

IDENTIFICATION OF MERCURY-CONTAINING PHASES IN DENTAL AMALGAMS BY DIFFERENTIAL SCANNING CALORIMETRY

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Differential scanning calorimetry was used to differentiate between γ_1 and γ_2 phases in dental alloys. Four different types of dental amalgams were examined: conventional lathe cut alloy, conventional spherulite alloy, non- γ_2 dispersalloy and ternary alloy (sybralloy).

The results showed that the non- γ_2 alloy produced a characteristic endotherm around 105°C, which is 20–30°C higher than that of the conventional alloys.

This method is not only a simple means of identifying the presence of dominant γ_2 phases in dental amalgams, but also serves to check the homogeneity of phase distribution in alloy particles.

Dental amalgams have been common materials in the dental profession for about a century. One of the common amalgam-preparing materials is the silver–tin alloy commonly termed γ -alloy, which is an intermetallic compound of composition Ag_3Sn . When this alloy is heated, a liquidus phase starts to appear at around 470° [1]. Mixing with mercury yields an amalgam with the desired workability. Chemically, in addition of the original alloy, two phases appear: a mercury-rich silver–mercury phase, normally designated the γ_1 phase, with composition Hg_3Ag_2 , and a mercury-lean tin–mercury phase, normally designated the γ_2 phase, with composition Sn_{7-8}Hg [2].

It has been found that the weakest phase in amalgam restoration is the γ_2 phase and thus the present state of the art is to eliminate formation of the γ_2 phase in order to improve the durability of the amalgam restoration [3]. This is achieved by introducing copper into the alloy so that the γ_2 phase can react with copper to form a Cu–Sn intermetallic compound; mercury combined with Sn then reacts with silver to produce more γ_1 phase. Cu_7Hg_6 is not easily formed in such systems at room temperature, since the solubility of Cu in Hg is less than the solubility of Ag in Hg by a factor of 10. Thus, copper can be included in the original Ag–Sn alloy to yield either a ternary mixture or an admixture of Ag–Cu eutectic mixed physically with the Ag–Sn alloy in what is called dispersalloy [4].

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So far very little work has been published on the mechanism of elimination of the γ_2 alloy [5, 6]. Furthermore, it is not easy to check the quality of the non- γ_2 alloy except either by X-ray diffraction or by the laborious method of etching and microscopic examination.

Thermal analysis has been used to characterize the components of dental materials and components of tooth structure, but, when applied to amalgams, it failed to differentiate between γ_1 and γ_2 phases in dental alloys [7, 8]. In this communication we report a simple method for characterizing both conventional and non- γ_2 alloys, using differential scanning calorimetry (DSC). Information can also be obtained about the homogeneity of distribution of composition throughout the particles.

Experimental

Four types of dental alloys were used as follows:

(a) Conventional lathe cut alloy (Amalcap) from Vivadent Co., zinc-free, capsulated, Ag content 70%, the recommended alloy mercury ratio being 1:8.

(b) Conventional spherallloy from Kerr Co., zinc-free, capsulated, recommended alloy mercury ratio 1:1.

(c) Non- γ_2 dispersalloy from Johnson & Johnson, composed of 2 parts by weight of conventional lathe cut alloy and 1 part of spherical particles of silver-copper eutectic Cu_6Ag_5 (71.9% Ag, 28.1% Cu). It contains zinc capsulated, and the recommended alloy mercury ratio is 1:1.

(d) Ternary alloy (Sybralloy), Ag-Cu-Sn alloy (spherical particles), zinc-free, capsulated, recommended alloy mercury ratio 1:1.

The amalgam alloys were triturated mechanically in an S. S. white cap master amalgamator [9] according to the instructions recommended by each manufacturer and then manually pressed in a standard mould to produce a pellet of dimensions 1 X 2 mm. The samples were placed in a covered aluminium crucible in a DSC cell of a Heraeus TA 500 thermal analysis system with a Pt-100 temperature sensor thermocouple. The sample was measured against a reference, which was an empty aluminium crucible. The temperature range used was 30–180°, with a heating rate of 5 degree/min, but a heating rate of 10 degree/min was also used to check its effect on the produced results. The heating rate was found to affect neither the location nor the area of the peak. This observation was different from previous literature reports [7, 8]. The thermal curves were made for both fresh and aged samples.

Results and discussion

The DSC curves showed endothermic peaks for conventional alloys at around 80°. This endotherm for the lathe cut alloy had an onset at 82° and a maximum at 86°,

while for the spheralloy it had an onset at 78° and a maximum at 82°. The areas of the two peaks were the same for the same sample weights (Fig. 1).

The non- γ_2 amalgams showed endothermic peaks at around 110°. Thus the dispersalloy had an onset at 104° with a maximum at 112°, while the ternary alloy (sybralloy) had an onset at 104° with a maximum at 108° (Fig. 2). Such patterns did not show significant changes upon aging of the samples.

In order to find a plausible explanation for the difference in phase behaviour of the non- γ_2 and the conventional amalgams, experiments were made with samples which were rich and lean in mercury content as compared to the recommended ratios.

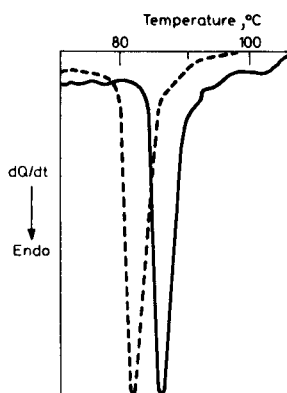


Fig. 1 Differential scanning calorimetric curves of two conventional amalgams: ——— Amalcap, - - - - spheralloy

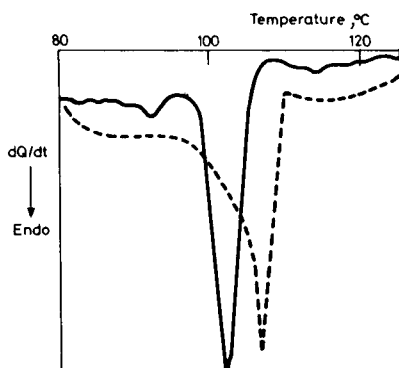


Fig. 2 Differential scanning calorimetric curves of two non- γ_2 amalgams: ——— sybralloy, - - - - dispersalloy

For the dispersalloy it was found that the mercury-rich mixture showed two endotherms, one with an onset at 85° and maximum at 88°, and the other with an onset at 110° and maximum at 114° (Fig. 3).

For the sybralloy, neither the mercury-rich nor the mercury-lean mixture showed extra endotherms or change in peak position (Fig. 4).

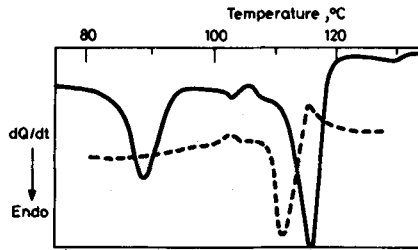


Fig. 3 Differential scanning calorimetric curves of dispersalloy: ——— rich in mercury, - - - - poor in mercury

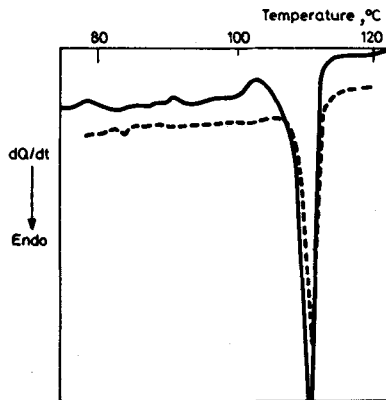


Fig. 4 Differential scanning calorimetric curves of sybralloy: ——— rich in mercury, - - - - poor in mercury

In order to rationalize the results, one has to consider detailed phase diagrams (either ternary or quaternary diagrams), which makes the analysis of the results extremely complicated. A much simpler, yet accurate approach is to consider the distinct phases which form upon trituration, and then treat those as separate phases, assuming that equilibrium is not established between the different phases during the heating time at such low temperatures where the diffusion rate is expected to be small. This situation would be feasible after the amalgamation process and the appearance of the plastic mass. During the heating of the samples in the DSC apparatus,

which takes about 15 min for the whole temperature rise range (from 30 to 115°), quasi-equilibrium between the phases might exist only near the temperatures where liquid phases do exist. The two important phases which form after amalgamation are the Ag_2Hg_3 (γ_1) phase and the Sn_{7-8}Hg (γ_2) phase.

We shall focus attention on the Ag–Hg binary phase diagram, the Sn–Hg binary phase diagram and the Ag–Sn–Hg ternary diagram. The following phases might exist:

For conventional alloys: Ag_3Sn (γ_0), Ag_2Hg_3 (γ_1) and Sn_{7-8}Hg (γ_2).

For dispersalloy and sybralloy: Ag_3Sn (γ_0), CuAg , Ag_2Hg_3 (γ_1), Sn_{7-8}Hg (γ_2), Cu_7Hg_6 (γ_3), Cu_3Sn (ϵ) and Cu_6Sn_5 (η_1).

Considering the Sn–Hg phase diagram, one finds that for the composition Sn_{7-8}Hg liquid starts to appear at about 85°. Thus, the endotherm at around 80° is correlated to the transformations involving the γ_2 phase. On the other hand, upon considering the Ag–Hg diagrams, one sees that the temperature at which liquid starts to appear is 127°. One might thus explain the endotherm at around 108° by the appearance of liquid phases during the decomposition of the γ_1 phase.

Furthermore, the results indicate that for the conventional alloys the γ_1 phase is formed intact with the γ_2 phase. On increase of the temperature, the decomposition of γ_2 takes place so that diffusion of the liquid would take place concurrently through the solid matrix. As a consequence of such a process, decomposition of the γ_1 phase would take place, leading to a homogeneous distribution of Ag–Hg compound throughout the matrix alloy. This would explain the non-existence of a higher-temperature endotherm of a separate γ_1 phase transformation in the conventional alloys.

On the other hand, the non- γ_2 alloys do not show the endotherm at around 80°, but the higher-temperature endotherm occurs at temperatures of 103–108°, which is lower than the phase transformation temperature of the pure γ_1 phase (127°). The lowering is attributed to the solid solubility of the Sn–Hg compound in the γ_1 phase, which would lead to the decrease of the temperature at which liquid appears on the Ag–Hg phase. In the case of dispersalloy, due to the presence of isolated particles of AgSn and AgCu , phase segregation (isolation) of γ_1 and γ_2 occurs upon increase of the mercury content, since the AgCu particles form only the γ_1 phase, but AgSn can form both γ_1 and γ_2 , which would lead to the appearance of both the low- and high-temperature endotherms characteristic of γ_2 and γ_1 , respectively. This is in agreement with previous work on the influence of the mercury content on the formation of the γ_2 phase [11, 12].

In the case of ternary alloy we failed to produce a low-temperature endotherm by enriching with mercury. This is understandable since in the system all particles are of homogeneous composition which might contain phases like Ag_3Sn (γ_0), Cu_3Sn (ϵ), Cu_6Sn_5 (η), $\beta\text{-AgSn}$ (β), Ag (α), Sn or Cu, depending on the composition. Such a homogeneous distribution of phase throughout the particles would render phase segregation in some particles unlikely once the liquid mass traverses the whole matrix. In support of this view it was found that, in all the sources, once those phases are decomposed the endotherm can not be obtained by cooling and reheating.

Looking at the ternary isothermal section of the Ag–Sn–Hg diagram, one finds a wide range of solid coexistence of γ_1 and γ_2 , either with γ_0 or with Hg [13].

In summary it could be concluded that:

1. In systems with a homogeneous distribution of phases throughout the particles it is possible only to identify either the γ_2 or the γ_1 phase. The γ_2 would be identified with an endotherm at around 80° for systems containing a significant quantity of this phase (conventional alloys). The γ_1 phase would be identified with an endotherm at around 105° for systems containing a small quantity of γ_2 phase (non- γ_2 alloys).

2. For systems with inhomogeneity of distribution of phases through the particles, like dispersalloys, it is possible to obtain both endotherms, depending on the quantity of mercury.

This method is not only a simple means of identifying the presence of dominant γ_2 phases in dental amalgams, but also serves to check the homogeneity of phase distribution in alloy particles.

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Zusammenfassung – DSC wurde zur Unterscheidung zwischen γ_1 - und γ_2 -Phasen in Zahnfüllungslegierungen herangezogen. Vier verschiedene Typen von Dentalamalgamen wurden untersucht: konventionelle "lathe cut"-Legierungen, konventionelle "spherally", Nicht- γ_2 -disperslegierung und ternäre Legierung ("sybrally"). Die Nicht- γ_2 -legierung ergibt ein endothermes Signal bei 105° , das um $20\text{--}30^\circ$ höher liegt als bei den konventionellen Legierungen. Diese Methode ermöglicht nicht nur die Anwesenheit von γ_2 -Phasen in Dentalamalgamen auf einfache Weise festzustellen, sondern dient auch zur Prüfung der Homogenität der Phasenverteilung in Legierungspartikeln.

Резюме – Дифференциальная сканирующая калориметрия была использована для определения различий между γ_1 и γ_2 фазами в четырех различных зубных сплавах: обычных сплавах, отшлифованных на токарном станке, обычном сферическом сплаве, нерассипном- γ_2 сплаве и тройном сплаве. Результаты показали, что нерассипной- γ_2 сплав показывает характерный эндотермический пик около 105° , который на $20\text{--}30^\circ$ выше такового в обычных сплавах. Метод позволяет не только просто идентифицировать наличие доминирующих γ_2 фаз в зубных амальгамах, но также служит для проверки гомогенности фазового распределения в частицах сплава.