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EARLY PHASE CHANGES DURING THE SETTING OF HIGH COPPER AMALGAMS

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Abstract

X-ray diffraction analysis has been used to evaluate the phase composition of two (spherical and lathe cut) HCSC amalgam alloys and early phase changes in these amalgam in the time interval 2.5 min to 7 days after trituration. A method appropriate for the evaluation of these changes was developed. Only two phases were found in alloys Valiant and Ana 2000: gamma(Ag_3Sn) and epsilon(Cu_3Sn). In amalgams, no diffraction peaks were observed corresponding to gamma 2 phase in the time interval form 2.5 min to 7 days after trituration. The relative concentration changes of the reaction products of an amalgamation (gamma 1 and eta) were observed already at 2.5 min after trituration. Twenty minutes after trituration there were some differences in the setting rate between spherical and lathe cut amalgams: the spherical amalgam rate was higher. The formation of the reaction phases was fastest during the first 60 min after trituration and continued for at least the next 7 days.

KEY WORDS: amalgam, setting reaction, diffraction analysis.

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Introduction

The amalgams with high copper content have been shown to have advantages over conventional ones in clinical performance and mechanical properties (1-3,8,15,19,20). The improvement of the clinical and mechanical performance has been attributed to the higher copper content in an amalgam alloy. 9–30 percent of copper in the alloy participates in the reaction mechanism of hardening and reduces or eliminates formation of the weakest tin-mercury phase in the amalgam (4,5,13). In the high copper amalgams, eta phase (Cu_6Sn_5) was found instead of gamma 2 (Sn_7Hg) (6,9,10,11). As for the lathe cut high copper single composition (HCSC) amalgam it was surmised that gamma 2 phase was formed and then eliminated by solid state reactions (3).

Most of the previous studies evaluated time-dependent phase changes which occured in amalgams older than one hour (14,22). In contrast to them, Okabe evaluated hardening of the dental amalgams already in 9.5 min after trituration. He found that, at first, crystals of eta phase were formed, followed by crystals of gamma 1 phase (16,17,18).

The aim of our work was to evaluate the phase changes in the spherical and lathe cut HCSC amalgams. The question was whether a gamma 2 phase is formed and then is eliminated or whether its formation is suppressed from the beginning of the setting reaction. Thereafter, we studied the dependence of the setting reaction on the two types of amalgam alloy. Finally, we evaluated the phase composition of these amalgam alloys in connection with the different technology of the manufacturing process.

Materials and Methods

Phase composition of amalgam alloys

Two commercial alloys of a high copper single composition Ana 2000 and Valiant have been used (see table 1). The compositions given by the manufacturers were in good agreement with those obtained by absorption spectrophotometry (see table 2), on Varian AA 275 spectrophotometer (Australia) with flame atomization. X-ray diffractograms of both alloys were performed on goniometer Kristalloflex, type F, Siemens (West Germany), using Bragg–Brentano focusing geometry , CoK alpha radiation, continuous scanning at a scanning speed 0.5 of 2 theta per min. The only diffraction lines found were those of epsilon and gamma. From the mass balance and elementary compositions results obtained by absorption spectrophotometry, phase composition was calculated:

$$\% \, Cu_3Sn = \% \, Cu \cdot \frac{M_{Cu_3Sn}}{3 \cdot M_{Cu}} \quad (1)$$

$$\% \, Ag_3Sn = \% \, Ag \cdot \frac{M_{Ag_3Sn}}{3 \cdot M_{Ag}} \quad (2)$$

where M is the relative atomic or molecular mass of the element or phase. The concentration of Hg in alloy Ana 2000 and Pd in alloy Valiant were neglected in the calculation.

Table 1. Selected dental alloys studied.

Dental alloy	Manufacturer	Batch No.	Hg/alloy	trituration
Valiant	L. D. Caulk, USA	022486	43/57	6 sec
Ana 2000	A. B. Nordiska Aff., Sweden	000177	50/50	12 sec

Table 2. Chemical composition of amalgam alloys (w%).

Dental alloy	Ag	Sn	Cu	Zn	Pd	Hg	particle shape
Valiant +)	—	—	—	—	1	—	spherical
++)	51.5	28.5	19.45	0.1	0.45	0	
Ana 2000 +)	43	29.6	25.3	0.1	—	2	lathe-cut
++)	44.7	29	24.6	0.1	—	1.6	

+) results reported by manufacturer
++) results by absorption spectrophotometry

Preparation of amalgam specimens

Amalgams were prepared by trituration in a Duomat 2 amalgamator Degussa (West Germany). Trituration times are given in table 1. Amalgams were condensed by hand into the cavity (13 × 15 × 1.5 mm) of a PMMA holder, overfilled and carved by a glass spatula.

Qualitative phase analysis of amalgams

Diffractograms were obtained under the same conditions as the ones of the alloys above mentioned. The range of measuring was 30–80 2 theta degrees. Amalgams were measured 1 and 24 hours and 7 days after trituration. The presence of the gamma 2 phase was already controlled 2.5 min after trituration. A qualitative phase composition of the amalgams 7 days old was checked after grinding them in the ball mill (Specamill, Specac, UK).

The determination of the phase changes in amalgams

On a basis of qualitative analysis we decided to evaluate setting reaction of the amalgams as a process of formation of Ag_2Hg_3 and Cu_6Sn_5 phases and dissolution of Ag_3Sn and Cu_3Sn phases.

As a criterion of phase concentration changes, intensity changes of the selected diffraction lines of the phases in the peak maximum were regarded. As the shape of the diffraction lines did not change during the setting of amalgam, we consider the use of these intensities to be adequate. Intensity measurements in the peak maximum is more rapid than determination of integral intensity. For kinetic measurements, such intensity is the only suitable method when no position sensitive detector is available. The intensities determined this way are less influenced by the lines from the surroundings.

Table 3. Diffraction patterns used for detection of phase changes in amalgams.

Phase	JCPDS Powder Diffraction File	d-spacing from the File	d-spacing found	hkl
gamma	4–0800	0.228 nm	0.2276 nm	(111), (021)
epsilon	1–1240	0.216 nm	0.217 nm	not known
gamma 1	11–67	0.267 nm	0.269 nm	(321)
eta	2–0713	0.298 nm	0.297 nm	(101)
gamma 2+)	—	0.278 nm	—	(100)

+) data obtained from literature (9,12).

The selected reflexions of the phases are introduced in table 3. The exact positions of peak maxima were determined by measuring in their surroundings by step scanning with a step magnitude of 0.01 degree. We have found that neither the position of the peaks nor the intensity of background changed during the process of amalgamation.

The dependence of intensity on time was determined as follows: The exact position of the selected peak maximum was presect on the diffractometer. An amalgam specimen was placed into the diffractometer and the counting of impulses started 1 min after the end of trituration. Each counting time was 75 seconds.

The counting was continuously repeated for 100 min after trituration. The counting was repeated 1 and 7 days after trituration, again. Each of the evaluated phases were analysed on a new amalgam specimen. From the number of impulses, values of linearly interpolated background were subtracted and the intensity was determinated as a number of impulses per 60 seconds.

Because the linear absorption coefficient of the matrix during the setting did not change, the relation between the concentration $C_i(t)$ of the i phase and intensity $I_{ij}(t)$ of the j line of the i phase in the time t can be written as follows:

$$C_i(t) = k_{ij} \cdot I_{ij}(t) \quad (3)$$

where the constant k_{ij} for the j line of the i phase is independent of time and the concentration ratio for time 1 and 2 is given by:

$$\frac{C_i(1)}{C_i(2)} = \frac{I_{ij}(1)}{I_{ij}(2)} \quad (4)$$

With respect to the phases which increased, ratios of the intensity in a given time to the intensity of the same line 7 days after trituration were determined. This is expressed in percent. For the phases whose content decreased, intensity ratios are related to the intensity 2.5 min after trituration, and determine how many relative percent of the phase from the mass of the phase present in amalgam in 2.5 min after trituration remained.

SEM evaluation

Amalgam alloys for SEM analysis were powdered on the specimen holder of the microscope.

Amalgams for SEM/energy-dispersive X-ray microanalysis (EDX) were condensed by hand into the form of a 4 × 4 mm of cylindrical shape. After 1 week of storage at 37 °C, the specimens were mounted in a ring using epoxy resin and the surface was ground and polished in the following sequence: silicone carbide papers 320 grit, 400 grit, 600 grit, diamond paste 6, 3, 1 and 0.25 micrometer particles.

The specimens were analysed in a scanning electron microscope JEOL JSM 25 (Japan) with attached EDX analyser (Tractor Northern TN 2000, USA). The microprobe settings were as follows: excitation potential 25 keV, counting time 100 seconds, analysed lines CuK, AgL, HgM, SnL. EDX analysis qualitatively defined the presence of elements of the known phases in the specimen.

Table 4. Calculated phase composition of dental alloys.

Dental alloy	Ag_3Sn(gamma)	Cu_3Sn(epsilon)
Valiant	70.5 w%	31.5 w%
Ana 2000	61.2 w%	39.9 w%

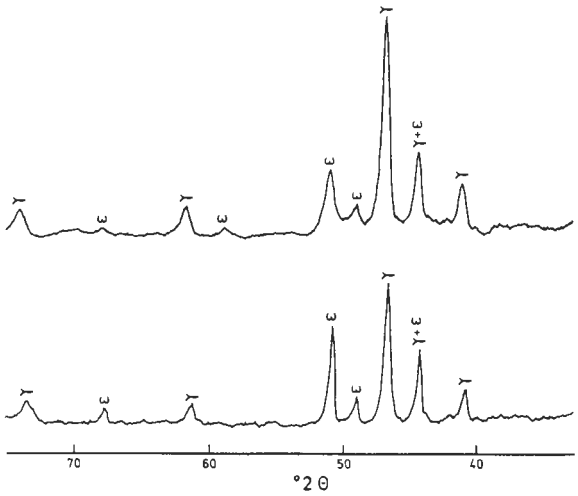

Fig. 1. X-ray diffraction patterns obtained from alloys.

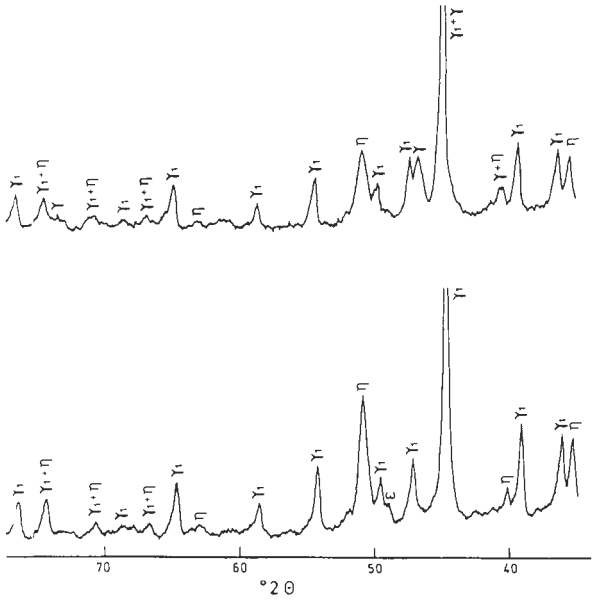

Fig. 2. X-ray diffraction patterns obtained from amalgams 7 days after trituration.

Results

X-ray diffractograms of the amalgam alloys confirmed the two-phase composition (gamma and epsilon) in each alloy. No other phases were found, see fig. 1. Table 4 shows the phase composition of the alloys calculated from the mass balance and elementary composition obtained by absorption spectrophotometry.

X-ray diffractograms of amalgams obtained 1 hour after trituration and 24 hours and 7 days after trituration did not reveal any line characteristic of a gamma 2 phase, formerly reported (3) as an interproduct of the lathe cut HCSC amalgam setting. The characteristic line (100) of the phase was not found even 2.5 min after trituration.

X-ray diffractograms of evaluated amalgams 7 days after trituration are shown in fig. 2. In Valiant only Ag_3Sn, Ag_2Hg_3 and Cu_6Sn_5 phases were found, in Ana 2000 only Cu_3Sn, Ag_2Hg_3 and Cu_6Sn_5 phases were found after this period.

The formation of the phases

Figs. 3 and 4 show the phase intensity changes of amalgams in the evaluated time interval after subtraction of interpolated value of background.

The time, after which the evaluated phases reached 50 percent of the final/initial concentration, was determined from figs. 3 and 4 is shown in table 5 as the half-time.

Concentration changes of phases, expressed as intensity ratios are shown in table 6.

gamma phase

As the reaction proceeded, the relative gamma content tended to decrease as is shown in figs. 3 and 4, table 6. This decrease was especially noticeable in Valiant. In Ana 2000, which contained less initial content (see table 3), the reaction continued and after 7 days there was no noticeable amount of the gamma phase. On the other hand, Valiant contained 18 rel.% of unreacted gamma phase. The half-time of the gamma phase was 38 min for Valiant and 86 min for Ana 2000 (table 5).

epsilon phase

During amalgamation the relative content of epsilon phase tended to decrease as shown in figs. 3 and 4, table 6. In the first 10 min after trituration the rate of decrease was more pronounced in Valiant, where there was about 58 rel.% of the initial content, while in Ana 2000 it was 80 rel.%. The half-time of the consumption was 13 min for Valiant and 30 min for Ana 2000. Because of the low initial intensities (see figs. 3 and 4) of the peaks, statistical fluctuation and possible inaccuracies in the values of the background, the relative content could be subject to certain errors.

gamma 1 phase

Gamma 1 phase is the major reaction product of the amalgamation reaction. The relative content of this phase

Table 5. The half-time of formation/consumption of the phases in amalgams.

Dental amalgam	Phase	Half-time
Valiant	gamma	38 min
Ana 2000	gamma	86 min
Valiant	epsilon	13 min
Ana 2000	epsilon	30 min
Valiant	gamma 1	23 min
Ana 2000	gamma 1	26 min
Valiant	eta	28 min
Ana 2000	eta	31 min

Table 6. Concentration changes of phases in time interval 2.5 min — 7 days after trituration in dental amalgams (relative %).

Dental amalgam	Phase	2.5 min	10 min	20 min	40 min	60 min	1 day	7 days
Valiant	gamma	100	88	71	49	38	24	18
Ana 2000	gamma	100	87	80	67	59	10	0
Valiant	epsilon	100	58	26	0			
Ana 2000	epsilon	100	80	61	45	39	not measured	
Valiant	gamma 1	8.6	28	47	70	85	97	100
Ana 2000	gamma 1	22	34	45	59	68	89	100
Valiant	eta	7.1	29	42	59	70	87	100
Ana 2000	eta	22.8	35	44	55	62	79	100

increased during the setting (see figs. 3 and 4, table 6).

There were no important differences in the formation rate of this phase between Valiant and Ana 2000 during the first 20 min. The more pronounced difference appeared in 40 min after trituration. There was 70 rel.% of the final gamma 1 formed in Valiant compared to 59 rel.% of the gamma 1 in Ana 2000. This difference continued after one hour as well as 24 hours after trituration, when Valiant formed 85 rel.% and 97 rel.% compared to Ana 2000 with 68 rel.% and 89 rel.%. The half-time of the formation was 23 min for Valiant and 26 for Ana 2000 (see table 5).

eta phase

This phase is supposed to be the reaction product of the amalgamation reaction. In our measurement, the relative content of this phase increased (see figs. 3, 4, table 6). In the first 20 min after trituration it reached higher relative concentrations overcame Ana 2000. The half-time of the formation was nearly the same for Ana 2000 and Valiant 28 min and 31 min, respectively after trituration see table 5.

SEM/EDX evaluation

Figs. 5 and 6 show SEM micrographs of evaluated alloys and their amalgams. The micrograph of Valiant amalgam shows the presence of spherical alloy particles with the reaction ring. These particles are surrounded by light phase consisting mainly of Ag and Hg: gamma 1 phase. The reaction ring consisted mainly of Cu and Sn, then Ag and Hg. The thickness of the ring was approximately 2—5 μm. Greater particles showed unreacted centers of original alloy. These centers were free of Hg, consisting of Ag, Sn, Cu.

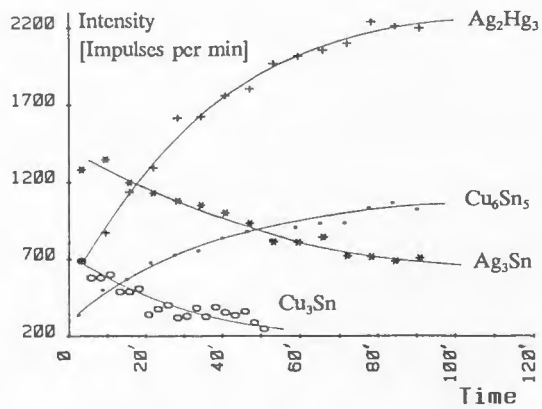

Fig. 3. Time dependent changes of intensities during amalgamation — Ana 2000.

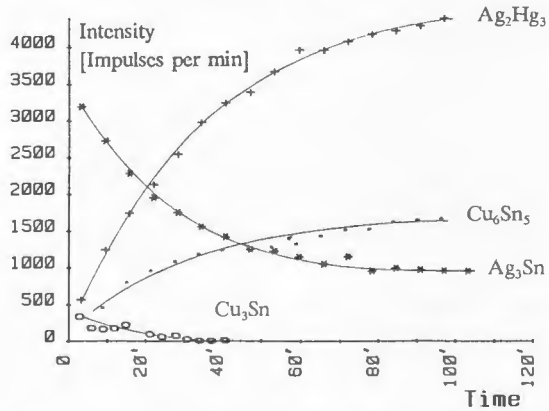

Fig. 4. Time dependent changes of intensities during amalgamation — Valiant.

The micrograph of Ana 2000 amalgam shows dominant light gamma 1 phase. In addition to this phase there were found two types of phases: light grey and the dark one. They were frequently in contact. No unreacted particles were found in this amalgam but the SEM showed the presence of areas with the shapes similar to the original alloy particles. Four phases were found in these areas: the lightest gamma 1 phase, rounded dark grey particles of unreacted Cu—Sn (epsilon), fringed grey areas of Cu—Sn (eta) phase and among them, a limited amount of particles consisting only of Ag and Sn (gamma) phase.

Discussion

Because of the difference in preparation technology and chemical composition of some spherical and lathe cut alloys, the presence of the eta phase could be suspected in some of them. The X-ray analysis by Malhotra and Asgar (11) showed the presence of the eta phase in "as received" alloy Sybraloy, but this phase was not detected by the work of Mahler and Adey (10) who used the same but annealed alloy. The beta (Ag—Sn) phase was identified in annealed alloys Tytin and Sybraloy and was not found in Valiant and Indiloy (10).

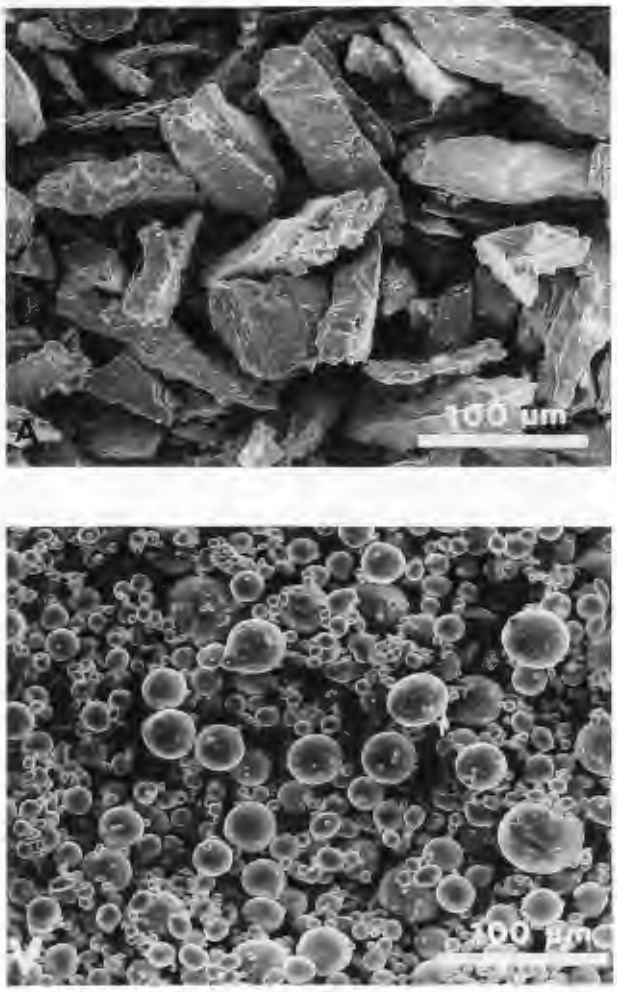

Fig. 5. SEM micrographs of amalgam alloys.
A — Ana 2000, V — Valiant.

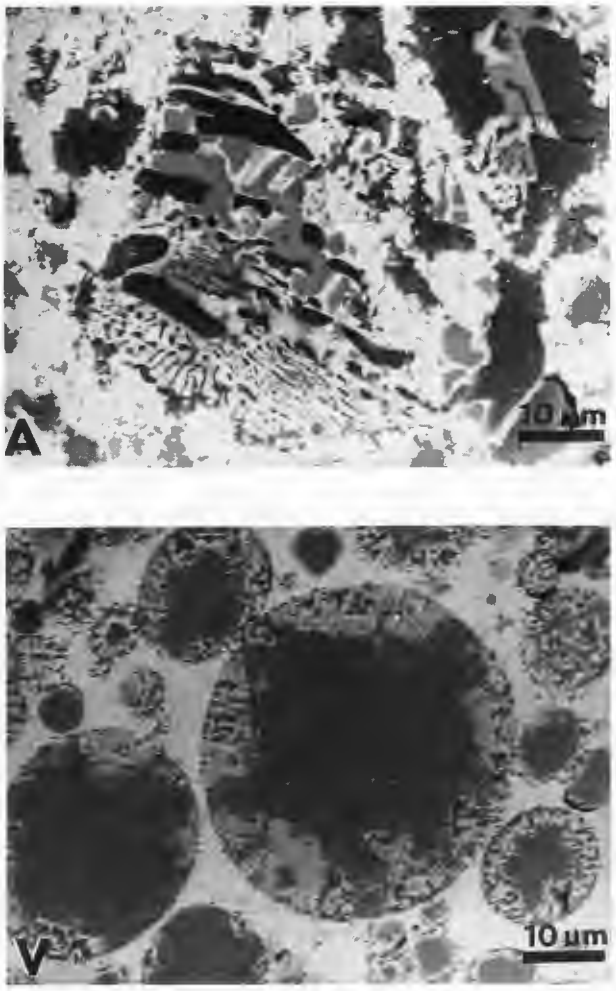

Fig. 6. SEM micrographs of amalgams.
A — Ana 2000, V — Valiant.

X-ray diffraction analysis of evaluated alloys Ana 2000 and Valiant revealed only two phases, gamma and epsilon in each alloy.

Differences were found between the results obtained by X-ray diffraction and SEM/EDX analyses of amalgams:
a) In Valiant amalgam, unreacted centers of original alloy particles were found by SEM analysis. According to the results of the X-ray diffraction, this alloy consists of epsilon and gamma phases, but X-ray diffraction of the amalgam did not reveal the presence of epsilon phase in it.
b) In Ana 2000 amalgam, the limited amount of the gamma phase was found in the rest of the reacted original alloy particles by SEM analysis. But this phase was not proved by X-ray diffraction analysis.

The following explanation is postulated: X-ray diffraction enables one to investigate the layer of the specimen dependent on perpendicular penetration thickness of X-rays. The actual thickness of layers for each phase was calculated (table 7) from the linear absorption coefficients according to the equation (7):

$$x = \frac{\ln (I/I_o) \cdot \sin \theta}{2\mu} \cdot 10\,000 \qquad (5)$$

I is the X-ray intensity of the uncovered surface of material, I_o is X-ray intensity of the layer at an x distance (µm) beneath the surface of material, µ is the linear absorption coefficient of surface layer and θ is the Bragg angle. Linear absorption coefficients were calculated in the usual way from mass absorption coefficients and specific weights of each phase. These were found either in tables (21) or calculated from the crystallographic data.

As a first approximation it can be said that the most distinct will be phases lying beneath the surface in the thickness less than the one calculated for the ratio $I_o/I = 10$. Phases with a distance greater than the thickness calculated for ratio $I_o/I = 100$ are not detectable. The most relevant values are those for the dominant gamma 1 phase and for mercury. This could explain the observation that in the Valiant, epsilon phase was not detected by X-ray diffraction 7 days after trituration, while SEM/EDX analysis revealed the presence of unreacted particles of this phase in the same amalgam. Similarly, the rest of gamma phase is hidden in the other phases of Ana 2000 amalgam.

The presence of the phases was controlled by X-ray diffraction on the powdered samples, but neither epsilon phase in Valiant nor gamma phase in Ana 2000 were identified. This can be explained by the study by Bayne (1) who found that fracture lines in HCSC amalgams proceeded

Table 7. Perpendicular penetration thickness of Co K alpha for $\theta = 20°$ (μm).

Phase	$I_o/I = 10$	$I_o/I = 100$
Ag_3Sn	1.15	2.29
Cu_3Sn	7.77	15.54
Cu_6Sn_5	1.8	3.61
Ag_2Hg_3	0.88	1.75
Hg	0.88	1.75

above the Cu–Sn reaction zone at the surface of the particles. We consider our method suitable for kinetic evaluations of amalgam setting but the evaluation of amalgam composition needs some more (e.g., SEM) analysis.

The X-ray diffraction analyses of the setting of amalgams did not show any noticeable reflection of the gamma 2 phase as an intermediary product of the setting in any of evaluated amalgams. On the basis of these results we assume that either there is a need to revise the supposed formula describing the mechanism of the elimination of the gamma 2 phase in the lathe-cut HCSC amalgams, or that the concentration of the gamma 2 phase was below the limit of the detection. This latter phase could react with Cu_3Sn to form Cu_6Sn_5 before its actual concentration reaches the limit of detection. The following reaction is postulated: as mercury reacts with Ag_3Sn of the original particles to form gamma 1 phase, the tin, released from Ag_3Sn reacts with Cu_3Sn and forms the Cu_6Sn_5 phase. In this way no gamma 2 phase is formed and the final products are: gamma 1, eta and unreacted alloy particles. This is in agreement with published data about the setting of the spherical HCSC but not of the lathe-cut HCSC amalgams (3,12).

Okabe used SEM to evaluate the setting and phase formation of high copper amalgams. He found that eta crystals were already fully formed by 9.5 min while gamma 1 phase crystals were formed within 30 min after trituration (16,17,18,22). We have found (table 5) that gamma 1 and eta reflexions were already present 2.5 min after trituration. It is impossible to determine which of the phases was formed first.

Conclusions

From the results of our work we can draw the following conclusions:

1. A new method, convenient for evaluation of the phase changes in the early stages of amalgamation was developed.
2. There were only two phases (gamma and epsilon) found in the HCSC amalgam alloys Valiant and Ana 2000.
3. In the time interval from 2.5 min to 7 days after trituration we did not identify noticeable reflexions of gamma 2 phase in any of the evaluated amalgams.
4. The formation of the reaction phases (gamma 1 and eta) was fastest during the first 60 min after trituration and continued for at least the next 7 days.
5. As early as 2.5 min after trituration, there were noticeable peak intensities of the reaction phases gamma 1 and eta.
6. There were some differences in the reaction rate between the spherical and lathe-cut amalgams: these became more pronounced 20 min after trituration, when Valiant overcame Ana 2000.

Acknowledgements

We are very thankfull to Z. Kohoutek who made AAS analysis of alloys, V. Buzek for EDX data of amalgams.

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Discussion with Reviewers

Reviewer III: Are there not several deviations from the background which coud be gamma 2 peaks in the pattern shown?

Authors: No deviations was found near the interplanar spacing 0.278 nm of the characteristic line of the gamma 2 phase. If the phase was present, its concentration was below the limit of the detection.