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STUDY OF THE DEAMALGAMATION PROCESS IN SILVER–TIN–BASE AMALGAMS [1]

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Dedicated to Professor Mladen Paić on the occasion of his 90$^{\mathbf{th}}$ birthday

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Deamalgamation of the common dentistry amalgam scrap, as well as of a model $Ag_{70}Sn_{17}Cu_{13}$ prealloy amalgam, was studied by metallography, microhardness, X-ray diffraction and differential thermal analysis techniques. The results are discussed from the view–point of the possible powder-metallurgical application of the process.

1. Introduction

The use of metal powders for dental purposes represents one of the oldest technical applications of powder metallurgy [1]. On the other side, the so-called amalgam

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process [2-5] played a significant role in the early history of tungsten powder metallurgy. The Cd-Bi amalgam served as a binder to refractory tungsten–powder in production of incandescent lamp filaments. In that process the amalgam was completely expelled from refractory tungsten matrix at subsequent high-temperature sintering of the green compact. Although obsolete, this process, in a slightly modified version, may still have the virtue appealing for its revival. In fact, it could prove worthy to distil-off fractionally mercury alone from the amalgam binder of a refractory powder matrix and to keep the amalgam prealloy rest as the solid metallic binder of the consolidated body. The key prerequisite to approach this renovelled amalgam process efficiently is to study the deamalgamation in relation to crystallographic, physical, mechanical and chemical properties of the deamalgamated metallic or intermetallic products, as well as to their metallurgical and structural compatibility with promising refractory powder matrices. Besides, the study of deamalgamation process of dentistry scrap should obviously bear very positive ecological implications.

2. *Experimental*

We designed and constructed the simple vacuum distillation apparatus, shown in Fig. 1 [6], which was used for the deamalgamation experiments.

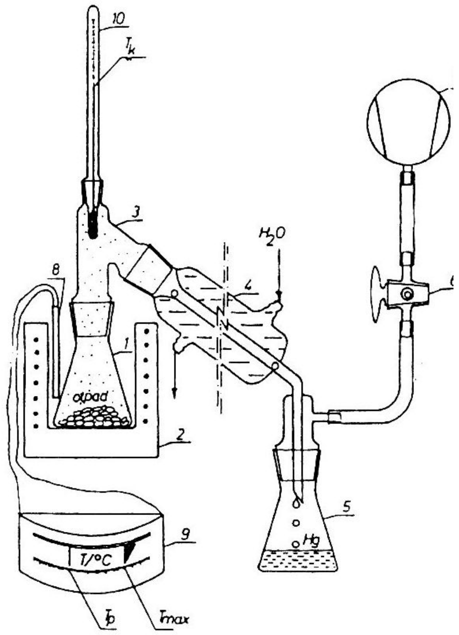
Processing parameters were adjusted by treating the unsorted amalgam filling scrap with a minor share of retrieved restoratives from a dentistry laboratory. An optimized temperature-time diagram for a 50 g amalgam scrap charge in shown in Fig. 2.

The synthesis of a representative $Ag_{70}Sn_{17}Cu_{13}$ (weight percentages) prealloy was made to ensure compositionally well defined and highly practice–matching research material. The highly homogenized mixture of 99.9^+ wt.% pure component metal powders was encapsulated into a quartz tube, evacuated to 10^{-3} Pa, melted at 1120 K, and filed down to a fine powder. The X–ray diffraction (XRD) of powders was performed using a Philips PW 1820 diffractometer with CuK_α graphite–monochromated radiation. For identification of the phases present in the samples, we used the data collected in Ref. 7. Specimens for metallographic observation and for determination of Vickers microhardness were prepared by a standard mechanical polishing procedure. A Leitz light microscope, Aristomet type, supplied with an automatic camera, was used to record the microstructure in specimens. Also, a Leitz Metallux 3 microscope in conjuction with Miniload 2 type attachment, supplied with the RZD DO computing device, was used for microhardness determination. The pyramide load during the measurement was 0.981 N. Differential thermal analysis (DTA) was performed by means of a Gebruder Netsch equipment. All DTA measurements were made in a helium atmosphere applying a heating rate of 5 K/min.

3. *Results and discussion*

The microstructure of amalgam scrap observed in the specimens before and after deamalgamation is shown in Figs. 3a and b and (c and d), respectively.

The micrographs (e and f) in the same figure represent microstructure observed in the model Ag70-Sn17-Cu13 prealloy. The corresponding hardness numbers for the above mentioned alloys are included in Table 1.



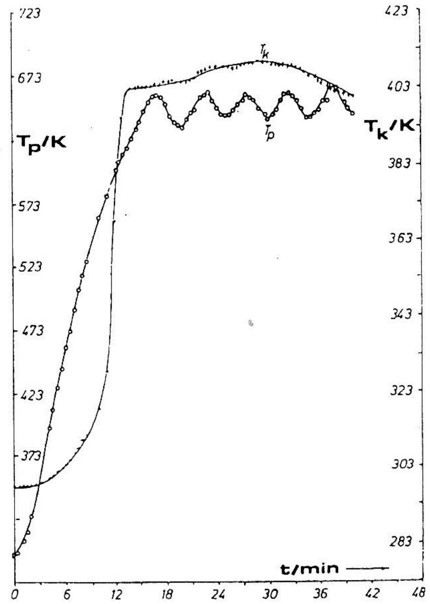


Fig. 1. Shematic drawing of the deamalgamation equipment; legend: glass container - 1, pot furnace - 2, joining glass piece - 3, vapour condenser - 4, glass container for liquid Hg *- 5, two-way valve - 6, vacuum pump - 7, thermocouple (T_p) - 8, temperature controller and display - 9, and mercury thermometer (T_k) - 10.*

Fig. 2. The temperature-time diagram for a 50 g *amalgam scrap charge. Temperatures T_p and T_k were measured by thermocouple and by mercury thermometer (right).*

The obvious cause of the significant decrease of hardness on deamalgamation is an enormous population of pores of an average diameter of about 10 μm in the deamalgamated specimen (see Figs. 3c and d).

TABLE 1.
Vickers microhardness determined on studied samples.

Amalgam scrap	(1.09 + 0.24) GPa
Deamalgamated amalgam scrap	(0.45 + 0.08) GPa
Model alloy $Ag_{70}Sn_{17}Cu_{13}$	(1.40 + 0.17) GPa

When preparing an amalgam tooth filling ("trituration"), one admixes small quantity of prealloyed metallic powder and approximately the same mass of liquid mercury. It is known that the microstructure of a typical low-copper Ag-Sn-base amalgam (LCA) consists of roughly 30 vol.% of unconsumed prealloy γ-Ag_3Sn particles embedded in minute γ_1-Ag_2Hg_3 grains participating with about 60 vol.%, and of about 10 vol.% of irregular discrete γ_2-Sn_7Hg grains [8]. A simple calculation

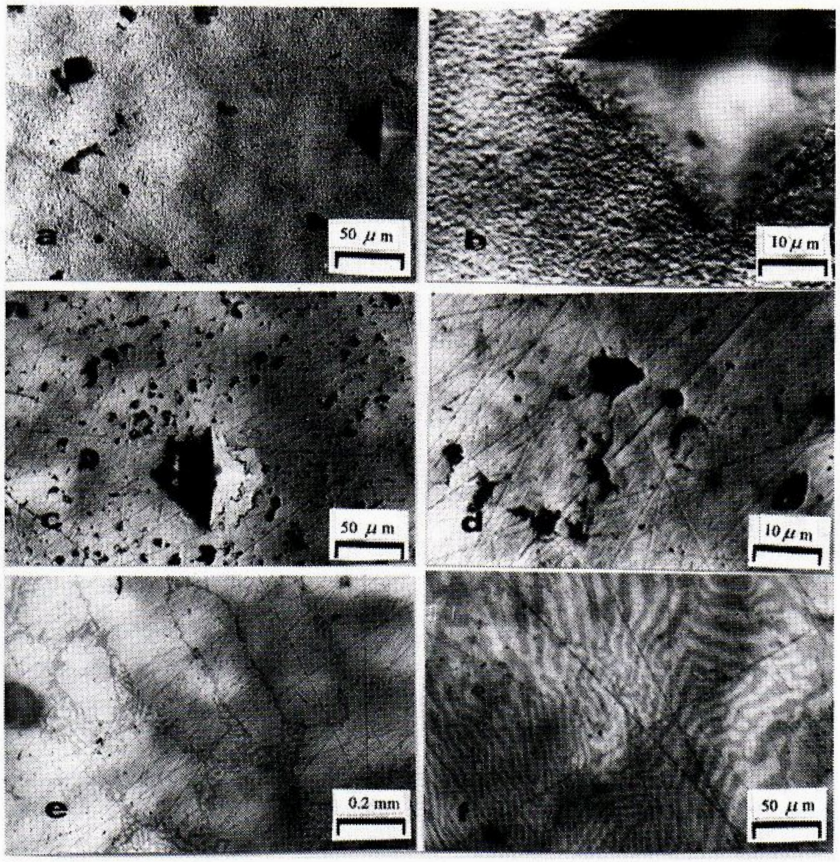


Fig. 3. Light micrographs of a dental amalgam scrap (a and b), of a deamalgamated dental amalgam scrap (c and d), and of a model $Ag_{70}Sn_{17}Cu_{13}$ prealloy (e and f), at two magnifications, respectively.

shows that mercury should be completely structurally engaged in these phases after setting, i.e. no free mercury in the amalgam should exist. Beside the microstructure uniformity (Figs. 3a and b), this statement supports the XRD pattern of amalgam scrap filings, exhibiting sharp diffraction lines, identified as: γ_1-Ag_2Hg_3 ([7], card number: 11-67), Cu_7Hg_6 ([7], card number: 33-470), and ζ-Cu_6Sn_5 ([7], card number: 2-713) (see Fig. 4a). In the same figure two lines which do not belong to the above phases are denoted by x. Hence, the origin of the cavities in the deamalgamated samples observed in Figs. 3c and d cannot be explained by assuming that they were the emptied space of former free-mercury wells. These cavities are due to a kind of "internal shrinkage", whose nucleation and growth mechanisms chalenge for a rational explanation.

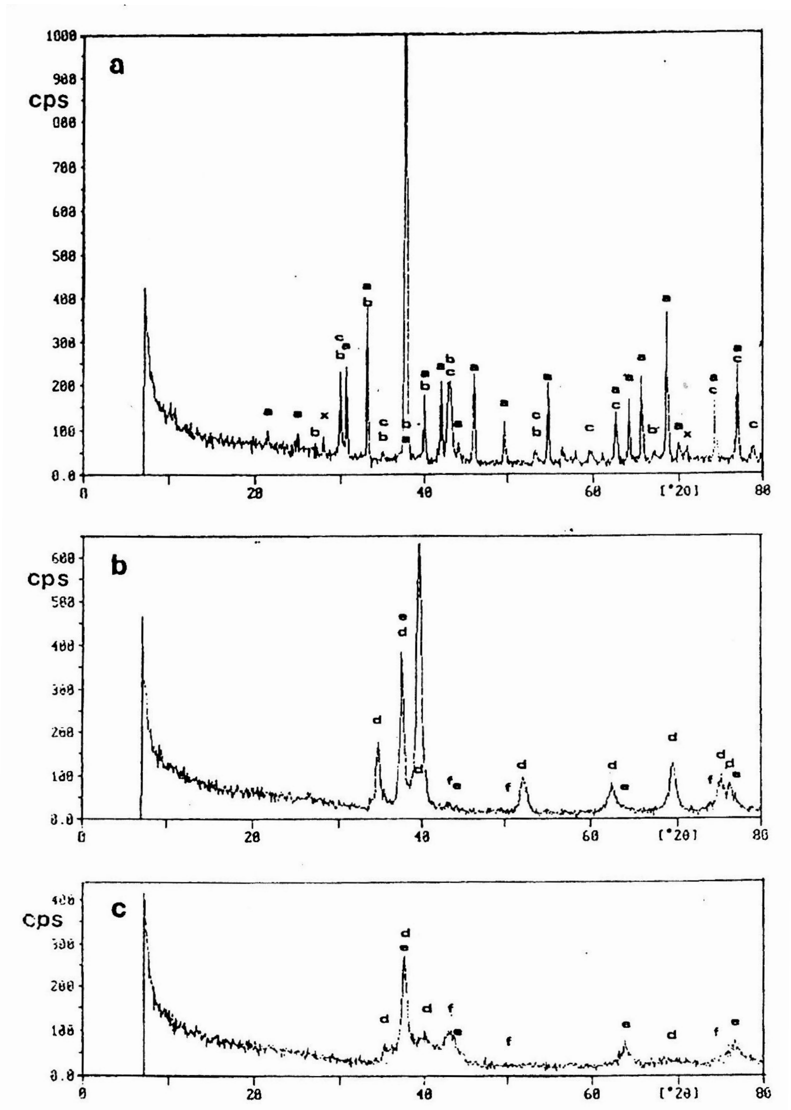


Fig. 4. XRD patterns of a dental amalgam scrap before (a) and after deamalgamation (b), and of the model $Ag_{70}Sn_{17}Cu_{13}$ *prealloy (c), respectively. The angular positions of observed diffraction lines belonging to the* γ_1-Ag_2Hg_3, Cu_7Hg_6, ζ-Cu_6Sn_5, γ-Ag_3Sn, Ag *and* Cu *phases are marked by a, b, c, d, e and f, respectively.*

The mass loss in the deamalgamation procedure applied was on the average 50% of the input amalgam scrap charge which means that the process of deamalgamation goes to completion (or at least very nearly so). This statement is convincingly confirmed by XRD pattern taken from a deamalgamated sample (Fig. 4b). The observed diffraction pattern belongs entirely to the γ-Ag_3Sn prealloy phase (the expected slight marks of the strogest Cu- and Ag-lines in the pattern indicate an LCA prealloy composition). This observation leads to an important conclusion that the deamalgamation process does not affect the phase structure of the original prealloy powder. In other words, the amalgamation is a reversible crystallographical process. This is decisive for the renewed amalgam process mentioned in Introduction. One can generally rely upon the expectation that the original crystal structure of the amalgam prealloy binder within a refractory powder compact matrix will not dramatically change after deamalgamation. This is a base for programming the material's properties.

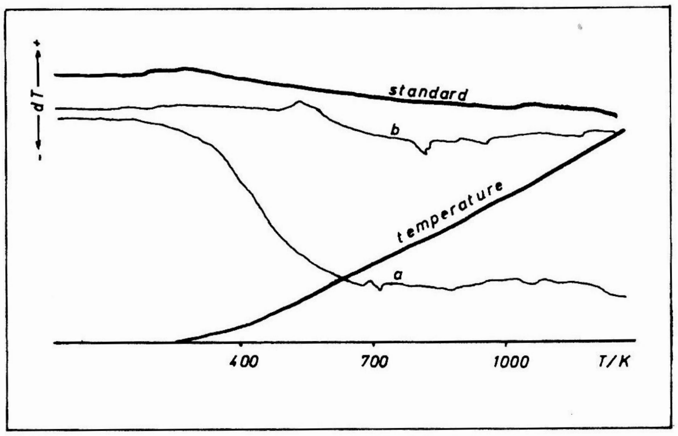


Fig. 5. DTA curves of a deamalgamated dental amalgam scrap (a), of the $Ag_{70}Sn_{17}Cu_{13}$ *prealloy (b), and the curve denoted "standard" representing the run without sample in place.*

Naturally, this general prospect comprises a number of problems that should be solved. For example, with regard to the compactness and the mechanical properties of the deamalgamated binder, one should interpret unusually large endothermic slope in the DTA diagram of deamalgamated sample (curve a in Fig. 5), beginning practically at room temperature and ending at a temperature of nearly 700 K. An apparently logical doubt about the rest-mercury evaporation is inconsistent within the previously represented facts. The actual origin of XRD line broadening of the γ-Ag_3Sn phase (see Fig. 4b) has also to be rationalized. It was very easy to prepare filings for XRD analysis, and this cannot be considered as a possible cause of broadening. One balances between the rather narrow compositional range (26.0–26.7 mass % Sn) of this intermetallide and the eventual powder particle comminution upon deamalgamation as the possible causes, and this is the puzzle to be considered carefully.

Micrographs in Figs. 3e and f show the microstructure of the vacuum melted model high–copper–single–composition (HCSC) $Ag_{70}Sn_{17}Cu_{13}$ amalgam prealloy. It is highly compact and uniform and is harder than the amalgam itself (see Table 1). XRD pattern of this prealloy (Fig. 4c) confirms the expectation that the dominating grains (of 5 to 100 μm in diameter) belong to the Ag-base solid solution, while the minor grain-boundary phases are identified as γ-Ag_3Sn and pure Cu. In this case the XRD line broadening is probably a consequence of very difficult sample preparative filing. The corresponding DTA diagram (curve b in Fig. 5) shows some interesting details of both the endo- and exothermic nature, but the most important information obtained from DTA measurement seems to be the absence of the large downward slope at low temperatures. The difference in DTA behaviour of deamalgamated and original amalgam prealloy, curves (a) and (b) in Fig. 5, calls for further investigation.

4. *Conclusion*

Our results point to the following conclusions: The efficiency of a simple vacuum distillation system has been successfully tested. The processing parameters of the procedure applied were properly optimized by using the dentistry filling amalgam scraps and retrieved restoratives as testing materials. The amalgamation process proves crystallographically reversible, i.e. the original prealloy crystal structure gets restored on deamalgamation. Beside these positive statements mentioned above a number of unanswered questions, like "internal shrinkage" or endothermic slope, should be explained. Furthermore, the reaction between the liquid mercury and the fine Ag-Sn-Cu-base prealloy powder should be considered as a process of liquid phase sintering with a transient liquid phase in which mercury is used in the reaction [4,9]. Therefore, answering this and similar questions will promote an economic and comfortable study of sintering process at room temperature, which otherwise occurs at high- temperatures, as well as applications of the obtained results, particularly regarding the sintering procedure, to other available and promising systems.

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ISTRAŽIVANJE DEAMALGAMACIJSKOG PROCESA U AMALGAMIMA SLITINA BOGATIH SREBROM I KOSITROM

Proces deamalgamacije u amalgamima slitina bogatih srebrom i kositrom istraživan je metalografijom, mjerenjem mikrotvrdoće, rentgenskom difrakcijom i diferencijalnom termičkom analizom. Dobiveni rezultati raspravljeni su s gledišta regeneracije otpadnog amalgama (reciklaže, tj. obnavljanja strukture i svojstava polaznih komponenti), kao i moguće uporabe ovog procesa u metalurgiji praha.