Evaluation of the Amalgamation Reaction of Experimental Ag-Sn-Cu Alloys Containing Pd Using a Mercury Plating Technique

Marie KOIKE, Jack L. FERRACANE¹, Hiroyuki FUJII
and Toru OKABE²

Nagasaki University Graduate School of Biomedical Sciences,
Course of Medical and Dental Sciences,
Department of Developmental and Reconstructive Medicine,
Division of Removable Prosthodontics and Management of Oral Function,
1-7-1 Sakamoto, Nagasaki, 852-8588 Japan

¹Department of Biomaterials & Biomechanics,

Oregon Health and Science University School of Dentistry, Portland, OR, USA

²Department of Biomaterials Science, Baylor College of Dentistry,
Texas A&M University System Health Science Center,
3302 Gaston Ave., Dallas, TX 75246, USA

Received March 31, 2003/Accepted June 26, 2003

A mercury plating technique was used to determine the phases forming on experimental Ag-Sn-Cu alloy powders (with and without Pd) exposed to electrolytically deposited mercury. Four series of alloy powders were made: a) 1.5% Pd with 10-14% Cu (CU series); b) 1.0% Pd with 10-14% Cu (1PD series); c) 1.5% Pd with different ratios of Ag₃Sn (γ) to Ag₄Sn (β) with 12% Cu (AGSN series); and d) 9-13% Cu with no Pd (NOPD series). Each powder was pressed on a freshly prepared amalgam specimen made from the same powder and metallographically polished until cross sections appeared; mercury was electroplated on the alloy particles. Alloy powders, amalgams and electroplated specimens were examined using XRD and SEM/EDS. XRD confirmed the presence of γ_2 in amalgams made from alloys with Cu<13% or with Ag₃Sn/Ag₄Sn>0.8. Specimens with moderately plated Hg showed γ_1 (Ag₂Hg₃) polyhedra and η' -Cu₆Sn₅, but not γ_2 . This method effectively identifies alloys prone to forming γ_2 .

Key words: amalgamation reaction, mercury-plating, palladium

INTRODUCTION

It is estimated that over 100 million posterior amalgams are placed annually in the USA. Despite improvements in esthetic alternatives, such as composites, dental amalgam continues to be the direct posterior restorative material of choice for more than 80% of practitioners¹. However, significant anti-amalgam sentiment exists due to concerns over the use of Hg-containing fillings in dentistry. Although studies have shown that the danger from Hg release from dental amalgams is minimal², research continues on the development of alloys that make amalgams with reduced Hg release. Recently, it was reported that small amounts of Pd (0.5 to 9.0 wt%) added to an alloy have a beneficial effect of decreasing Hg vaporization during setting and after abrasion of set amalgam^{3,4}. Apparently, Pd stabilizes the amalgam structure, as evidenced by thermal analysis^{3,5} and dilatometry⁶. Based on recent studies, it is

hypothesized that the Pd stabilizes the γ_1 matrix, possibly by affecting the amount of Sn dissolving in this phase during setting, which results in less overall Hg vaporization. A series of alloys was prepared to test several hypotheses regarding the effects of alloying Pd, altering the Ag and Sn ratio (and thus, the $\gamma\text{Ag}_3\text{Sn}$ to $\beta\text{Ag}_4\text{Sn}$ ratio), and changing the Cu content. This study investigated the amalgamation reaction of these experimental alloys, as part of the total characterization of these experimental amalgams.

The objective of this study was to use a Hg-plating technique to determine the phases forming on various experimental Ag-Sn-Cu alloy powders with and without Pd, and three commercial alloys, when exposed to electrolytically deposited Hg.

MATERIALS AND METHODS

Alloys used

Four series of experimental alloy powders were fabricated for this project: a) CU series- 1.5% Pd with different Cu concentrations (10-14%); b) 1PD series- 1.0% Pd with different Cu concentrations (10-14%); c) AGSN series- 1.5% Pd with different Ag_3Sn (γ) to Ag_4Sn (β) ratios at the same Cu concentration (12%); and d) NOPD series- different Cu concentrations (9-13%) with no Pd. As the controls, three commercial alloys (Tytin: Kerr Manufacturing Co., Romulus, MI, USA; Dispersalloy: The L.D. Caulk Division, Dentsply International Inc., Milford, DE, USA; Spheraloy, Kerr Manufacturing Co., Romulus, MI, USA) were employed. Tytin consists of spherical particles of a ternary Ag-Sn-Cu alloy. Dispersalloy is a mixture of spherical Ag-Cu alloy particles at its eutectic composition and lathe-cut Ag-Sn alloy particles. Spheraloy is the spherical powder of a Ag-Sn alloy. Since Tytin and Dispersalloy were supplied in tablet form, we pulverized them into powder using an amalgamator (Caulk VariMix III, L. D. Caulk, Milford, DE, USA). All other alloys were originally in the powder form. The chemical compositions (wt%) of both the experimental powders and commercial alloys tested in the study are listed in Table 1. The experimental powders consisted of spherical particles and were made to our specifications by an alloy powder manufacturer (Special Metals Corporation, Ann Arbor, MI, USA). The chemical compositions of the commercial alloy powders were obtained from published data⁷⁾. In the present paper, Tytin or Dispersalloy are referred to as high-Cu alloys and Spheraloy is referred to as a low-Cu alloy. Note that Table 1 lists the ratio of Ag_3Sn and Ag_4Sn for each alloy. As shown, the series of AGSN powders was designed to span a range of $\text{Ag}_3\text{Sn}/\text{Ag}_4\text{Sn}$ from 23.9 to 0. The rate of amalgamation was considered to increase from AGSN1 to AGSN5, since the reaction with mercury is much faster for $\beta\text{Ag}_4\text{Sn}$ than for $\gamma\text{Ag}_3\text{Sn}$ ⁸⁾. Indeed, the amalgamation reaction of AGSN5 was too fast to prepare the amalgam specimens. Therefore, alloy powder AGSN5 was not included in the present study.

Knowing the composition of each of the phases present in the alloys, the weight percent of each phase could be calculated by solving a series of simultaneous equations. To determine the compositions of the phases for the Pd-containing alloys, the

Table 1 Chemical compositions (wt%) of the alloys used for the amalgams

Series	Alloy Code	Ag	Sn	Cu	Pd	Ag ₃ Sn/Ag ₄ Sn
CU series	CU1	60.3	28.2	10.0	1.5	3.4
	CU2	59.1	28.4	11.0	1.5	3.3
	CU3	58.0	28.6	12.0	1.5	3.3
	CU4	56.8	28.8	13.0	1.5	3.3
	CU5	55.6	29.0	14.0	1.5	3.3
IPD series	IPD1	61.2	27.8	10.0	1.0	3.6
	IPD2	60.0	28.0	11.0	1.0	3.7
	IPD3	58.9	28.2	12.0	1.0	3.7
	IPD4	57.7	28.3	13.0	1.0	3.4
	IPD5	56.5	28.5	14.0	1.0	3.5
AGSN series	AGSN1	57.0	29.5	12.0	1.5	23.9
	AGSN2	57.9	28.6	12.0	1.5	3.3
	AGSN3	58.7	27.8	12.0	1.5	1.5
	AGSN4	59.5	27.0	12.0	1.5	0.8
	AGSN5	61.6	24.9	12.0	1.5	0
NOPD series	NOPD1	63.7	27.3	9.0	0.0	3.4
	NOPD2	62.5	27.5	10.0	0.0	3.3
	NOPD3	61.2	27.8	11.0	0.0	3.3
	NOPD4	60.0	28.0	12.0	0.0	3.3
	NOPD5	58.8	28.2	13.0	0.0	3.3
Commercial alloys	Tytin	59.3	27.1	13.3	0.0	1.8
	Dispersalloy	69.6	17.7	11.8	0.0	*
	Spheraloy	71.0	25.5	3.5	0.0	6.7

*Cannot be accurately determined since this is not a single-composition alloy

powders from the AGSN2 and AGSN5 alloys were vacuum-sealed in Vycor tubing and annealed in a furnace at 350°C for 7 days. The annealed alloys were then mounted in epoxy and polished for analysis in the scanning electron microprobe (6400 SEM, JEOL, Peabody, MA) using wavelength dispersive spectroscopy (LINK eXL, Oxford Analytical, Concord, MA) following the general procedures previously described by Mahler and Adey⁹⁾.

For alloys containing Ag, Sn, Cu, and Pd, four phases form in the alloy particles: 1) γ -Ag₃Sn, composed of 71.4% Ag, 27.0% Sn, 1.6% Cu; 2) β -Ag₄Sn, composed of 78.4% Ag, 20.6% Sn, 1.0% Cu; 3) ϵ -Cu₃Sn, composed of 3.6% Ag, 38.4% Sn, 54.2% Cu, 3.8% Pd; and a Pd-containing phase composed of 1.3% Ag, 51.5% Sn, 24.4% Cu, 22.8% Pd. The compositions of the γ -Ag₃Sn and Cu₃Sn were determined from the AGSN2 alloy, and the composition of the β -Ag₄Sn was determined from the AGSN5 alloy. This procedure was followed because γ -Ag₃Sn was the predominant phase in AGSN2, and β -Ag₄Sn was the predominant phase in AGSN5. The composition of ϵ -Cu₃Sn was consistent in both AGSN2 and AGSN5. Because the Pd-containing phases were too small to be measured accurately in either the AGSN2 or AGSN5 alloys, the composition of this phase was determined from another experimental alloy containing 5 wt% Pd used in previous experiments³⁾.

For alloys containing Ag, Sn, and Cu, but no Pd, three phases form in the alloy

particles: 1) γ -Ag₃Sn, composed of 71.4% Ag, 27.0% Sn, 1.6% Cu; 2) β -Ag₄Sn, composed of 78.4% Ag, 20.6% Sn, 1.0% Cu; and 3) ϵ -Cu₃Sn, composed of 2.0% Ag, 39.4% Sn, 58.7% Cu. The compositions of the γ -Ag₃Sn and β -Ag₄Sn were those used for the AGSN2 and AGSN5 alloys. The composition of the ϵ -Cu₃Sn was taken from a previous analysis of Tytin by Mahler and Adey⁹⁾. In this study, the same type of calculations were made for Tytin and Spheraloy, using the compositions reported by Mahler and Adey for Tytin, and these values have been included in Table 1 as Ag₃Sn/Ag₄Sn values.

X-ray diffractometry

Amalgam specimens from all the experimental alloy series and the commercial alloys were prepared for x-ray diffractometry by condensing a triturated alloy powder into a steel die having a cross-sectional area of 10 mm×15 mm with approximately 14 MPa pressure, which is similar to the pressure specified in the ANSI/ADA specification for dental amalgam. The experimental alloy powders were triturated with Hg (initially 50% to the powder) by adjusting the trituration conditions on a Caulk VariMix III (L. D. Caulk, Milford, DE, USA), so that the consistency of the resultant amalgams was similar to that of Tytin. The commercial alloys were triturated using

Table 2 Trituration conditions for the alloy tested

Series	Alloy Code	Initial %Hg	Speed	Time	Pestle	Residual Hg (%) (Mean/SD)
CU series	CU1	50.00	M	10	small*	46.18/0.26
	CU2	50.00	M	9	small	45.36/0.46
	CU3	50.00	M	11	small	45.22/0.69
	CU4	50.00	M	10	small	45.64/0.70
	CU5	50.00	M	9	small	45.06/0.43
1PD series	1PD1	50.00	M	10	small	44.83/0.21
	1PD2	50.00	M	14	large**	44.45/0.29
	1PD3	50.00	M	14	large	43.80/0.57
	1PD4	50.00	M	12	large	44.23/0.54
	1PD5	50.00	M	10	large	45.30/0.33
AGSN series	AGSN1	50.00	M	10	small	45.76/0.56
	AGSN2	50.00	M	11	small	45.22/0.69
	AGSN3	50.00	M	10	small	45.73/0.27
	AGSN4	50.00	M	7	no	46.69/0.46
	AGSN5	50.00				
NOPD series	NOPD1	50.00	M	13	large	44.83/0.29
	NOPD2	50.00	M	12	large	44.44/0.55
	NOPD3	50.00	M	12	large	44.67/0.38
	NOPD4	50.00	M	12	large	45.24/0.61
	NOPD5	50.00	M	12	large	45.48/0.45
Commercial alloys	Tytin	44.70	M	10	no	42.04/0.30
	Dispersalloy	50.00	M	7	no	48.22/0.54
	Spheraloy	52.03	M	16	no	47.99/0.37

*Small Pestle: 3.18 mm diameter; 11.5 mm long; 0.680 g

**Large Pestle: 3.94 mm diameter; 12.6 mm long; 1.138 g

the conditions recommended by each alloy manufacturer. The trituration conditions, including the initial Hg%, speed, time, type of pestle, and the mean of the residual Hg%, are given in Table 2. The residual Hg% (R) was estimated by collecting and weighing the mercury exuded from around the die plunger using the following calculation:

$$R = [\{ M - E - 0.5 (P + M) + 0.5 (E + A) \} / A] \times 100,$$

where M is the initial weight of mercury prior to trituration; E is the weight of mercury exuded; P is the weight of alloy powder triturated; and A is the weight of the amalgam specimen.

After aging for 3 days, the height of the specimens was adjusted to approximately 4 mm, and then one of the large surfaces was polished to 4000 grit silicon carbide paper. The finished surfaces were examined using an x-ray diffractometer (XRD; Miniflex CN2005, Rigaku, Japan) operating at 30 kV and 10 mA. Cu-K α radiation was used at a scanning speed of 0.02/step and 6 sec per step over a 2θ range of 29 to 45°. The peaks of the XRD patterns were indexed according to the ICDD (International Center for Diffraction Data, Swarthmore, PA, USA) polycrystalline powder diffraction files. In addition, x-ray diffraction information for each alloy powder was obtained. Two specimens were analyzed for each alloy powder and amalgam.

Preparation of specimens for Hg plating

The present study intended to examine the amalgamation reaction on the cross-sectional surface of the alloy particles. Thus, it was necessary to first "glue" together alloy particles into a solid mass, which was accomplished by embedding the particles into a freshly made amalgam prepared using the corresponding alloy powder. The freshly prepared amalgams were condensed for 15 seconds in a steel die with a cross-sectional area of 13 mm $\times$ 13 mm under a pressure of approximately 14 MPa. The height of the condensed amalgam was approximately 2 mm for most specimens. Directly after removing the plunger from the die, a layer or two of the same alloy powder was spread over the open surface of the amalgam. Immediately, the surface was pressed again with the same pressure for 60 seconds. After initial setting, the condensed amalgam with the powder was removed from the die and stored for 24 hours. An electric lead wire was connected using silver paint (14810, Ernest F. Fullam, Latham, NY, USA) at the center on the surface of the condensed amalgam, opposite the surface where the alloy powder was compressed. After the silver paint dried, the condensed amalgam was mounted with the powder surface side down in a resin mounting material (Epoxide, Buehler Ltd., Lake Bluff, IL, USA). The surface with the alloy powder was located at the bottom of the mount, and was metallographically polished up to 2,000 grit silicon carbide paper so that the cross sections of the powder were revealed. A solution of 0.53 g HgCl₂, 0.71 g NH₄Cl, 1.42 g NaCN, and 47.30 ml distilled water¹⁰⁾ was used to electrolytically plate the mercury on the alloy particle cross sections, as in an earlier study¹¹⁾. The plating was

performed for 2 to 5 minutes with the current density of 25 mA/cm² in a room temperature bath.

Metallography

The Hg-plated specimens were examined using a scanning electron microscope (SEM; JSM 6300, JEOL, Peabody, MA, USA) equipped with an energy dispersive spectrometer (EDS; Voyager x-ray microanalysis and digital imaging system, Noran Instruments, Middleton, WI, USA). Selected individual crystals formed on the alloy particles were observed in the SEM and semi-quantitatively analyzed by EDS. Results were subjected to ZAF correction¹²⁾. Identification of crystals of intermetallic compounds formed on the specimens were made by comparing various identified reaction phases found in our previous studies^{13,14)}.

RESULTS

X-ray diffractometry

Fig. 1 shows typical XRD patterns of alloy powders in the entire CU series (CU1 through 5) and those of the three commercial alloys as well. As expected, peaks associated with γ Ag-Sn (Ag_3Sn) were found for all alloy powders. The diffraction angles for β Ag₄Sn (PDF# 29-1151) overlap with those of γ Ag₃Sn (PDF# 44-1300), so these two intermetallic compounds could not be differentiated. ϵ Cu-Sn (Cu_3Sn) phases were identified for all powders, including the low-Cu Spheralloy. No peaks were associated with any Pd-containing phases in any of the Pd-containing powders.

Fig. 1 XRD patterns of powder of CU series vs. commercial alloys.

Fig. 2 XRD patterns of amalgams prepared from CU series compared with those of the three commercial amalgams tested.

The XRD patterns from the Dispersalloy powder suggested the existence of α Ag and α Cu. The XRD patterns of all the other experimental powders were very similar in diffraction angles and intensities to those of the CU series powders.

Fig. 2 shows the XRD patterns of amalgams prepared from alloys in the entire CU series (CU1 through 5) and those of the three commercial amalgams. Two phases, γ (Ag_3Sn) and γ_1 (Ag_2Hg_3), were identified in all of the amalgams. The γ_2 Sn-Hg ($\text{Sn}_{7.8}\text{Hg}$) phase was identified in the amalgams made from CU1, CU2 and CU3 and Spheralloy. The γ' (Cu_6Sn_5) phase was detected in all the amalgams. The intensity of the γ' (Cu_6Sn_5) phase increased with increasing Cu concentration in the experimental and commercial alloys. As found in the XRD patterns for the experimental CU series amalgams, the formation of γ_2 and change in the intensity of γ' followed a similar trend in the other experimental alloy series. In other words, in each experimental alloy series, the γ_2 phase was detected in all amalgams prepared from powders 1 through 3 (for example, AGSN1-AGSN3, etc.). These alloy powders all had $\text{Cu} < 12\%$ and/or γ (Ag_3Sn)/ β (Ag_4Sn) > 0.8 . The intensity of γ' increased with increasing alloy number (1 to 5) in three of the experimental alloy series (CU, 1PD, and NOPD), but not in the AGSN series.

SEM metallography

Figs. 3-10 show representative SEM micrographs of Hg-plated specimens of two selected alloy powders from all of the experimental alloy series (Nos. 1 and 4 for the

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8 (a)

Fig. 8 (b)

Fig. 9

- Fig. 3 Secondary SEM image of an amalgam made from CU1. A: γ_1 ; B: γ_2 .
 Fig. 4 Secondary SEM image of an amalgam made from CU5. A: γ_1 .
 Fig. 5 Secondary SEM image of an amalgam made from IPD1. A: γ_1 ; B: γ_2 .
 Fig. 6 Secondary SEM image of an amalgam made from IPD5. A: γ_1 .
 Fig. 7 Secondary SEM image of an amalgam made from AGSN1. A: γ_1 ; B: γ_2 .
 Fig. 8 (a) Secondary SEM image of an amalgam made from AGSN4. A₁: γ_1 ; A₂: γ_1 .
 (b) Close-up view of Fig. 8 (a). C: η' .
 Fig. 9 Secondary SEM image of an amalgam made from NOPD1. A: γ_1 ; B: γ_2 .

AGSN series and Nos. 1 and 5 for the other series). Figs. 11-13 show representative SEM micrographs of the Hg-plated specimens of the three commercial alloys.

Fig. 3 shows CU1 particles, which were densely covered by γ_1 crystals (A) with γ_2 crystals (B) formed on top of them. Fig. 4 shows that γ_1 polyhedra (A) were closely packed on the CU5 particles. On this alloy, neither γ_2 crystals nor η' crystals were found. Fig. 5 shows polyhedral crystals of γ_1 (A) densely formed on the IPD1 particles. γ_2 crystals (B) formed, but were not as well defined as on CU1 as shown in Fig. 3. Fig. 6 shows closely packed γ_1 crystals (A) formed on IPD5 particles. No γ_2 crystals or η' crystals were found. The AGSN1 particles in Fig. 7 were covered by clearly defined γ_1 polyhedra (A). Some of the γ_1 crystals were larger than those on other alloys. Irregularly shaped γ_2 crystals (B) were also found on the surface. Fig. 8 (a) shows γ_1 crystals (A₁) formed in the center of the AGSN4 particle surface. Inside the "rim" of γ_1 around the periphery of the surface, there were also γ_1 crystals (A₂) that were smaller compared with other γ_1 polyhedra. Fig. 8 (b) is a magnified

Fig. 10 (a)

Fig. 10 (b)

Fig. 11 (a)

Fig. 11 (b)

Fig. 12 (a)

Fig. 12 (b)

Fig. 13 (a)

Fig. 13 (b)

Fig. 10 (a) Secondary SEM image of an amalgam made from NOPD5. A: γ_1 ; C: η' .

Fig. 10 (b) Secondary SEM image of an amalgam made from NOPD5. B: γ_2 .

Fig. 11 (a) Secondary SEM image of an amalgam made from Tytin. A: γ_1 .

(b) Close-up view of Fig. 11 (a). A: γ_1 ; C: η' .

Fig. 12 (a) Secondary SEM image of an amalgam made from Dispersalloy. A: γ_1 .

(b) Close-up view of Fig. 12 (a). A: γ_1 ; C: η' .

Fig. 13 (a) Secondary SEM image of an amalgam made from Spheralloy. A: γ_1 ; B: γ_2 .

(b) Close-up view of Fig. 13 (a). A: γ_1 ; B: γ_2 .

view of the peripheral area in the AGSN4 particle shown in Fig. 8(a). Some of the smaller crystals (C) are composed of η' . Fig. 9 shows NOPD1 particles, which were covered by γ_1 polyhedra (A) and elongated γ_2 crystals (B). No η' crystals were identified around the periphery. Fig. 10 (a) shows NOPD5 particles covered by γ_1 crystals (A) of various sizes. Areas containing η' phase (C) were also identified. In contrast to the Pd-containing alloys with a similar copper concentration, some γ_2 crystals (B) had formed in the NOPD5 specimens as shown in Fig. 10 (b). Fig. 11 (a) shows closely packed γ_1 polyhedra (A) formed on Tytin. No γ_2 crystals were found. Fig. 11 (b) is a magnified view of the γ_1 crystals (A) covering Tytin. At the periphery, areas (C) containing η' phase were found, similar to those found on AGSN4. Fig. 12 (a) shows γ_1 polyhedra (A) on a Ag-Cu eutectic particle and a lathe-cut Ag-Sn particle in Dispersalloy. Fig. 12 (b) provides a magnified view of the periphery of the Ag-Cu particle, showing rod-shaped η' crystals (C) between well defined γ_1 polyhedra (A). Fig. 13 (a) shows elongated γ_2 crystals (B) that grew longitudinally

on the surface of Spheraloy. Various sizes of γ_1 crystals (A) are also visible on the surface. Another Spheraloy particle with γ_1 (A) and γ_2 (B) crystals on the surface is shown in Fig. 13 (b).

DISCUSSION

In this study, four series of Ag-Sn-based alloy powders were prepared in order to investigate the effect on the amalgamation reaction of changing the Cu and/or Pd concentration and the Ag vs. Sn ratio. Phases of intermetallic compounds formed in the amalgamation reaction on the Hg-plated alloy particles correlated well with those found in the corresponding amalgams detected by XRD.

The γ_2 phase formed in alloys having less than 12% Cu and/or $\text{Ag}_3\text{Sn}/\text{Ag}_4\text{Sn}$ ratios exceeding 0.8. The mechanism whereby Cu reduces the formation of the unfavorable γ_2 phase in high-Cu amalgams is well documented^{8,15)}. The Cu serves as a "getter" of Sn, because it preferentially reacts with Sn and reduces the amount of Sn that is dissolved in Hg and available to form γ_2 .

In contrast, γ_2 crystals were often found on the Hg-plated specimens prepared from all of the NOPD series alloys, even when the Cu concentration exceeded 12%. This finding suggests that in the three series of alloys with Pd (CU, AGSN and 1PD), Pd assisted in reducing the amount of γ_2 formed. In previous studies in which 3.5-15% of Pd was added to Ag-Sn alloys, a number of investigators reported that the formation of the γ_2 phase was eliminated or limited, since Pd preferentially reacted with Sn¹⁶⁻¹⁸⁾. Considering the much smaller amount of Pd in the alloys evaluated in the present study (1.0-1.5%), the mechanism whereby Pd reduces the amount of γ_2 phase produced may not be the same as that described in previous studies¹⁹⁾ employing a higher amount of Pd.

Furthermore, the XRD data show a reduction in η' Cu_6Sn_5 , since less Cu is used in the alloys; this finding implies that less Sn is being reacted with copper, leaving more to be dissolved in the γ_1 grains. This mechanism has been hypothesized as the reason why lower mercury vaporization has been detected after abrasion of amalgams made from these Pd-containing alloys⁴⁾.

The Hg-plated surfaces of the three commercial alloys provided good comparative information for the experimental alloys. The surfaces of the low-Cu amalgam Spheraloy showed a considerable number of rods and plates of γ_2 crystals that grew either perpendicular or parallel, respectively, to the hexagonal-based plane⁸⁾. Another interesting feature of the γ_2 crystals observed was that they formed consistently on top of the γ_1 crystals. This pattern is due to the mechanism presented earlier¹⁵⁾. Less Ag dissolves into Hg than Sn, and thus, the saturation concentration of Ag in Hg is lower than that of Sn in Hg (1/20). Both factors cause γ_1 crystals to nucleate and grow before the majority of the Sn reaches saturation. Once the Sn saturates in the mercury, γ_2 crystals begin to nucleate and grow on top of the already formed γ_1 crystals.

As expected, no γ_2 was formed on the Hg-plated Tytin and Dispersalloy. It is

widely agreed that dissolved Sn is removed from the Hg either by reacting with Cu dissolved in the Hg to make η' Cu_6Sn_5 or by the diffusion of Sn to Cu (in Dispersalloy) or ϵ Cu_3Sn sites (in Tytin), where η' Cu_6Sn_5 is produced^{8,15}. In the Hg-plated Dispersalloy, η' rod crystals are seen [Fig. 12(b)] on a Ag-Cu eutectic alloy particle. The amount of Hg electrolytically plated was maintained at a similar level for all the specimens in this study. It was found that when the amount of Hg plated was two or more times greater than the amount used in this study, γ_2 crystals formed on the surfaces of all of the experimental alloy particles, excluding the two commercial high-Cu alloys. Apparently, these commercial alloys are well designed to prevent the formation of γ_2 .

CONCLUSION

The reaction phases obtained by the Hg-plating method on various Ag-Sn-Cu (+Pd) alloy particles correlated with the x-ray diffraction data of the amalgam specimens. The effect of a small amount of Pd (1.0-1.5%) in reducing the formation of the γ_2 phase was confirmed. This method could be used for effectively identifying alloys that are prone to the formation of γ_2 .

ACKNOWLEDGMENTS

A portion of this study was supported by a research grant (R01 DE 07644) funded through the National Institutes of Health/National Institute of Dental and Craniofacial Research, Bethesda, MD. The authors thank Mr. Jerry Adey for his work in designing the experimental alloys. They also thank Mrs. Lucyna Carrasco for her assistance with the x-ray diffractometry and are grateful to Dr. David R. Treadwell, Special Metals Corporation, for producing the experimental alloy powders for the present study. Finally, the authors appreciate editorial assistance by Mrs. Jeanne Santa Cruz.

REFERENCES

- 1) CRA (Clinical Research Associates): Subjects: Product Use Survey-1995. *CRA Newsletter* **19**: 1-4, 1995.
- 2) Wahl M. J.: Amalgam - Resurrection and redemption. Part 2: The medical mythology of anti-amalgam, *Quintessence Int* **32**: 696-710, 2001.
- 3) Okabe, T., Ohmoto, K., Nakajima, H., Woldu, M. and Ferracane, J. L.: Effect of Pd and In on mercury evaporation from amalgams, *Dent Mater J* **16**: 191-199, 1997.
- 4) Ferracane, J. L., Adey, J. D. and Okabe, T.: Hg release after abrasion of Pd-containing amalgams with varied Cu, *J Dent Res* **81**: A-424, Abstr. No.3440, 2002.
- 5) Omar, I. M., Chern Lin, J. H., Greener, E. H. and Marshall, S. J.: Solubility of Pd in γ_1 and its effect on the γ_1 to β_1 transformation in dental amalgam, *Northwestern Dent Res* **1**: 10-15, 1989.
- 6) Mante, F., Chern Lin, J. H., Moser, J. B. and Greener, E. H.: Palladium effects on thermal expansion and phase changes in amalgam, *J Dent Res* **67**: 308, Abstr. No.1563, 1988.
- 7) de Freitas, J. F.: A survey of the elemental composition of alloy for dental amalgam,

Australian Dental J 24: 17-25, 1978.

- 8) Okabe, T. and Mitchell R. J.: Setting reactions in dental amalgam, Part 2. The kinetics of amalgamation, *Crit Rev Oral Biol Med* 7: 23-35, 1996.
- 9) Mahler, D. B. and Adey J. D.: Microprobe analysis of a high Cu amalgam alloy, *J Dent Res* 56: 379-384, 1977.
- 10) Gray, A. G., ed. Modern electroplating. *John Wiley & Sons, Inc.*, New York; *Chapman & Hall, Ltd.*, London, 1953, p.492.
- 11) Okabe, T. and Hochman, R. F.: Amalgamation reaction on mercury-plated dental alloy (Ag_3Sn), *J Biomed Mater Res* 9: 221-236, 1975.
- 12) Goldstein, J. I., ed. Scanning Electron and X-ray Microanalysis. A text for biologists, materials scientists, and geologists., 2nd ed., *Plenum Press*, New York, 1992, pp.395-416.
- 13) Okabe, T., Mitchell, R., Butts, M. B., Wright, A. H. and Fairhurst, C. W.: A study of high copper amalgams. I. A comparison of amalgamation on a Hg-plated high copper alloy tablets, *J Dent Res* 57: 759-767, 1978.
- 14) Okabe, T., Mitchell, R., Wright, A. H. and Fairhurst, C. W.: A study of high copper amalgams. II. Amalgamation on a Hg-plated high copper alloy containing 30 wt.% Cu, *J Dent Res* 57: 768-771, 1978.
- 15) Mitchell, R. J. and Okabe T.: Setting reactions in dental amalgam, Part 1. Phases and microstructures between one hour and one week, *Crit Rev Oral Biol Med* 7: 12-22, 1996.
- 16) Mante, F., Greener, E. H., Gilbert, J. and Chern Lin J. H.: The effect of matrix phase morphology on the structure of Ag-Cu-Pd dispersed phase dental amalgam, *J Oral Rehabil* 22: 711-715, 1995.
- 17) Mante, F. K., Chern Lin, J. H., Mante, M. O. and Greener, E. H. The effect of noble metals on the mechanical properties of dispersed phase dental amalgam, *J Oral Rehabil* 25: 279-284, 1998.
- 18) Chern Lin, J. H., Chung, K. H. and Greener, E. H.: Microstructures of admixed amalgams produced from Pd-containing dispersants, *Dent Mater* 8: 85-88, 1992.
- 19) Szurgot, K., Greener, E. H., Marshall, G. W. and Marshall, S. J.: Microstructure of Ag-Cu-Pd dispersed phase amalgam, *J Dent Res* 60: 481, Abstr. No.685, 1981.