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DYNAMIC THERMAL EXPANSION AND SCANNING CALORIMETRY OF MERCURY PHASES IN DENTAL AMALGAMS

S. H. Kandil, A. S. El-Kady, M. A. El-Gamal* and *S. E. Morsi*

DEPT. OF MATERIALS SCIENCE,
INSTITUTE OF GRADUATE STUDIES AND RESEARCH AND
*DEPT. OF CONSERVATIVE DENTISTRY, FACULTY OF DENTISTRY;
ALEXANDRIA UNIVERSITY, ALEXANDRIA, EGYPT

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Thermomechanical analysis, TMA, was used to evaluate the linear thermal expansion coefficient, α, of four different types of dental amalgams: Conventional lathe-cut alloy, conventional spheralloy, high copper dispersalloy and high copper ternary alloy. Dynamic thermal expansion studies showed an interesting contraction behaviour around 85 °C for conventional amalgams and 105 °C for high copper amalgams which coincided with the endotherms produced by differential scanning calorimetry, DSC, and was attributed to the existence of the γ_2 and γ_1 phases, respectively. Pure single phases were prepared and characterized by DSC at 210 °C for γ_2 and 120 °C for γ_1. When the γ_2 was enriched with mercury, the decomposition endotherm showed gradual shift to lower temperatures and reached 85 °C. The value of the linear coefficient of thermal expansion ranged between 15 and 35 ppm/°C for all the investigated brands.

Thermomechanical analysis has confirmed previous results achieved by DSC in characterizing mercury-containing phases in dental amalgams.

Previous work has been undertaken to investigate the different mercury-containing phases in dental amalgams by differential scanning calorimetry DSC [1]. Conventional and high copper amalgams showed endothermic peaks around 84 and 107° respectively.

In high copper amalgams (the so called non γ_2 amalgams), the slightly higher endotherm appearing around 107° was attributed to the existence of γ_1 phase. The endothermic peak in conventional amalgams appearing around 84° was attributed to the presence of the γ_2 phase and not representing a separate phase by itself. Both endotherms were obtained for systems of high copper amalgam having inhomogeneity in the microstructure.

Several high copper single composition alloys exist where the amount of γ_2 in their respective amalgams can be varied by changing the final mercury content. As

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the final amount of mercury is increased, and at a specific mercury content, a transition occurs from γ_2 free state to a γ_2 containing state. The γ_2 phase affected the corrosion behaviour while the γ_1 grain boundaries influenced the creep behaviour [2].

Other workers [3] identified the γ_1 phase by DSC while failed to identify the presence of γ_2 in specific amalgam alloys. They attributed the low temperature peak to the extremely high sensitivity of the DSC technique in detecting and quantifying Hg–Sn–Ag segregations in dental amalgams.

The dimensional stability of amalgams is an important aspect in clinical behaviour. Most of the previous research on dimensional stability has dealt with the dimensional change that occurs during hardening within the first 24 hours and with the different coefficient of thermal expansion of the amalgam restoration (25 ppm/deg) and the tooth (10 ppm/deg). Phase changes in amalgam restoration were found to result in dimensional changes. As observed clinically, these dimensional changes partly cause some of the extrusion of amalgam restorations [4].

The isothermal setting up of the various types of alloys when mixed with mercury showed different characteristic dimensional change curves depending on the microstructure of such alloys [5]. The lathe-cut conventional low copper amalgam and the admixed high copper dispersion amalgams showed the classical picture of dimensional change in which the specimen undergoes an initial contraction for about 40 minutes after the beginning of trituration, and then begins to expand. The spherical conventional low copper amalgams and the ternary unicomposition spherical high copper amalgam showed dimensional changes in the form of contraction only.

Although numerous authors [6, 7] have investigated different aspects of the design of amalgam restoration, no references have been found where the mechanical effects of the amalgam setting (i.e. prestress) and thermal expansion have been correlated. In a finite element stress analysis of class I amalgam restoration subjected to setting and thermal expansion, it was concluded that these effects can produce significant stresses and distortion of tooth structure regardless of those caused by imposed loading such as masticatory forces [8].

In the present study, a dynamic thermomechanical study was carried out on conventional and high copper amalgams. The linear thermal expansion coefficient was correlated to the phase behaviour of the materials. Pure single amalgam phases were prepared and studied with the objective of determining the structural origin of the transitions occurring in both DSC and TMA investigations.

Materials and methods

Materials

Types of amalgams used are presented in Table 1.

Table 1 Composition of alloys used in the amalgam formation

Material	Manufacturer	Particle form	Approximate composition, %				Mercury alloy ratio
			Ag	Sn	Cu	Zn	
Amalcap	Vivadent Lichtenstein	Lathe-cut	70	25.8	2.4		1:8
Spheralloy	Kerr Michigan, USA	Spherical	69.8	24.0	4.5		1:1
Dispersalloy	Johnson and Johnson New Jersey, USA	Blend*	68.9	18.5	11.3	0.75	1:1
Sybralloy	Kerr Manufacturing Europe, Scafati, Italy	Spherical	41.4	30.8	27.6		1:1

* Composition is a mixture of two comminuted alloys: one powder having the conventional flake shaped particles based on Ag, Sn, the other powder of spherical Ag–Cu alloy.

Preparation of amalgam specimen

Amalgam alloys were triturated mechanically in an S. S. White cap master amalgamator according to the instructions recommended by each manufacturer. The amalgam was then manually pressed in a standard mould to produce a pellet of dimensions 1 × 2 × 2 mm for DSC measurements or a cylinder, of 4 mm diameter and 8 mm height, for TMA measurements.

Preparation of single phases

Pure γ_1 and γ_2 phases were prepared using the methods previously reported in literature [7, 8].

Thermal measurements

Thermomechanical analysis

A Heraeus TMA 500 dilatometer was used. The sample temperature was monitored by means of a NiCr–Ni thermocouple fitted in a sample holder of standard design which was made of quartz. The linear expansion coefficient was calculated on the assumption that the quartz expansion coefficient has an insignificant effect on the measured values. The heating rate used was 5 deg/min, in the temperature range 20–150°. Samples were measured 24 hours after the start of the mixing.

DSC measurements

The samples were placed in aluminium lidded pans in a Heraeus DSC cell connected to a Heraeus DTA thermal analyser. A Pt–100 temperature sensor was used while the heating rate was kept at 5 deg/min in the temperature range 30–300°.

Results and discussion

The measurements of the thermal expansion coefficients for the four types of amalgam showed specific characteristic contractions at varied temperatures while they were linearly increasing in the temperature range of 20–150° (Fig. 1).

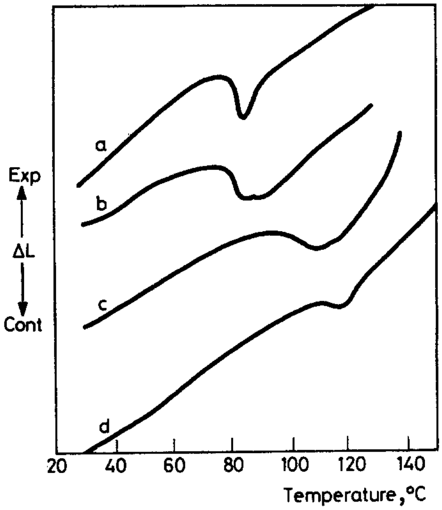

Fig. 1 Thermomechanical measurement of the various types of dental amalgams over the temperature range 30–160 °C. a: Amalcap, b: Spheralloy, c: Dispersalloy, d: Sybralloy

The values of the linear expansion coefficients varied from one type of amalgam to the other. Each amalgam showed a value for the linear thermal expansion above the contraction temperature different from the value obtained below the contraction temperature (Table 2).

Generally, the thermal coefficient of expansion has increased at temperatures above the transition temperature except in the case of the lathe-cut conventional

Table 2 Dimensional changes for the conventional and high copper amalgams in the temperature range 20–150 °C

Type of amalgam		First phase of expansion, α, ppm/deg	Range of transition, °C	Amount of contraction, %	Second phase of transition, α, ppm/deg
Conventional	Lathe-cut	25.5	70– 93 (87)	0.032	15.6
	Spherical	14.0	67–100 (83)	0.025	20.0
High copper	Dispersion	15.6	90–117 (107)	0.017	35.7
	Ternary spherical	18.5	90–113 (105)	0.007	25.0

amalgam. This would indicate a general loss of binding strength along the matrix as a result of this transition.

The most interesting finding in the thermomechanical behaviour of all investigated types is the occurrence of contraction at lower temperature in the case of the conventional amalgams when compared with the high copper ones. Thus in conventional amalgams (Amalcap and Spheralloy) the contraction minima appeared at 87 and 83° respectively, while in the high copper amalgams (Dispersalloy and Sybralloy) the contraction minima appeared at 107 and 105° respectively. When the samples were cooled and reheated, this contraction behaviour disappeared.

This agrees well with previous findings [1] for the same amalgams based on DSC studies where endothermic peaks around 80° in conventional amalgams were attributed to transformations associated with the presence of the γ_2 phase. For the high copper amalgams, the endotherms appearing around 108° were attributed to the decomposition of the γ_1 phase.

It is possible to extend the same interpretation to the observation of the dimensional contraction which may involve interphase diffusion and solid dissolution. The dimensional loss in conventional amalgams was more significant as compared to the high copper ones. This may be attributed to the formation of mercury enriched γ_2 phase which may subsequently involve exudation and interdiffusion of mercury to the γ_1 phases. In other words one could say that the γ_2 phase has an initial high affinity to mercury in non-stoichiometric amounts and at a later stage interdiffusion of non-stoichiometric mercury occurs in favour of the thermodynamically stable γ_1 phase. This process is favoured by an increase of both temperature and time.

To resolve the literature dispute concerning the structural origin of the DSC endotherms and to identify the origin of this contraction behaviour, single phases including pure γ_2 and γ_1 were prepared and investigated by DSC analysis to show endotherms at 210 and 120° respectively. These were attributed to the decom-

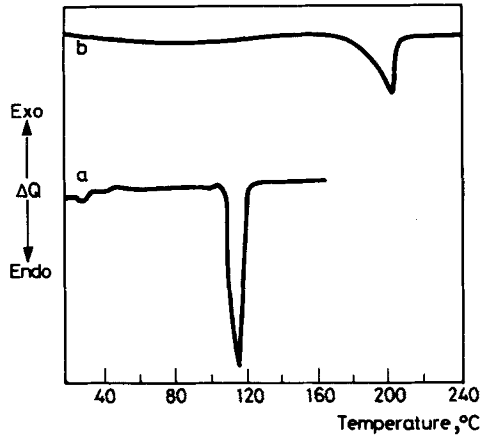

Fig. 2 DSC curve of pure γ_1 (a) and pure γ_2 phases (b)

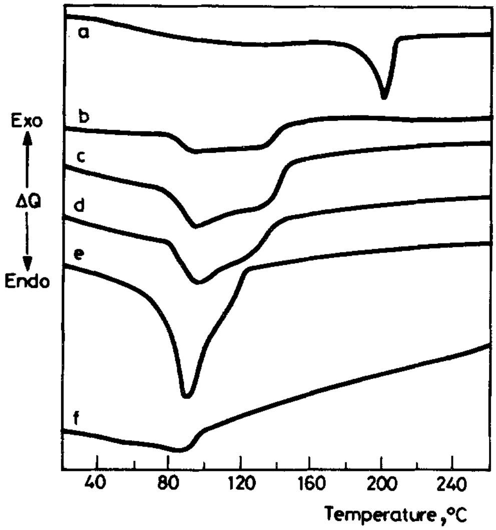

Fig. 3 DSC curves of γ_2 phase enriched with mercury. a: Standard tin-mercury ratio, b–f: Mercury doubled each time

position of the pure phases (Fig. 2). When the γ_2 phase was enriched by mercury, a broad endotherm appeared suggesting the existence of non-stoichiometric phases (Fig. 3). Also a continuous shift towards lower temperature endotherm occurred which is in agreement with the previous results of other workers [3]. This strongly confirms that the endotherm appearing at 80° in conventional amalgam is due to mercury enriched γ_2 phase and the appearance of such endotherm is a criterion for the existence of the phase and is usually associated with it.

On the other hand, an endotherm around 100° was produced when mercury enriched tin sample was analysed by DSC (Fig. 4a). When this phase was left to set, a shift towards higher temperature (Fig. 4b–d) occurred and this is attributed to interdiffusion of mercury between the mercury rich and mercury lean grains.

Previous reports [1] showed the existence of two endotherms at 82 and 108° when dispersalloy containing isolated particles of Ag–Sn and Ag–Cu was enriched with mercury. TMA measurements on such mercury enriched dispersalloy (Fig. 5), indicated the existence of both low and high temperature contractions in correspondence to the endotherms obtained by DSC measurements. Thus both

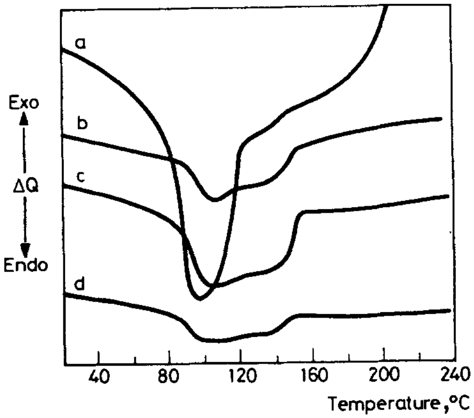

Fig. 4 DSC curves of tin-highly enriched with mercury. a: 1 hour after addition, b: 24 hours after addition, c: 48 hours after addition and d: 96 hours after addition

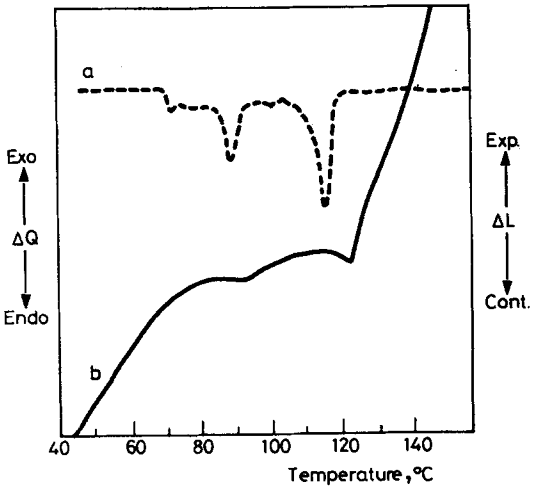

Fig. 5 Thermal curves for Dispersalloy enriched with mercury. a: DSC, b: TMA

DSC and dimensional changes could be useful tools in indicating the existence of both γ_1 and γ_2 phases.

In conclusion, we confirm our previous work on utilizing DSC as a powerful tool for characterizing γ_2 containing amalgams. We may not totally exclude the arguments of Sarkar et al. [3] on the possibility of segregation of Hg–Sn–Ag but we confirm that such low temperature endotherm is associated with the presence of γ_2 phases and in the case of non-γ_2 forming amalgams such endotherm is absent.

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Zusammenfassung — Mittels thermomechanischer Analyse (TMA) wurde der lineare Ausdehnungskoeffizient α von vier verschiedenen, stomatologisch eingesetzten Amalgamen ermittelt. Die dynamischen Thermoexpansionsuntersuchungen zeigten für herkömmliche Amalgame bei 85 °C und für Hochkupferamalgame bei 105 °C ein interessantes Kontraktionsverhalten, welches mit den bei DSC-Untersuchungen beobachtbaren Endothermen zusammenfällt und das der Existenz der Phasen γ_2 und γ_1 zugeschrieben werden kann. Reine Einphasen wurden gefertigt und mittels DSC für γ_2 bei 210 °C und für γ_1 bei 120 °C charakterisiert. Wird die γ_2 Phase mit Quecksilber angereichert, sinkt die Zersetzungsendotherme allmählich bis auf 85 °C ab. Der lineare Ausdehnungskoeffizient liegt für alle untersuchten Marken in einem Bereich von 15–35 ppm/deg. Die thermomechanische Analyse bekräftigt die früheren Ergebnisse bei der Charakterisierung von quecksilberhaltigen Phasen in stomatologisch eingesetzten Amalgamen mittels DSC.

Резюме — Термомеханический анализ был использован для определения коэффициента теплового расширения (α) четырех различных типов зубных амальгам: обычный токарно-обработанный сплав, обычный шарообразный сплав, дисперсионный сплав с высоким содержанием меди и тройной сплав с высоким содержанием меди. Исследования динамического термического разширения показали интересный характер сжатия около 85° для обычных амальгам и при 105° для амальгам с высоким содержанием меди, что совпадает с эндотермами, полученными методом ДСК, и что было отнесено за счет наличия, соответственно, γ_2 и γ_1 фаз.

Обе фазы в отдельности были получены и были охарактеризованы методом ДСК при 210° для γ_2 и при 120° для γ_1. При обогащении фазы γ_2 ртутью эндотерма разложения постепенно сдвигалась в сторону более низких температур и достигала температуры 85°. Для всех исследованных образцов коэффициенты теплового расширения находились в интервале 15–35ппм/град. Термомеханический анализ подтвердил полученные ранее методом ДСК результаты исследования ртутьсодержаших фаз в зубных амальгамах.