# DENTAL AMALGAM – RELATION BETWEEN MICROSTRUCTURE, CORROSION AND MERCURY RELEASE

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The study was aimed at evaluating the effect of the composition and structure of dental amalgams on their corrosion behaviour and mercury release. A group of materials currently available on the market was chosen for the measurements. On the basis of results it is possible to conclude that the composition of the alloy influences both the phase structure and the corrosion properties of the resulting material. The technology of the alloy powder preparation does not have significant influence on the corrosion behaviour of the resulting material, but it affects the rate of mercury release.

Key words: dental amalgam, corrosion, mercury release

# DENTÁLNÍ AMALGÁM – VZTAH MEZI MIKROSTRUKTUROU, KOROZÍ A UVOLŇOVÁNÍM RTUTI

Cílem práce bylo zhodnotit vliv složení a struktury dentálních amalgámů na jejich korozní chování a uvolňování rtuti za modelových podmínek. Pro měření byl vybrán soubor materiálů, které jsou běžně dostupné na trhu. Na základě výsledků bylo konstatováno, že složení slitiny použité pro přípravu dentálního amalgámu má vliv jak na fázovou strukturu, tak na korozní chování výsledného materiálu. Způsob výroby prášku slitiny nemá na korozní vlastnosti výrazný vliv, ovlivňuje však rychlost uvolňování rtuti.

## 1. Introduction

Dental amalgam as a material used for dental cavities filling after caries removal has a long history [1]. In terms of composition, there are currently two basic types of dental amalgams: low-copper amalgam with the copper content in the alloy up to 8 %, and high-copper one, which is further divided into several sub-groups [2]. Silver is the major component of the alloy, the rest consists of tin, copper and also other elements in low concentrations. The alloy is mixed with mercury in about 1:1 mass ratio. According to the powder production technology and

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resulting particle shapes, amalgams are divided into lathe-cut, globular and hybrid, with the latter containing various types of powders. Amalgam with admixed AgCu particles (termed as admix system) represents a transition between low- and high-copper ternary alloys. It is based on an alloy with a copper content mostly up to 8 %, most often in the form of lathe-cut grains, with spherical particles of a silver-copper eutectic (AgCu28) added. In this material, the overall copper content is higher than 8 %, and the material mostly corresponds to the high-copper type of amalgam in terms of its phase composition [3].

After an amalgam powder has been mixed with mercury, the amalgamation reaction starts, leading to the hardening of the originally plastic mixture. A number of inter-metallic compounds originate in the course of this reaction. An overview of the most important of them is shown in Table 1. In the $\gamma_1$ phase, which is the matrix of all dental amalgams, phases $\eta'$, and in some materials $\varepsilon$, are dispersed. In case of insufficient copper content, mercury also binds to tin, and the $\gamma_2$ phase appears in the structure. Its presence is typical for low-copper amalgams, but it should not occur in high-copper materials. The microstructure of admix amalgams is characterized by the so-called reaction rings which cluster around eutectic particles and contain higher concentration of the $\eta'$ phase. Non-reacted grains of the initial alloy are always present in microstructure of all dental amalgam types.

Table 1. Structural phases of dental amalgams

| Phase | Composition |
|---|---|
| $\gamma$ | $Ag_3Sn$ |
| $\gamma_1$ | $Ag_2Hg_3$ |
| $\gamma_2$ | $Sn_{7\text{-}8}Hg$ |
| $\eta'$ | $Cu_6Sn_5$ |
| $\varepsilon$ | $Cu_3Sn$ |

Corrosion resistance of amalgams has been studied fairly extensively [e.g. 4–9]. Mercury release as a strongly controversial property of dental amalgams has been studied primarily in terms of its evaporation into air [10–14]. Its release into a solution modelling the oral environment, which is closer to *in vivo* conditions and may provide different results due to a number of possible electrochemical reactions, has been embraced in experimental studies less often [15–17].

The presented study was aimed at evaluating the influence of the composition and structure of dental amalgams on their corrosion behaviour under model conditions, and on mercury release from them.

## 2. Experimental

A set of materials currently available on the market was chosen for the measurements. Table 2 presents the mean composition of the tested alloys as given by manufacturers, and the recommended mixing ratio with mercury. The study was not intended to compare commercial products, materials are therefore labelled with codes. Amalgam specimens were prepared according to manufacturers instructions, by mixing in amalgamator Capmix (Espe, FRG) and its subsequent preparation into the form of testing cylinders was done according to ISO 1559 [18]. Typical microstructures of individual types of materials are presented in Figs. 1–3.

Sets of four cylinders were fixed to a brass carrier by electrically conductive adhesive, and vacuum-cast in epoxy resin. The specimens were machined into a

Table 2. Composition of studied dental amalgams

| Code | Composition [%] | | | | Alloy : Hg ratio | Hg in amalgam [%] | Alloy powder |
|---|---|---|---|---|---|---|---|
| | Ag | Sn | Cu | Hg | | | |
| LC | 70.3 | 22.4 | 4.1 | 3.2 | 1.09 | 51.6 | lathe-cut |
| L | 43.0 | 29.6 | 25.4 | 2.0 | 1 | 51 | lathe-cut |
| A1 | 43.2 | 29.7 | 24.9 | 2.2 | 1 | 51.1 | admix |
| A2 | 56.0 | 27.9 | 15.4 | | 1.09 | 47.9 | admix |
| A3 | 70.0 | 14.7 | 12.3 | 3.0 | 1 | 51.5 | admix |
| G1 | 48.0 | 30.0 | 22.0 | | 1.33 | 43.5 | globular |
| G2 | 60.0 | 28.0 | 12.0 | | 1.35 | 42.5 | globular |

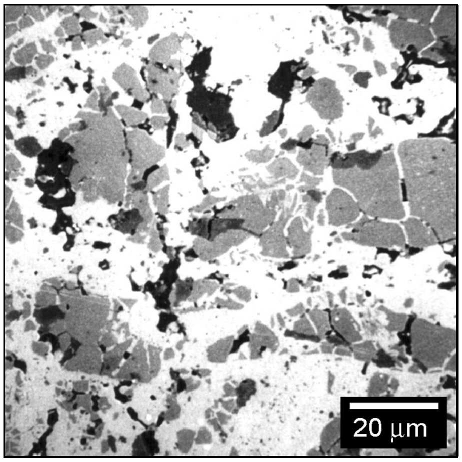

Fig. 1. Low-copper amalgam (material LC).

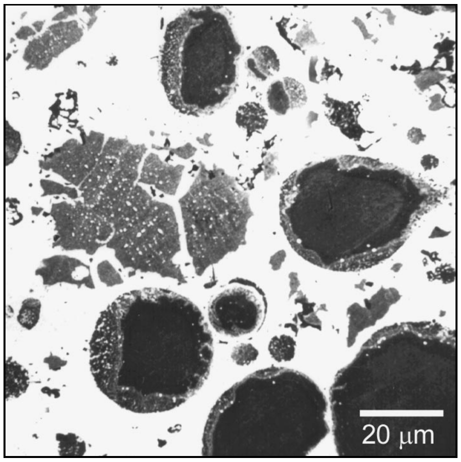

Fig. 2. Amalgam containing dispersed globular AgCu particles (material A3).

shape allowing for their use as weighing bottle stoppers while determining the rate of mercury release. The measurements were conducted at 37.0±0.5 °C in model saliva solution (20.1 mmol/l KCl; 17.9 mmol/l $NaHCO_3$; 3.6 mmol/l $NaH_2PO_4$; 5.1 mmol/l KSCN; 0.1 mmol/l lactic acid; pH = 6.8). Oxygen content was modified to two levels: for the purpose of potentiodynamic measurements it was minimized by bubbling nitrogen through the solution for two hours, while for other measurements, air was bubbled through the solution for the period of one hour. The electrochemical study was performed using the PC4/FAS measurement system and CMS 105 software (Gamry Instruments, USA).

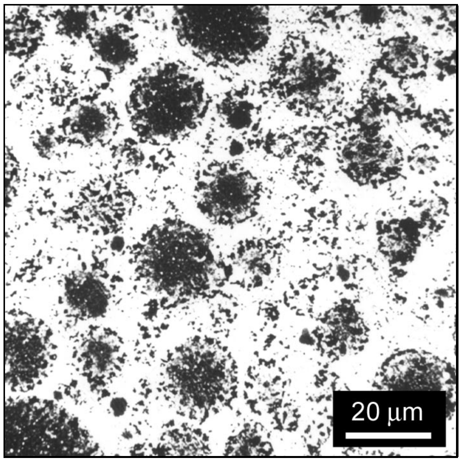

Fig. 3. High-copper globular amalgam (material G2).

In order to determine the rate of mercury release, a weighing bottle filled with an aerated model solution was closed with a wet-ground specimen (P2500/10s). The weighing bottle was then placed upside down in an air thermostat. The specimens were exposed at 37 °C for 22 hours. After that time, the electrolyte was stabilized with a solution of potassium dichromate in nitric acid and analyzed using the AAS method (TMA Mercury Analyzer, Altec). The measurements were repeated at least four times.

## 3. Results and discussion

### 3.1 Corrosion of amalgams

Fig. 4 shows typical potentiodynamic curves for studied amalgams, together with curves for tin and copper, whose influence on the corrosion behaviour is clearly the most significant. Given that the main amalgam components are mercury and silver, corrosion potential on the most curves is relatively negative. Oxidation of tin, resulting in a creation of insoluble corrosion products (hydrated $Sn(OH)_2$ and $Sn(OH)_4$ [19]), is the only electrochemical reaction under these conditions. Amalgam surface is covered by a layer of tin corrosion products in a relatively broad range of potentials. In the region around 0 V/SHE, which is at the same time the region of free corrosion potentials of long term exposed amalgams in an oral cavity [20, 21], the behaviour of materials differs in dependence on the tin and copper content. Amalgams with a relatively low copper content are characterized by a sharp current increase resulting from the breakdown of the tin oxide layer. In practice,

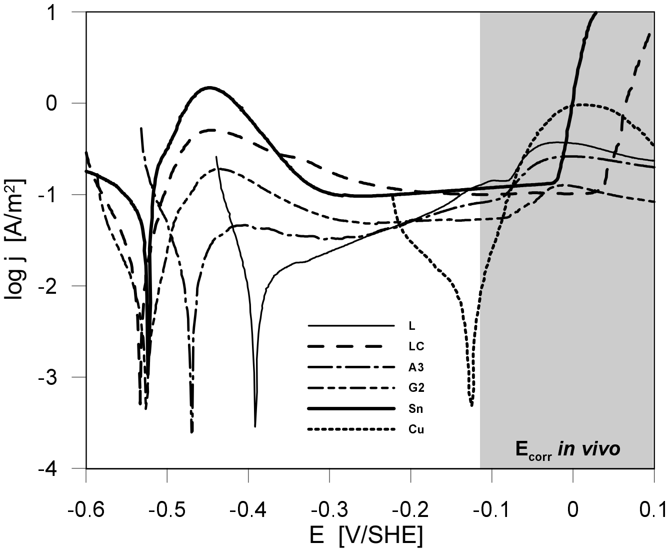

Fig. 4. Typical potentiodynamic curves for low- and high-copper amalgams, copper and tin (model saliva, deaerated, 37 °C, 1 mV/s).

it means mainly degradation process of the $\gamma_2$ phase which constitutes the major corrosion problem of low-copper dental amalgams. This phase is usually precipitated along the grain boundaries, and its corrosion causes marginal breakdown of the filling resulting in decrease of its life-time [22].

In the region of free corrosion potentials in the oral cavity, high-copper amalgams exhibit an increase of current, which is due to the electrochemical activity of copper containing phases. An analysis of the amalgams exposed *in vivo* revealed that a selective attack on the $Cu_6Sn_5$ ($\eta'$) phase creating continuous regions around AgCu particles in admix amalgams is the only more significant corrosion problem of high-copper amalgams [23]. In ternary materials copper containing phases are dispersed in the matrix, and negative impact of corrosion on the fillings life-time is, thus, in both cases lower than in the case of corrosion of the $\gamma_2$ phase in low-copper amalgams.

In order to minimize corrosion, the free corrosion potential of amalgams should be as negative as possible. Fig. 5 sumarizes stabilized values of the free corrosion potentials of all studied amalgams under model conditions, and it shows their obvious dependence on the mean tin content. Materials L and A1 are exceptions, with their copper content being so high that an X-ray diffraction analysis revealed the presence of the $\varepsilon$ phase.

The composition of the alloy used for the preparation of dental amalgam affects

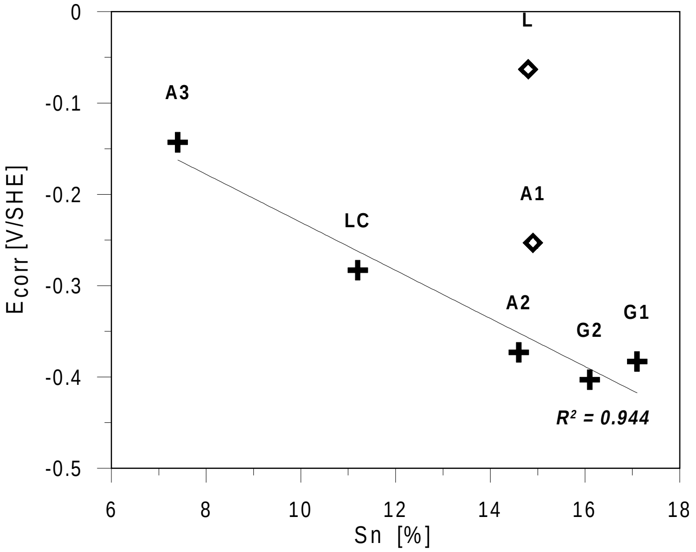

Fig. 5. Free corrosion potential of amalgams as a function of the mean tin content in amalgam (L and A1 not included in regression analysis; model saliva, aerated, 37 °C).

both the phase structure and the corrosion resistance of the resulting material. The presence of the $Sn_{7\text{-}8}Hg$ phase indicates possibility of localized corrosion attack. Very high concentration of copper results in shift of the free corrosion potential in a positive direction. This process increases the danger of copper corrosion products release, which may cause negative (allergic) response in sensitive individuals.

The technology of the alloy powder preparation or alloy powder particles shape does not affect the corrosion behaviour. High-copper amalgams of the admix type, in which the reaction rings around the grains of the AgCu alloy represent the localization of corrosion, are less advantageous. However, the resulting effect of the corrosion process on the filling life-time is far less fatal than in the case of low-copper materials containing $\gamma_2$ phase.

### 3.2 Mercury release

During amalgamation, mercury creates the two most important structural phases containing mercury: $\gamma_1$ matrix phase and structural component $\gamma_2$ in the case of the low-copper amalgam. The level of mercury release depends mainly on the volume of the $\gamma_1$ phase, and, as established by Ferracane and others [24–26], on its alloying by tin. The overall amount of mercury used for amalgam preparation is from practical point of view the only quantity known for the most of dental amalgams.

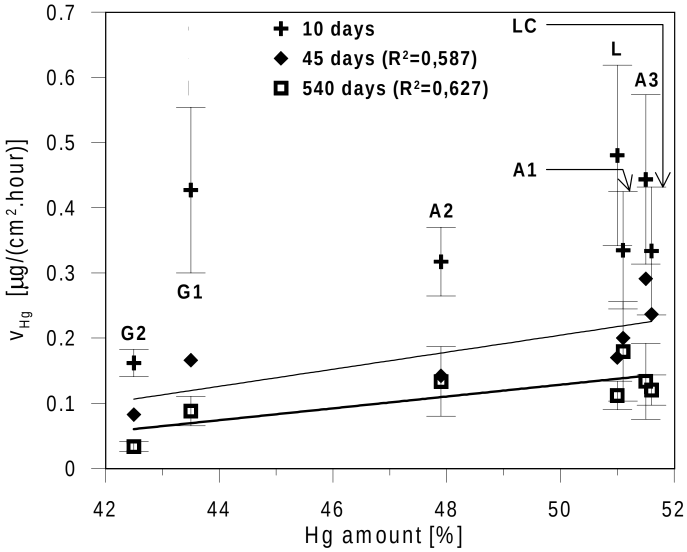

Fig. 6. Release of mercury as a function of the mean mercury content in amalgam (model saliva, aerated, 37 °C).

In the whole set, it is only material G2 that exhibits any statistically significant difference from the other tested materials in two out of three times selected for the measurement (10 and 540 days – see Fig. 6). It is a ternary material based on globular powder with a high tin content and the lowest amount of mercury used for amalgamation. As it results from the study [27] dealing with an analysis of the behaviour of amalgams prepared using various types of powders of the same high-copper ternary alloy, amalgam based on globular powder showed the lowest rate of mercury release. Very low values of the rate of mercury release were also stated in this study for the other globular amalgam (G1), but no statistically significant difference from the group of other materials was noticed in this case. In view of the above mentioned significant difference of material G2, particularly after 540 days of ageing, this specimen is not considered in the following discussion.

Dependence of the rate of mercury release as a function of its content in amalgams is shown in Fig. 6 for the whole set of the studied materials and for all exposure times. To facilitate orientation, the confidence intervals for the time of 45 days have been omitted. All amalgams show considerable data scatter in the 10th day after their preparation, but the differences are not statistically significant, and the data do not follow any trend. This period of time is obviously too short for stabilization of the structures. The mean rate of mercury release is 0.37 $\mu$g/(cm$^2 \cdot$h), its minimum value is 0.17 $\mu$g/(cm$^2 \cdot$h), and maximum 0.48 $\mu$g/(cm$^2 \cdot$h).

The mean rate of mercury release in the 45th day after preparation is 0.20 $\mu$g/(cm$^2\cdot$h). In comparison with the measurement in the 10th day, the mean value dropped 1.9 times. The maximum and minimum rates are 0.29 and 0.14 $\mu$g/(cm$^2\cdot$h), respectively. Specimens LC, A1 and A3 exhibit higher than average rates of mercury release.

The differences in the rate of mercury release between materials are not statistically significant in the set aged for 540 days, with the mean rate being 0.131 $\mu$g/(cm$^2\cdot$h). The difference between the maximum (0.179 $\mu$g/(cm$^2\cdot$h)) and minimum (0.088 $\mu$g/(cm$^2\cdot$h)) rates is similar to that measured in the 45th day of exposure, i.e. 2.0 times in this case. A higher than average rate of mercury release was determined for specimens A1, A2 and A3. There is also interesting the difference in the behaviour of materials L (0.112 $\mu$g/(cm$^2\cdot$h)) and A1 (0.179 $\mu$g/(cm$^2\cdot$h)), which seems to differ only in terms of their preparation (lathe-cut vs. admix). All admix amalgams exhibit an above average rate of mercury release and also higher scatter if compared with the other materials under study.

### 3.3 Differences in the rate of mercury release as a function of the type of amalgam alloy powder

Globular powders – the lowest amount of mercury was used for preparation of these amalgams, and the rate of its release from long-term aged specimens is the lowest. A higher rate of mercury release was noticed for material G1, where the tin content in the alloy is of 2 % higher than in material G2, but it contains more mercury. Difference in the behaviour of these two materials is also evident from the time dependence of mercury release. Material G1 is similar to the other amalgams in this respect, while material G2 exhibits the lowest rate of mercury release from the time of preparation. The free corrosion potential of both materials is comparable.

Lathe-cut powders – there were two materials in the set, one of them was low-copper amalgam (LC). Material L contains 29.6 % and LC 22.4 % of tin, in the case of LC some tin is mercury-bound in the $\gamma_2$ phase. Both materials differ importantly in copper content and in free corrosion potentials. Nevertheless, specimens aged for a longer time display practically the same rate of mercury release, which is the lowest measured after amalgams based on globular powder. The results also demonstrate that in terms of mercury release, low-copper amalgams do not swerve the spectrum of other materials behaviour.

Admix powders – the set contains three materials. The rate of mercury release from specimens aged for 540 days is above average in all three of them. Surprising is the difference in behaviour of specimens A1 and A3, which have a different tin content in the alloy (A1 roughly twice as much as A3) and displayed a clearly opposite trend in the rate of mercury release. The free corrosion potential of specimen A3 is more positive than that of specimen A1, and the material is therefore exposed under conditions which are more favourable for passivation. As a result, the rate of mercury release is lower. From the practical point of view, however, too positive free corrosion potential may be a drawback.

Explanation of the above mentioned unexpected or opposite trends in mercury release rate will require more detailed study mainly focussed on the tin content in $\gamma_1$ phase analysis.

## 4. Conclusions

The corrosion behaviour of the set of studied amalgams and mercury release from them may be summarized in the following general points:

1. The free corrosion potential of amalgams depended predominantly on the overall tin content, which increase leads to a drop in the free corrosion potential. More negative free corrosion potentials negatively influence, to some extent, conditions for passivation, but at the same time counteract the corrosion potential shift to an undesirable region.

2. High content of copper (in the studied set it was at the level of 25 % in the alloy) and silver (at the level of 70 % in the alloy) caused an undesired shift of the free corrosion potential in the positive direction, particularly, when $\varepsilon$ phase is present in the structure. An amalgam alloy must contain a sufficient amount of copper in order to prevent formation of $\gamma_2$ phase, but any further increase in copper content may have a negative impact from the corrosion point of view.

3. The technology of the alloy powder preparation did not have any significant effect on the corrosion behaviour of materials in the studied set.

4. The rate of mercury release depended, to a certain extent, on the amount of mercury in the structure only in the case of specimens aged for 45 and 540 days.

5. The technology of the alloy powder preparation affected the rate of mercury release, rising in the globular<lathe-cut<admix order.

6. Besides amalgam A1 (45 days), all admix specimens displayed an above average rate of mercury release. All three specimens of this type also showed higher scatter as compared with specimens of other types.

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