X-ray Diffraction Analysis of $\gamma 2$ (Sn-Hg) Phase in High Copper Amalgams of Varying Mercury Content

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Microstructures of high copper commercial amalgams containing varying amounts of mercury, ranging from 20% above to 25% below recommended values, were primarily investigated by x-ray diffraction. Mechanisms relating to the absence or presence of γ_2 (Sn-Hg) phase in these amalgams were discussed in relation to the presence of copper and tin elements in their original alloys. The optimum mercury concentration in some amalgams was determined in order to keep them free of the γ_2 (Sn-Hg) phase.

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Introduction.

Recently, some high copper amalgams have been added to the certified list of the American Dental Association.[1-3] The promising laboratory and clinical test results of these amalgams indicate a great potential for use in future restorations.[4-7] The superior physical properties obtained from most high copper amalgams resulted from the absence of γ_2 (Sn-Hg) phase in their microstructure. However, the absence of γ_2 phase in some high copper amalgams was only true when the recommended mercury concentration was used. Jensen[8] has shown that Tytin amalgam containing 50% and 60% mercury showed the presence of γ_2 phase. Mahler and Adey[9] found that in three high copper amalgams certain changes occurred when the mercury content reached a specific range. These changes were: a relatively large increase in creep, an increase in susceptibility to etching at the γ_1 (Ag-Hg) grain boundaries, and an increase in tin content in the γ_1 phase.

The above results initiated the present study to investigate microstructure in some high copper amalgams (made from commercial alloys) containing different mercury concentrations in their set amalgams. The mercury concentrations were varied from 20% above to 25% below their recommended values. Commercial dental amalgam alloys selected were Tytin, Sybraloy, Indiloy, Dispersalloy, Optaloy II, and Micro II.

Materials and methods.

Table 1 shows the brand of the selected alloys, their manufacturers, recommended mercury-to-alloy ratios, mechanical amalgamators used, trituration times, and the weight of the pestles used in their specified capsules. Table 2 shows their approximate chemical composition and the shape of the original alloy particles. Amalgams of varying mercury content (Table 3) were prepared and allowed to set at 37°C for two wk prior to study. Amalgams were crushed to small-sized particles for x-ray diffraction measurements. The x-ray machine used was a Phillip's (XRG-3000) x-ray generator with copper K_α radiation (λ = 1.54 Å) and a nickel filter. In order to obtain accurate values for 2 $\theta°$, the diffractometer scanning speed was adjusted to 1° per min. The x-ray signal, after being amplified, was recorded on a chart recorder and calibrated for one-inch equivalent to 1°. The 2 $\theta°$ values obtained from diffraction peaks were converted into d-spacings using standard conversion tables. The observed d-values of all the diffraction peaks in conjunction with the ASTM tables were used to identify the presence of metallic phases containing crystallites of different orientations.

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TABLE 1

Dental Alloy	Manufacturer	Batch No.	Recommended Hg (%)	Amalgamator Used	Trituration Time (sec)	Weight of Pestle (gm)
Tytin (predispensed)	S. S. White Philadelphia, PA	17511	43.0	Capmaster	6	--
Sybraloy (predispensed)	Kerr Mfg. Company Romulus, MI	1009751277	46.0	Caulk Vari-Mix II (M-2 setting)	10	0.206
Indiloy (powder)	Shofu Dental Corp. Menlo Park, CA	307602	46.0	Capmaster	15	--
Dispersalloy (predispensed)	Johnson & Johnson East Windsor, NJ	HRI 8137-002841	50.0	Caulk Vari-Mix II (M-2 setting)	12	0.689
Optaloy II (pellets)	L. D. Caulk Company Milford, DE	1264-601624	54.0	Caulk Vari-Mix II (M-2 setting)	14	0.594
Micro II (pellets)	L. D. Caulk Company Milford, DE	1264-601452	54.0	Caulk Vari-Mix II (M-2 setting)	14	0.594

TABLE 2
APPROXIMATE CHEMICAL COMPOSITION (%)

Types	Alloys	Ag	Sn	Cu	In	Shape
	Tytin	60	27	13	–	Sphere
Uni-Comp.	Sybraloy	40	30	30	–	Sphere
	Indiloy	60	22	13	5	Sphere
	Dispersalloy	72	–	28	–	Sphere
		69	27	4	–	Irregular
Ad-Mix	Optaloy II	66	9	25	–	Sphere
		76	23	1	–	Irregular
	Micro II	65	9	26	–	Sphere
		72	26	2	–	Irregular

Results.

The Fig. shows partial x-ray diffraction patterns over the important range of 2 θ° values to detect γ_2 phase peaks in amalgams made from recommended mercury content. The identification of these diffraction patterns has already been discussed.[5] For amalgams containing varying amounts of mercury, the absence or presence of γ_2 phase in their microstructure is given in Table 3.

Discussion.

Before dealing with the observed x-ray diffraction patterns, the following mechanisms are described in order to understand the absence or presence of γ_2 phase in these amalgams.

Mechanisms for the absence or presence of γ_2 phase. – Amalgams made from uni-composition alloys. It is well known that the original alloy particles contain mostly Ag_3Sn

TABLE 3
MERCURY CONCENTRATIONS IN AMALGAMS

Amalgam	25% Below Recom. (%)	20% Below Recom. (%)	15% Below Recom. (%)	10% Below Recom. (%)	5% Below Recom. (%)	Hg As Recom. (%)	5% Above Recom. (%)	10% Above Recom. (%)	15% Above Recom. (%)	20% Above Recom. (%)
Tytin	32.2	34.4	36.5	38.7	40.8	43.0	45.2	47.3	49.5	51.6
Sybraloy	34.5	36.8	39.1	41.4	43.7	46.0	48.3	50.6	52.9	55.2
Indiloy	34.5	36.8	39.1	41.4	43.7	46.0	48.3	50.6	52.9	55.2
Dispersalloy	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0
Optaloy II	40.5	43.2	45.9	48.6	51.3	54.0	56.7	59.4	62.1	64.8
Micro II	40.5	43.2	45.9	48.6	51.3	54.0	56.7	59.4	62.1	64.8

Underline indicates the presence of γ_2 phase.

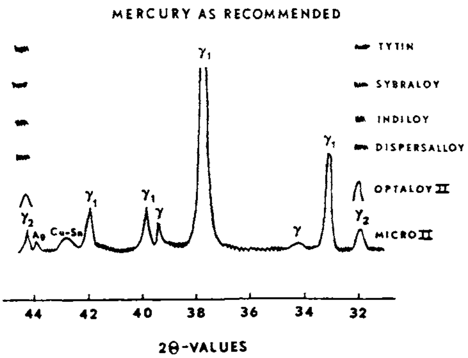

Fig. – Partial x-ray diffraction patterns over the important range of 2 $\theta°$ values, showing the absence or presence of γ_2 phase in amalgams made from recommended mercury content.

and Cu_3Sn phases. Also, the reaction of these alloy particles with mercury is limited to the outer surface layers of the particles, while most of the inner part of the particles remains unreacted. To explain this reaction, one of two possible mechanisms is probably taking place: 1) Initially, γ_1 (Ag-Hg) and γ_2 (Sn-Hg) phases are formed. Since the γ_2 phase is unstable, tin from this phase combines with Cu_3Sn to form Cu_6Sn_5 as observed in x-ray diffraction. Released mercury from γ_2 phase again reacts with original γ particles in the same fashion. Hence, the set amalgam becomes free from γ_2 phase, and the major amalgam products are γ_1, Cu_6Sn_5, and γ (unreacted) particles; or 2) as mercury reacts with Ag_3Sn of the original particle to form γ_1, the released tin from Ag_3Sn reacts with Cu_3Sn and forms Cu_6Sn_5 phase. In this manner no γ_2 is formed, and the final product is the same γ_1, Cu_6Sn_5, and the γ (unreacted) particle. Thus, the absence of γ_2 phase in Tytin, Sybraloy, and Indiloy amalgams when made from their recommended mercury values can be explained with one of these two mechanisms.

Amalgams made from ad-mixed composition alloys. Dispersalloy contains a blend mixture of lathe-cut Ag_3Sn particles, with spherical Ag-Cu eutectic particles. Initially, mercury reacts with Ag_3Sn and Ag-Cu eutectic separately. The γ_1 (Ag-Hg) and γ_2 (Sn-Hg) phases are produced from γ (Ag_3Sn) particle reaction, and small amounts of the additional γ_1 phase are also produced from silver of Ag-Cu eutectic particles. Because the γ_2 phase is unstable, the tin from this phase combines with copper of Ag-Cu eutectic and forms Cu_6Sn_5 phase, as observed in x-ray diffraction. The released mercury from γ_2 phase reacts with silver of Ag-Cu eutectic, forming some additional γ_1 phase. Hence, the set Dispersalloy amalgam becomes free from the γ_2 phase, and the major amalgamated products are γ_1, Ag-Cu eutectic surrounded by Cu_6Sn_5, and γ (unreacted particles). This mechanism explains the absence of γ_2 phase in Dispersalloy amalgam. The presence of 28% copper in Ag-Cu eutectic particle of Dispersalloy was sufficient to completely eliminate γ_2 phase in its amalgam for all mercury values used in this investigation.

However, Optaloy II and Micro II alloys contain about 9% tin in their Ag-Cu eutectic (Table 2). The presence of 9% tin in Ag-Cu eutectic is held responsible for the appearance of γ_2 phase in the amalgams, as explained in the following hypothesis. The reaction of mercury with these alloys produces γ_2 phase in two ways: 1) the reaction of mercury with tin from the surface layers of Ag_3Sn (γ) particles, and (2) the reaction of mercury with tin contained in the Ag-Cu eutectic particles. In fact, the presence of 9% tin in Ag-Cu eutectic produces some more γ_2 phase, and the copper in these alloys is not in sufficient quantities to be able to eliminate all of the γ_2 phase formed. This explained the presence of γ_2 phase in both Optaloy II and Micro II amalgams for all values of mercury ranging from 25% below to 20% above their recommended amounts.

The above mechanisms would be employed to explain the observed x-ray diffraction data from amalgams of varying mercury.

Amalgams containing mercury as recommended. – The Fig. shows a typical presentation of partial x-ray diffraction patterns from amalgams made from mercury, as recommended by their manufacturers. The analysis has shown (Table 3) that Tytin, Sybraloy, Indiloy, and Dispersalloy amalgams were free from γ_2 phase, while Optaloy II and Micro II amalgams contained γ_2 phase in their microstructure. The absence or presence of γ_2 phase in these amalgams has already been discussed.

Amalgams containing mercury above recommended levels. – Table 3 indicates that Indiloy amalgam containing mercury 5% or above the recommended value and Tytin amalgam containing mercury 15% or above the recommended value contained γ_2 phase in their microstructure. Since Tytin and Indiloy amalgams contained the same amount of copper in their original alloys (Table 2), the absence or presence of γ_2 phase in these amalgams would depend upon some optimum value of mercury concentration used in the reaction. Table 3 shows that Tytin amalgam made from 47.3% mercury (10% above recommended value) was free from γ_2 phase, while Indiloy amalgam containing 48.3% mercury (5% above recommended value) contained γ_2 phase. Approximately 48% mercury seemed to be the limit for these amalgams to be free from γ_2 phase. In practice, an amalgam made from recommended mercury is packed in the prepared tooth cavity, and the applied condensation force further reduces the mercury content in the bulk of the restoration. The mercury concentration of amalgam around the margins is known to be higher than the bulk; however, it is not any higher than 2 to 3 percent of the recommended values.[10] For example, for Tytin the mercury content would not exceed 44-45%, whereas for Indiloy it would reach 47-48%. As shown, Tytin amalgam with 44-45% mercury is free from γ_2, whereas 47-48% mercury for Indiloy would start to produce some γ_2 phase.

Sybraloy and Dispersalloy amalgams were totally free from γ_2 phase with up to 20% higher mercury than that which is recommended. With such a high mercury concentration it is almost impossible to pack amalgam. Optaloy II and Micro II amalgams always contained γ_2 phase in their microstructure for all mercury values up to 20% above those recommended.

Amalgams containing mercury below recommended values. – Table 3 shows the absence or presence of γ_2 phase in amalgams containing mercury up to 25% below their recommended values. The metallurgical behavior of these amalgams was similar to amalgams made from recommended mercury. Optaloy II and Micro II amalgams contained some γ_2 phase even when triturated with mercury at 25% below those values recommended. However, the amalgams were very dry and practically unusable.

Conclusions.

1. All high copper amalgams are not completely free of the weak γ_2 phase. Absence of the γ_2 phase in high copper amalgams depends on the composition of the original alloy, as well as the final mercury content in set amalgam.

2. Certain hardened high copper dental amalgams with higher mercury contents than recommended have a greater chance of containing γ_2 phase than when they contained lower amounts of mercury.

3. Set Micro II and Optaloy II amalgams showed γ_2 phase even when they contained the recommended mercury content.

4. Indiloy amalgam is free from γ_2 phase at recommended mercury-to-alloy ratios, but will show γ_2 phase in its microstructure when the mercury-to-alloy ratio is increased to 5% above that which is recommended. However, from a practical view it is difficult

to condense any spherical amalgam alloys when triturated with 5% higher mercury than that which is recommended.

5. Tytin amalgam is free of the γ_2 phase up to 10% above the recommended mercury-to-alloy ratios, and somewhere between 10 and 15% above the recommended ratios, the γ_2 phase appears.

6. X-ray diffraction patterns for Sybraloy and Dispersalloy do not show any γ_2 peaks, even when mercury-to-alloy ratios were increased 20% above their recommended values.

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