from conventional amalgams, and exhibit the same characteristic endotherm peak as seen in Fig. 1d. The presence of the 80° endotherm peak in the Hg-rich Dispersalloy observed by El-Hadary et al. should therefore be attributed to these segregations and not to γ_2. The absence of such an endotherm in Hg-rich Sybraloy observed by these authors and confirmed in our laboratory can be explained by its high Cu content (30%). As the amount of copper increases, the chances for the formation of segregations are minimized.

Referring to the DSC curves of Hg-rich Dispersalloy in the above paper, it is of interest to note that in spite of the presence of segregations, the γ_1 endotherm persists. This behavior is in contrast to that observed in conventional amalgams. The heterogeneous nature of Dispersalloy microstructure has been suggested as a possible explanation. Considering that the microstructure of all amalgams is highly heterogeneous and the co-existence of both endotherms is possible even in a socalled 'homogeneous' ternary alloy (Fig. 2), the above explanation cannot be tenable. Therefore a different explanation is offered below. This explanation is based on the observation that with an increase in the 80° endotherm peak, the γ_1 endotherm peak decreases (Fig. 2).

As noted before, the absence of the γ_1 endotherm does not suggest that this phase is absent but rather is evidence that the decomposition of γ_1 is a non-thermal process occurring at a temperature below its peritectic transition point. This decomposition of γ_1 has been attributed to the dissolution of γ_1 in Hg. There is reason to believe that a significant amount of Hg is necessary to destabilize γ_1. This in turn is dependent on the volume fractions of segregations—the source of Hg. For lack of suitable control, the volume fractions of these segregations in different amalgams have not been determined yet. However, for a constant mass, the area under the 80° endotherm (ΔH) is proportional to the volume fraction. It has been observed that this area is different for different types of amalgams. For a number of conventional amalgam studied, where γ_1 endotherm is always absent, the minimum (ΔH) has been found to be around 10 J/g. In γ_2-free dental amalgams showing both endotherms, the maximum ΔH is around 4 J/g. It appears therefore that when the volume fraction of segregation is below a certain critical level, $4\ \mathrm{J/g} < \Delta H\mathrm{cr} < 10\ \mathrm{J/g}$, necessary for the destabilization of γ_1, the γ_1 endotherm can persist.

The above discussion leads to the following answer to the question raised in the title of this note. For the amalgams tested, the differential scanning calorimetry technique was not able to identify the presence of γ_2 although it did identify γ_1 in certain situations. The technique is, however, extremely sensitive in detecting and quantifying Hg–Sn–Ag segregations in dental amalgams. Since in the past these segregations have eluded detection by such conventional techniques as optical and electron microscopy and X-ray diffraction, it is perhaps justified to conclude that the DSC may be the only viable tool to characterize segregations in dental amalgams.

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