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## X-RAY DIFFRACTION AND SCANNING ELECTRON MICROSCOPY ANALYSES OF A GALLIUM-BASED DENTAL RESTORATIVE ALLOY

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### Abstract

Specimens of a gallium-based dental alloy were prepared with different condensation techniques, with and without the removal of a surface layer, and after aging for 2 hours at 50°, 100° and 150°C. X-ray diffraction at times ranging from 10 minutes to 1 day showed the development of the four matrix phases ( $\beta$ -Sn, CuGa<sub>2</sub>, Ga<sub>28</sub>Ag<sub>72</sub>, and In<sub>4</sub>Ag<sub>9</sub>) during the setting reaction. Scanning electron microscope (SEM) examination of specimens loaded to failure revealed brittle fracture, with greater porosity for hand-condensed specimens, and provided insight into crack propagation processes. Aging increased the amount of  $\beta$ -Sn in freshly prepared specimens, and removal of the Ga-rich surface layer after condensation decreased the amount of this phase. For specimens stored for 5 weeks at room temperature, aging substantially increased the amount of the CuGa<sub>2</sub> phase but caused only moderate increases in the amount of  $\beta$ -Sn.

**Key Words:** Gallium, dental alloy, microstructure, X-ray diffraction, scanning electron microscopy, heat treatment, mechanical properties, fracture.

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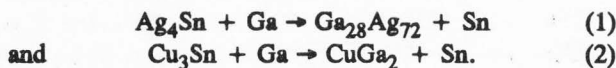
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### Introduction

Gallium was first suggested as a replacement for mercury in dental alloys by Puttkammer (1928), based upon the ability of liquid gallium to wet the surfaces of many solids, including human teeth. Smith and Caul (1956) subsequently described gallium alloys that could serve as possible alternatives to dental amalgam. Three commercial products (Gallium Alloy GF and Gallium Alloy GF II, Tokuriki Honten, Tokyo, Japan; and Galloy, Southern Dental Industries [SDI], Bayswater, Victoria, Australia) have been recently marketed as alternatives to dental amalgam with the goal of offering similar handling behavior, good physical properties and superior biocompatibility. Several studies have evaluated the setting dimensional changes and mechanical properties (Herø and Okabe, 1994; Berglund *et al.*, 1995; Osborne and Summitt, 1995), handling characteristics (Mash *et al.*, 1993; Momoi *et al.*, 1996), *in vitro* and *in vivo* corrosion characteristics (Oshida and Moore, 1993; Herø and Okabe, 1994; Kaga *et al.*, 1996), and biocompatibility (Motokawa *et al.*, 1987; Kaminishi *et al.*, 1990; Psarras *et al.*, 1992; Wataha *et al.*, 1994) of the gallium-based alloys.

For these restorative materials, the reaction of the Ga-based liquid with the two constituent phases (Ag<sub>4</sub>Sn and Cu<sub>3</sub>Sn) in the starting Ag-Sn-Cu pre-alloy particles can be written as (Herø and Okabe, 1994):



Both reactions result in the formation of a  $\beta$ -Sn phase. A fourth phase (In<sub>4</sub>Ag<sub>9</sub>) also forms as a result of reaction between Ag in the pre-alloy particles and In present in the Ga-based liquid. The formation of these microstructural phases is intimately related to the setting dimensional changes, mechanical properties, corrosion resistance and biocompatibility of these materials (Herø and Okabe, 1994). The objective of this study was to obtain greater insight into the setting reaction kinetics, microstructural stability and nature of crack propagation for a commercially popular gallium alloy prepared under different experimental conditions. Such information can

Table 1. Summary of specimens for X-ray diffraction experiments.

Experimental condition	Trituration time	Condensation procedure	Surface for XRD analysis	Holding or storage time (at room temperature)
1 (n = 2)	8 seconds	glass slide	condensed surface	1 day and 1 week
2 (n = 1)	8 seconds	glass slide	condensed surface	10 minutes, 30 minutes, 1 hour, 2 hours and 1 day
3 (n = 1)	8 seconds	hand	opposite from condensed surface	10 minutes, 30 minutes, 1 hour, 2 hours and 1 day
4 (n = 2)	8 seconds	hand	after 1-mm layer removed	10 minutes, 30 minutes, 1 hour, 2 hours, 1 day and 3 weeks
5 (n = 1)	8 seconds	hand	after 1-mm layer removed and specimen fractured	2 weeks
6 (n = 2 each temperature)	8 seconds	hand	after 1-mm layer removed	no storage; 2-hour heat treatment at 50°, 100° and 150°C
7 (n = 2 each temperature)	8 seconds	hand	after 1-mm layer removed	5-week storage; 2-hour heat treatment at 50°, 100° and 150°C

provide the basis for greater understanding of the clinical performance of the gallium-based alloys and yield insight for the scientific development of improved materials.

### Materials and Methods

A commercial product (Galloy) was contributed by the manufacturer (SDI) for this study. The product was in the standard encapsulated form, containing (in separate compartments) powder particles with a nominal composition of 60% Ag, 28% Sn and 12% Cu, and a eutectic liquid with an approximate composition of 62% Ga, 25% In and 13% Sn (values in weight percent). The recommended trituration time of 8 seconds (Ultramat 2, SDI) was used. There were seven X-ray diffraction (XRD) experiments (Table 1), corresponding to different condensation procedures, surface conditions, holding or storage times at room temperature, and heat treatments at elevated temperatures (50°, 100° and 150°C) to simulate long-term aging in the oral environment. The number of replicate specimens for each experimental condition is provided in Table 1. For example, two separate specimens were heat treated at each of the three elevated temperatures.

XRD was performed using Cu K $\alpha$  radiation and a diffractometer (PAD-V, Scintag, Sunnyvale, CA). Values of  $2\theta$  ranged from 25° to 95° with a scanning rate of 0.5° per min for the first experiment, and the

major peaks for all phases occurred between 28° and 48° (Herø and Okabe, 1994). Faster scanning rates of 1° or 2° per min were also used, with minimal shifting of peak positions (Shaker, 1997), and a scanning rate of 2° per min between 28° and 48° was used to study the early stages of setting. Peaks were identified by comparison to a published XRD pattern (Herø and Okabe, 1994) and ICDD (International Center for Diffraction Data, Swarthmore, PA) powder standards. The relative amounts of a particular phase for the different experimental conditions were estimated qualitatively from the relative areas under the appropriate XRD peaks. Replicate XRD specimens were typically used (Table 1) in an effort to account for the complicating effects of preferred crystallographic orientation that were typically observed, as will be discussed later.

A JEOL JSM 820 (JEOL, Tokyo, Japan) scanning electron microscope (SEM) was used to study the microstructures, and spot analyses were performed on phases with an X-ray energy-dispersive spectroscopic (EDS) system (Link eXL with a PentaFET detector and an ultrathin window, Oxford Instruments, High Wycombe, U.K.). Hand-condensed specimens were prepared (using a smooth, round-ended amalgam condenser of 2 mm diameter) in a 4.5 mm diameter x 4 mm high poly (methyl)methacrylate (PMMA) mold; typically three increments were applied. These specimens were stored for 1 day at room temperature and then fractured in diametral compression at a cross-head speed of 0.25 mm

**Table 2.** Summary of X-ray diffraction peaks for Galloy specimen in Figure 1 after 1 day and comparison of positions to ICDD standards.

Peak	Intensity (cps)	2 $\theta$ (deg)	d (Å)	Interpretation	d <sub>std</sub> (Å) and I <sub>std</sub>
1	110	30.85	2.90	$\beta$ -Sn	2.915 (100)
2	59	31.54	2.84	CuGa <sub>2</sub>	2.829 (35)
3	94	32.14	2.78	$\beta$ -Sn	2.793 (90)
4	68	34.75	2.58	Ag <sub>4</sub> Sn	2.568 (25)
5	113	35.20	2.55	CuGa <sub>2</sub>	2.545 (80)
				Ga <sub>28</sub> Ag <sub>72</sub>	2.543 (16)
6	103	37.57	2.39	Ag <sub>4</sub> Sn	2.391 (27)
				Cu <sub>3</sub> Sn	2.380 (60)
7	372	38.71	2.32	In <sub>4</sub> Ag <sub>9</sub>	2.339 (100)
				Ga <sub>28</sub> Ag <sub>72</sub>	2.312 (100)
8	223	39.58	2.28	Ag <sub>4</sub> Sn	2.263 (100)
9	67	40.12	2.25	Ga <sub>28</sub> Ag <sub>72</sub>	2.242 (100)
10	36	41.44	2.18	Ga <sub>28</sub> Ag <sub>72</sub>	2.187 (25)
11	44	43.18	2.09	Cu <sub>3</sub> Sn	2.080 (100)
12	56	44.11	2.05	$\beta$ -Sn	2.062 (34)
13	182	44.56	2.03	$\beta$ -Sn	2.017 (74)
				CuGa <sub>2</sub>	2.031 (100)
14	123	45.22	2.00	CuGa <sub>2</sub>	2.000 (80)
15	59	46.78	1.94	CuGa <sub>2</sub>	1.946 (16)

per min (N = 7). Other specimens were machine-condensed in the same mold, following ADA specification (ADA, 1977), stored for 1 day and fractured by diametral compression in the same manner (N = 6).

### Results

Figure 1 shows the XRD patterns between 28° and 48° at 10 minutes, 30 minutes, 1 hour, 2 hours and 1 day for a specimen condensed between microscope slides (experiment 2). There was little difference in the XRD patterns after 1 day and 1 week for the specimens that were condensed between microscope slides (experiments 1 and 2 in Table 1).

Table 2 provides matches of the interplanar spacings (d) for the phases (Herø and Okabe, 1994) with the values (d<sub>std</sub>) and relative intensities (I<sub>std</sub>) for the ICDD standards:  $\beta$ -Sn (4-673), CuGa<sub>2</sub> (25-275), Ga<sub>28</sub>Ag<sub>72</sub> (28-432), In<sub>4</sub>Ag<sub>9</sub> (29-678), Ag<sub>4</sub>Sn (29-1151) and Cu<sub>3</sub>Sn (3-1010). Small discrepancies in the interplanar spacings arise from the complex phase compositions (Herø

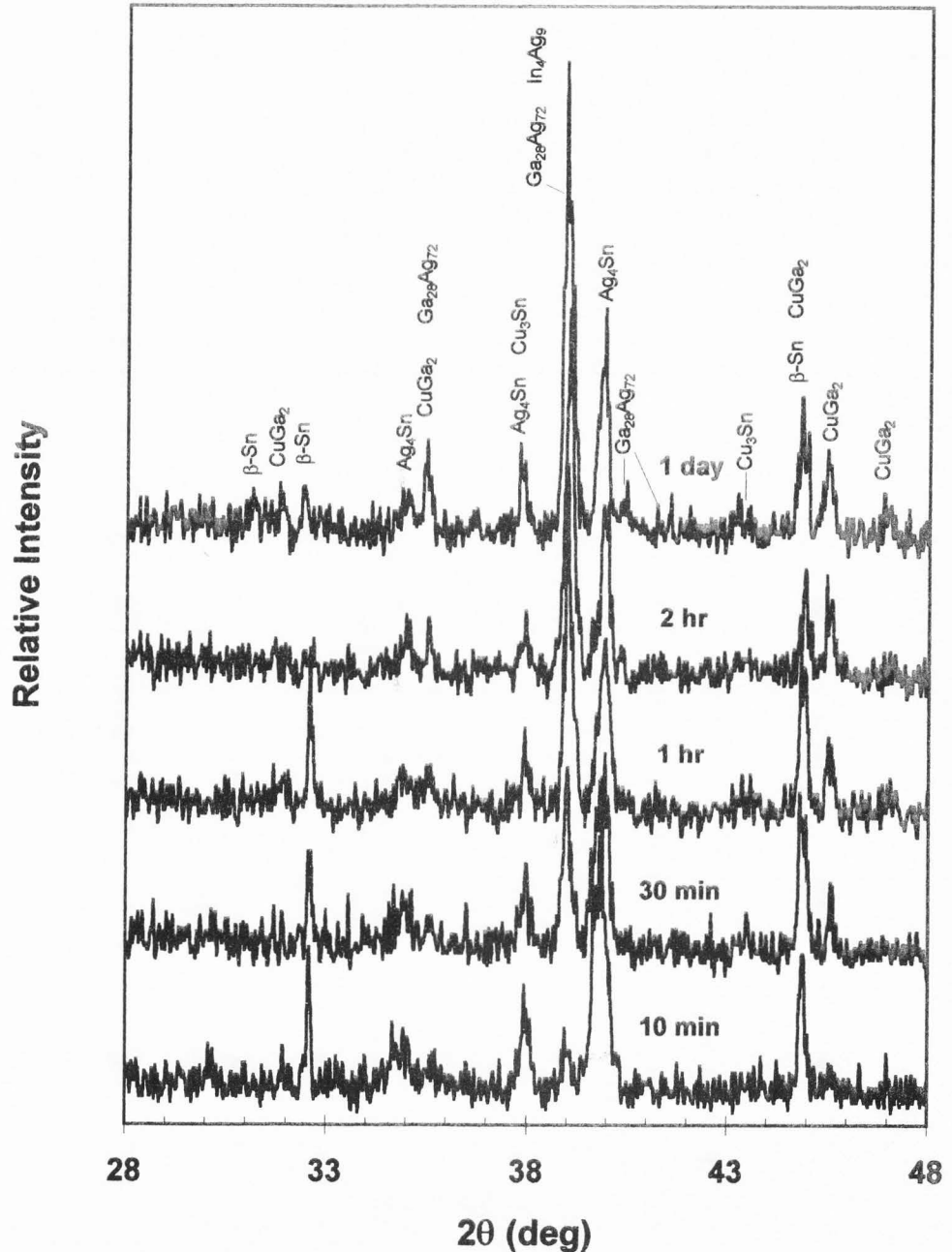
and Okabe, 1994). Figure 1 shows that the  $\beta$ -Sn, CuGa<sub>2</sub>, and In<sub>4</sub>Ag<sub>9</sub> phases began to form within 10 minutes after condensation. Peak 9 for Ga<sub>28</sub>Ag<sub>72</sub> (Table 2) also forms rapidly, appearing as a shoulder on the strong peak 8 for Ag<sub>4</sub>Sn at times up to 2 hours, and becomes a separate peak after 1 day. Although not designated in Figure 1, an apparent peak on the left shoulder of peak 1 for  $\beta$ -Sn in Table 2 may correspond to the peak at d<sub>std</sub> = 2.920 Å (I<sub>std</sub> = 7) for the ICDD CuGa<sub>2</sub> powder standard.

For the specimen that was hand-condensed in the PMMA mold and analyzed on the opposite surface (experiment 3), the XRD patterns at times ranging from 10 minutes to 1 day were similar to those for the corresponding times in Figure 1. Variations in the intensities of  $\beta$ -Sn peaks (Shaker, 1997) were attributed to differences in crystallographic orientation of this phase, as will be discussed later.

When specimens were hand-condensed in the mold and a 1-mm thick surface layer removed to simulate normal clinical conditions for the placement of a restoration



Figure 2. X-ray diffraction patterns at different times for a hand-condensed Galloy specimen, where a 1-mm surface layer was removed. Scanning rate:  $2^\circ$  per min.



Heat treatment also increased the amount of  $\text{CuGa}_2$  (see peaks 14 and 15, Table 2). When the specimens were stored for 5 weeks at room temperature prior to heat treatment (experiment 7), there were only moderate increases in  $\beta\text{-Sn}$  (Figure 4) but substantial increases in  $\text{CuGa}_2$ . Figure 4 also shows the XRD pattern for a control specimen that was stored for 5 weeks at room temperature without subsequent heat treatment.

Using Student's  $t$  test, it was found that the one-day diametral tensile strength (DTS) (mean  $\pm$  standard deviation) was significantly ( $p < 0.05$ ) higher for the machine-condensed specimens ( $53.0 \pm 8.1$  MPa) compared

to the hand-condensed specimens ( $39.2 \pm 11.8$  MPa). The present mean DTS for the machine-condensed specimens was approximately 15% lower than the one-day DTS of 63 MPa reported in the SDI product information literature for Galloy after 24 hours.

Figures 5a and 5c show secondary electron image (SEI) photomicrographs, and Figures 5b and 5d show corresponding backscattered electron image (BEI) photomicrographs of two different regions on the planar fracture surface of the strongest machine-condensed specimen. The microstructural phases have been designated by numbers in Figures 5b and 5d as follows: (1)  $\text{Ag}_4\text{Sn}$ ;



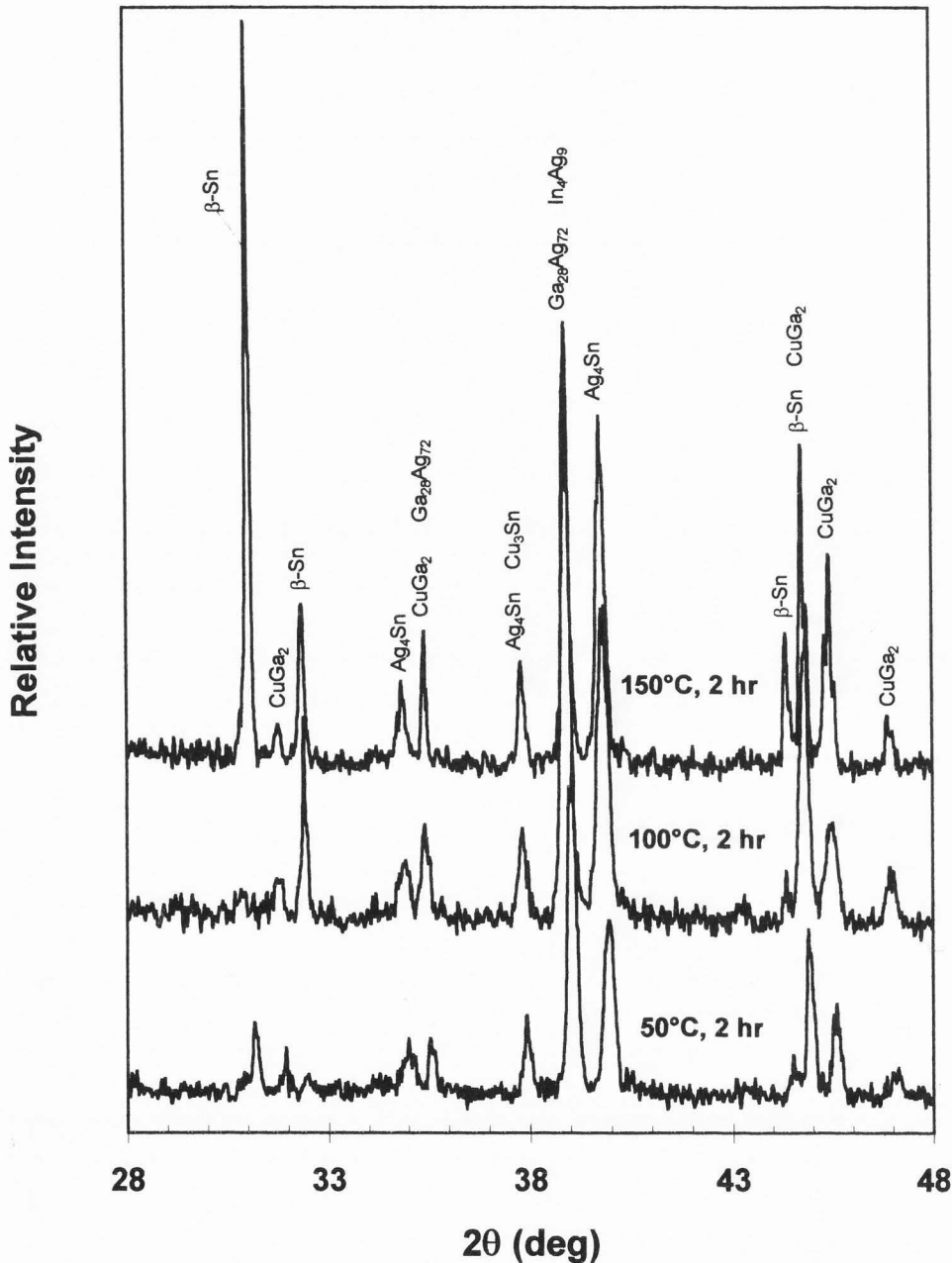


Figure 3. X-ray diffraction patterns for Galloy specimens that were heat treated for 2 hours at 50°, 100° and 150°C after minimal storage at room temperature. Three different specimens were used. Hand-condensed, with a 1-mm surface layer removed. Scanning rate: 0.5° per min.

(2)  $\text{Cu}_3\text{Sn}$ ; (3)  $\beta\text{-Sn}$ ; (4)  $\text{CuGa}_2$ ; (5)  $\text{Ga}_{28}\text{Ag}_{72}$ ; and (6)  $\text{In}_4\text{Ag}_9$ . The identities of the phases were determined by qualitative EDS spot analyses. Quantitative EDS analyses were not performed since individual grains of matrix phases often had dimensions of about 1  $\mu\text{m}$ , too small for accurate analyses without interference from adjacent grains of other phases (Lee, 1993). While the relative darkness of the phases in the BEI photomicrographs increases with decreases in their mean atomic numbers (Lee, 1993), the complex compositions of these phases (Herø and Okabe, 1994) must be considered in estimating the mean atomic numbers. The lightest-appearing phases in the BEI photomicrographs are  $\beta\text{-Sn}$ ,

$\text{Ag}_4\text{Sn}$  and  $\text{In}_4\text{Ag}_9$ , and the darkest-appearing phases are  $\text{CuGa}_2$  and  $\text{Cu}_3\text{Sn}$ . Figures 5b and 5d show that the  $\text{Cu}_3\text{Sn}$  phase appears much darker than the  $\text{Ag}_4\text{Sn}$  phase in the BEI photomicrographs and that these two phases intimately coexist in the pre-alloy particles.

Figures 6a and 6b compare the brittle fracture surfaces for the strongest machine-condensed and weakest hand-condensed specimens, respectively. Crack propagation occurred through and around the pre-alloy particles in Figure 6a, whereas crack propagation was around the large pre-alloy particle in the center of Figure 6b. Fracture also occurred at the boundaries between the matrix phases in all specimens examined. As shown in

Figure 4. X-ray diffraction patterns for Galloy specimens that were heat treated for 2 hours at 50°, 100° and 150°C after 5-week storage at room temperature, and for a control specimen that was stored for the same period of time without subsequent heat treatment. Four different specimens were used. Hand-condensed, with a 1-mm surface layer removed. Scanning rate: 0.5° per min.

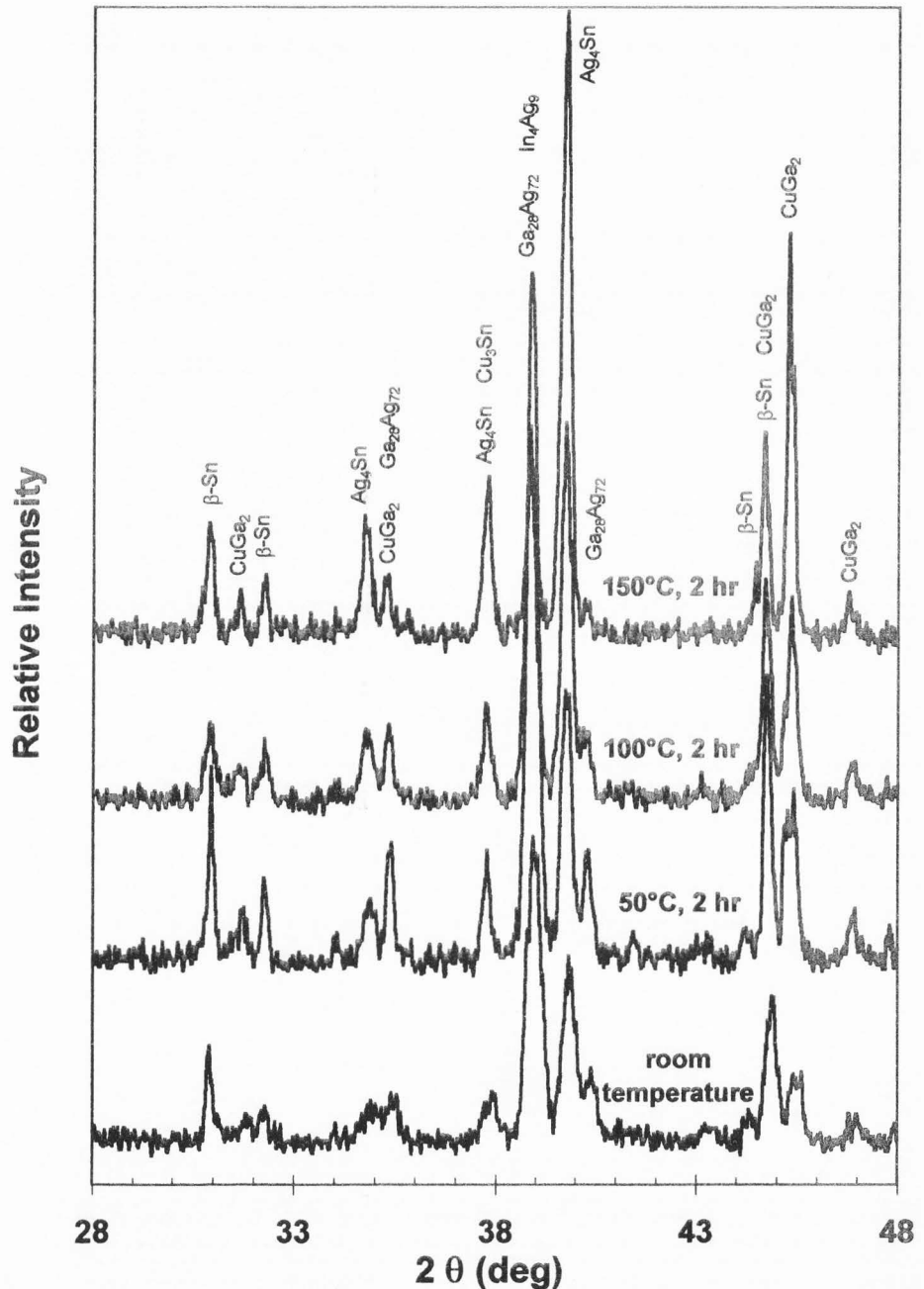


Figure 6b, the hand-condensed specimens typically contained large regions of porosity that were absent in the machine-condensed specimens.

#### Discussion

The brittle fracture of Galloy follows from the microstructure of this material, where most phases have tetragonal ( $\beta$ -Sn and CuGa<sub>2</sub>) and hexagonal (Ga<sub>28</sub>Ag<sub>72</sub>, Ag<sub>4</sub>Sn, and Cu<sub>3</sub>Sn) crystal structures with relatively few slip systems. The substantially different lattice parameters of these phases should result in poor interphase

bonding, which is consistent with the observed crack propagation between the matrix phases in Figures 5 and 6. The significantly lower DTS for the hand-condensed specimens, which was attributed to greater porosity, emphasizes the importance of proper condensation for this material. The BEI photomicrographs in Figures 5b and 5d, which show that all of the matrix phases can be located adjacent to the partially consumed pre-alloy particles, are consistent with the XRD patterns for early setting times. It is evident from Figure 5 that the crystallographic orientations of individual matrix phases might change as these grains grow or new grains form,



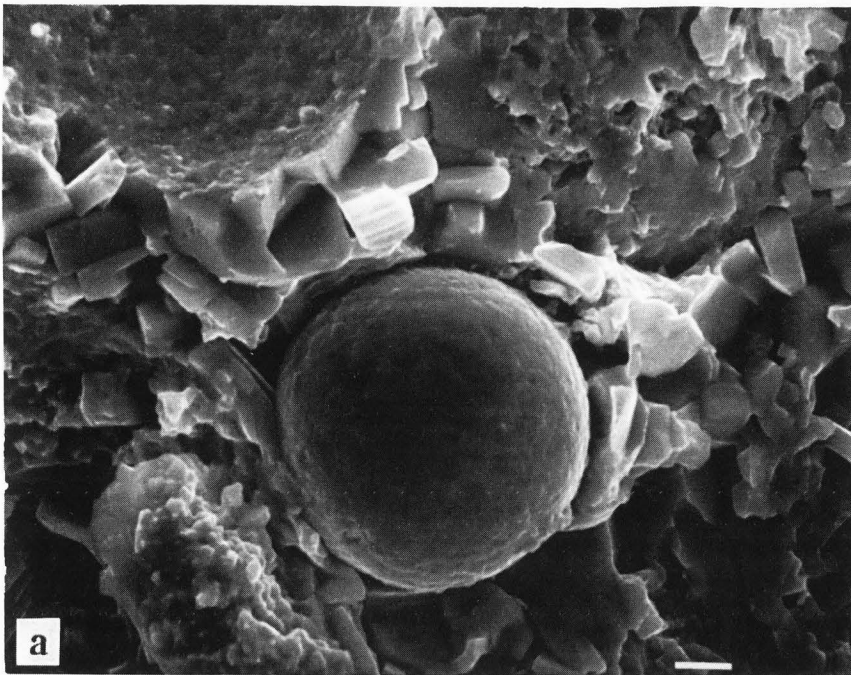
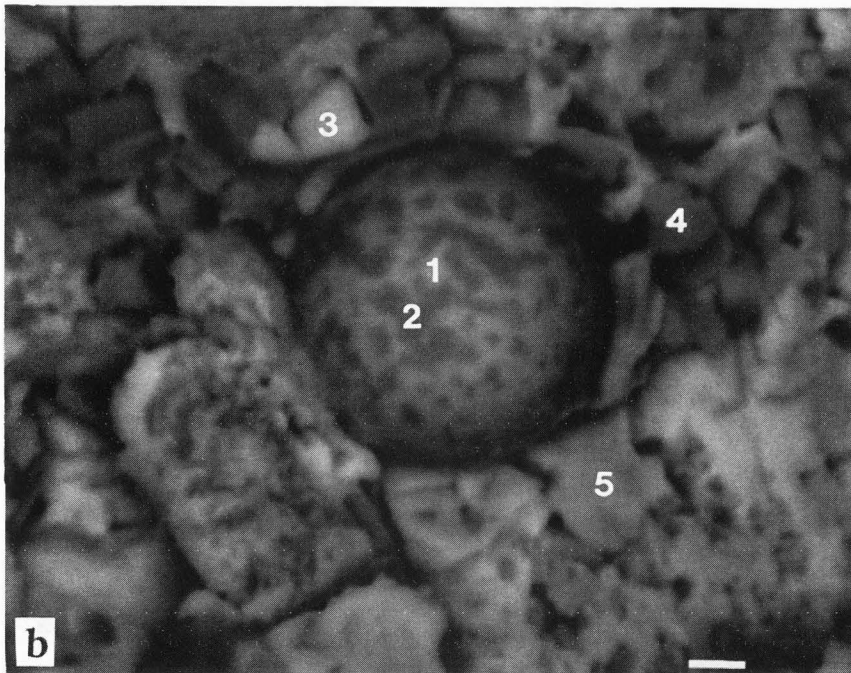


Figure 5 (5a and 5b at left; 5c and 5d on the facing page). Secondary (5a and 5c) and corresponding backscattered (5b and 5d) electron images at two different sites on the fracture surface of the strongest machine-condensed specimen. Bar = 1  $\mu\text{m}$ . Microstructural phases:

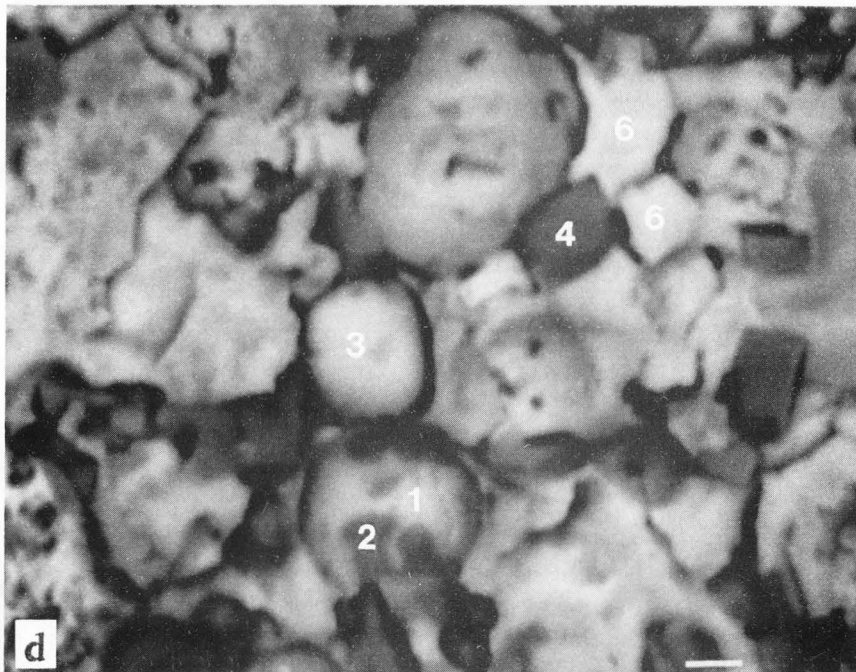
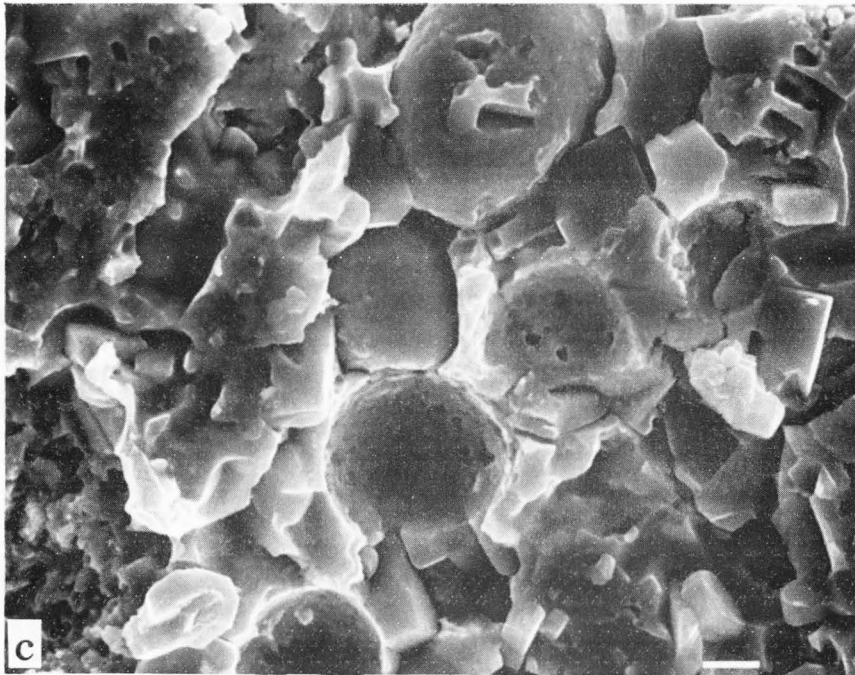
- (1)  $\text{Ag}_4\text{Sn}$ ;
- (2)  $\text{Cu}_3\text{Sn}$ ;
- (3)  $\beta\text{-Sn}$ ;
- (4)  $\text{CuGa}_2$ ;
- (5)  $\text{Ga}_{28}\text{Ag}_{72}$ ; and
- (6)  $\text{In}_4\text{Ag}_9$ .



accounting for effects of preferred orientation on the relative intensities for  $\beta\text{-Sn}$  and other phases in the XRD patterns.

The present XRD results (Figures 1 and 2) indicate that all four matrix phases have begun to form within 10 minutes after condensation. The transient peak at  $30^\circ$  in Figure 1 occurring at 10 minutes after condensation may be associated with an initial composition modification of either the  $\text{CuGa}_2$  or  $\beta\text{-Sn}$  phase that subsequently disap-

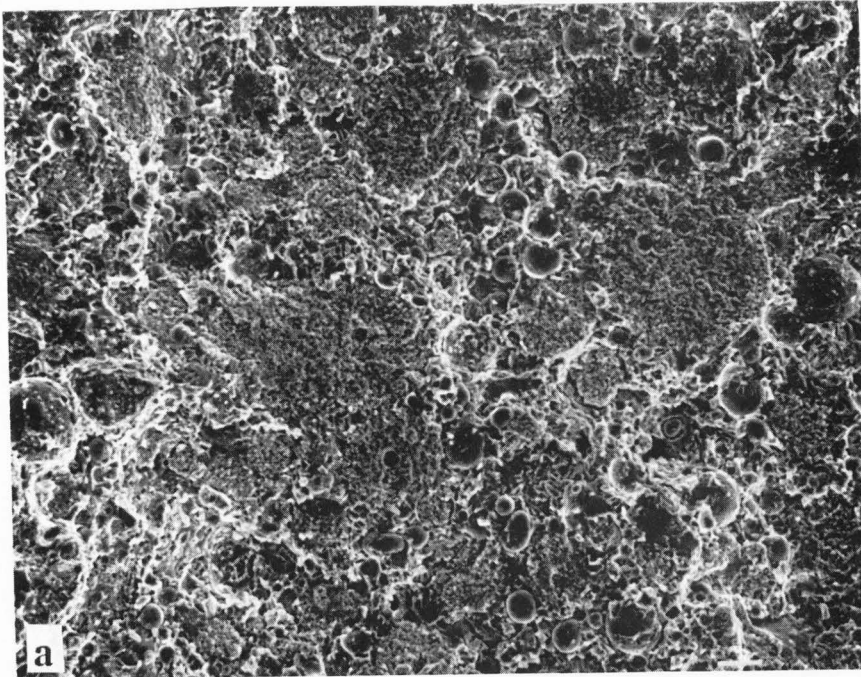
pears, although the agreement with corresponding peaks for the two ICDD binary standards is poor. Examination of XRD patterns from the same Galloy specimens at times up to 3 weeks after condensation (Shaker, 1997) indicated that the setting reaction was largely completed after 1 day. Comparison of Figures 1 and 2 shows that the amount of  $\beta\text{-Sn}$  in the near-surface region after setting was greatly reduced if the Ga-rich surface layer was removed from the freshly condensed specimens, which



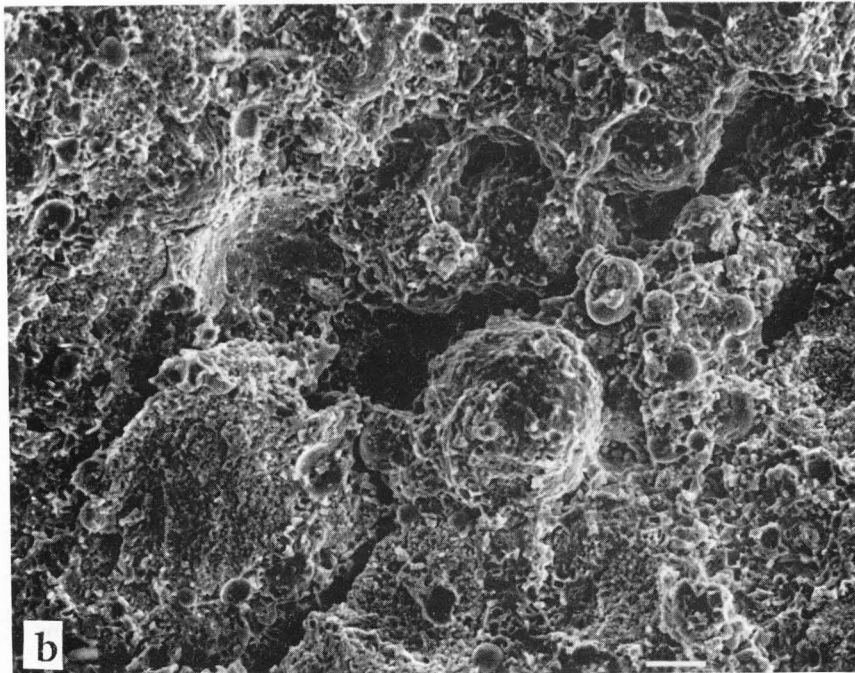
would be the procedure for the clinical placement of a restoration. When freshly prepared specimens were heated for 2 hours at 50°, 100° and 150°C, the available liquid Ga reacted to produce abundant amounts of  $\beta$ -Sn, particularly in the specimens that were heated at 100° and 150°C (Figure 3). However, when other specimens were stored for 5 weeks at room temperature (resulting in minimal residual liquid Ga), the amount of  $\beta$ -Sn after subsequent heating at 100° and 150°C was

only moderately increased from that in unheated control specimens stored at room temperature for the same period of time, although the amount of  $\text{CuGa}_2$  was substantially increased (Figure 4).

The formation of increased amounts of  $\text{CuGa}_2$  or  $\beta$ -Sn in aged Galloy specimens can have considerable importance for the problematic corrosion resistance of this material. Oshida and Moore (1993) investigated the *in vitro* corrosion of Gallium Alloy GF using Ringers



**Figure 6.** Lower-magnification secondary electron images comparing the fracture surfaces for the strongest machine-condensed specimen (a) with the weakest hand-condensed specimen (b). Bar = 10  $\mu\text{m}$ . Careful examination of Figure 6a shows planar areas corresponding to fracture through the pre-alloy particles. Some adhesive fracture at the matrix-particle interface can also be seen.



solution, and identified the corrosion products as  $\text{Ga}_2\text{O}_3$  and  $\text{SnO}_2$ . Herø and Okabe (1994) observed preferential attack of the  $\text{CuGa}_2$  phase during the *in vitro* corrosion of gallium alloys using  $\text{NaCl}$ /lactic acid solutions. Kaga *et al.* (1996) evaluated Gallium Alloy GF restorations after eight months and found corrosion products that were mainly gallium oxides and hydroxides. Herø *et al.* (1997) found that corrosion of the  $\text{CuGa}_2$  phase occurred in the Gallium Alloy GF under *in vivo* conditions,

whereas no detectable dissolution of the  $\beta$ -Sn phase was observed.

These studies show that further research is needed to develop a gallium restorative alloy with improved corrosion resistance. Recent SEM/EDS and XRD studies by Herø *et al.* (1996) have demonstrated the complex metallurgical structures of the gallium restorative alloys and the difficulty in precise identification of the microstructural phases. The pre-alloy particles of the present



commercial products have compositions that are very similar to those of the pre-alloy particles for the high-copper dental amalgams, and reduction or elimination of copper to minimize the CuGa<sub>2</sub> phase appears advisable. The favorable evidence of the biocompatibility of gallium (Masuhara *et al.*, 1987; Chandler *et al.*, 1994) warrants more study of the complex metallurgy of this element to achieve an optimum gallium restorative alloy.

### Conclusions

Under the conditions of this study, the following conclusions can be drawn:

(1). XRD showed that formation of the four matrix phases began within 10 minutes after trituration.

(2). Removal of the Ga-rich surface layer after condensation decreased the amount of  $\beta$ -Sn, and heat treatment of freshly prepared specimens greatly increased the amount of this phase.

(3). Similar heat treatment after five weeks storage at room temperature substantially increased the amount of CuGa<sub>2</sub>, but there were only moderate increases in  $\beta$ -Sn.

(4). Brittle fracture of Galloy occurred between matrix phases, and both around and through pre-alloy particles.

(5). There was considerably more porosity in the hand-condensed specimens compared to the machine-condensed specimens, accounting for the lower DTS of the former.

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### Discussion with Reviewers

**G.W. Marshall:** If the Sn is removed by carving excess material from the surface, as is implied by the experiment, would you expect a Sn-rich layer at the floor and walls of a Galloy restoration, and if so, what implications would this have for the corrosion characteristics of the restoration?

**Authors:** Further study may be necessary to answer this question. With a vertical condensation technique, one would not expect to have a Sn-rich layer at the walls and floor of a Galloy restoration. The objective of this condensation procedure is to bring the excess liquid to the surface, where the cavity preparation has been intentionally overfilled. The overfilled material is removed during subsequent carving. In their *in vivo* study, Herø *et al.* (1997) examined the cross-sections of retrieved gallium alloy disk specimens that had been exposed to the oral environment for periods of up to nine months. They found that only the CuGa<sub>2</sub> phase corroded substantially. It would be worthwhile to examine retrieved Galloy clinical restorations that have been exposed to *in vivo* conditions for longer periods of time.

**G.W. Marshall:** Recently, the American Dental Association has withdrawn approval of this alloy, and SDI has withdrawn it from the U.S. market, due to poor clinical performance. Can you comment on this relative to the findings from your work?

**Authors:** A major aspect of the poor clinical performance is the problematic *in vivo* corrosion characteristics of this material. Future development of gallium restorative alloys should focus on strategies to eliminate deleterious microstructural phases in the set material. Present formulations of the gallium-based alloy products employ pre-alloy powder compositions that are very similar to those of the pre-alloy powders for high-copper dental amalgams, and more innovative metallurgical approaches are needed. One strategy might be reduction of the copper content or the elimination of this element from the alloy composition to avoid the CuGa<sub>2</sub> phase that has been implicated as the principal corroding phase *in vivo*. Another aspect of the poor clinical performance appears to be the reports of fractured teeth containing Galloy restorations. Comments about this problem are provided below in answer to a question from Dr. Sarkar.

**N.K. Sarkar:** Is there any evidence that any of the constituent phases forms a continuous network, similar to  $\delta_2$  (Sarkar, 1992) in dental amalgams, and could contribute to intergranular corrosion and fracture?

**Authors:** There is no evidence, at present, of any reaction phases that form a continuous network, but further detailed microstructural studies are needed to investigate

this possibility.

**N.K. Sarkar:** Is  $\beta$ -Sn pure tin? Or, is it a solid solution of Sn with small amounts of Ag, Cu, Ga and In? This information is important from the standpoint of the corrosion resistance of Galloy. The presence of small amounts of other elements exercises profound influence on the corrosion behavior of Sn which, otherwise, is highly corrosion-prone in a chloride-containing environment.

**Authors:** According to the EDS analyses published by Herø and Okabe (1994), the  $\beta$ -Sn phase contains approximately 83 at.% Sn, so that this phase contains a substantial total percentage of atom species other than tin although the amount of each element is relatively small. However, the  $\beta$ -Sn phase does not appear to corrode *in vivo* (Herø *et al.*, 1997).

**N.K. Sarkar:** The Ag-Sn phase in the present manuscript has been identified as an intermetallic compound of the stoichiometric formula Ag<sub>4</sub>Sn. According to the Ag-Sn binary phase diagram, such an intermetallic compound does not exist. Please comment.

**Authors:** An ICDD powder X-ray diffraction standard (29-1151) exists for the Ag<sub>4</sub>Sn phase, which corresponds approximately to the  $\zeta$  phase in the Ag-Sn phase diagram (Massalski, 1986). The  $\beta$  and  $\gamma$  Ag-Sn phases that are found in the starting pre-alloy powders for dental amalgams, as described in traditional dental material textbooks (Anusavice, 1996), correspond to the  $\zeta$  and  $\epsilon$  phases, respectively, in the conventional Ag-Sn phase diagram for metallurgists (Massalski, 1986).

**N.K. Sarkar:** At the 1998 meeting of the American Association for Dental Research, Dr. John Osborne from the University of Colorado presented a paper summarizing the results of a three-year clinical study and said that Galloy should no longer be used as a restorative material (Osborne *et al.*, 1998). A relatively large proportion of the Galloy restorations exhibited a rough surface, and there were frequent tooth fractures due to expansion of the material. A similar report from Brazil on another Ga-containing alloy was published a few years ago (Navarro *et al.*, 1996). Which of the phases identified in the present study could be linked to such excessive expansion and the consequent tooth fracture? What metallurgical modifications can be done to avoid these problems?

**Authors:** We do not know of any study that has determined the phase(s) responsible for this excessive expansion. This is a very important area for future research on the gallium restorative alloys. The phase or phases interacting with the oral environment (or simply undergoing transformation *in vivo* with time) must be

identified and minimized or eliminated in improved compositions of the gallium restorative alloys. One broad aspect of this problem may simply be the relatively large number of matrix phases (four) formed during the setting reaction of the gallium-based alloys, compared to that for the dental amalgams (two phases, after the disappearance of the  $\gamma_2$  phase that initially forms during the setting of some high-copper alloys).

**H. Hersø:** The Ga-Ag phase is designated  $\text{Ga}_{28}\text{Ag}_{72}$ . Maybe the composition of this phase can vary more than this strict stoichiometry indicates? Gunnaes *et al.* (1997) have studied this hexagonal phase by transmission electron microscopy (TEM) and electron diffraction, and it is described in detail along with other observed phases.

**Authors:** The  $\text{Ga}_{28}\text{Ag}_{72}$  phase appears to correspond to the  $\beta'$  phase in the Ag-Ga phase diagram (Massalski, 1986), and it can have a varying composition. In the well-known Hansen (1958) and Elliott (1965) volumes on binary phase diagrams, this phase is instead labeled as  $\zeta'$ .

**H. Hersø:** The heat treatments at 50°, 100° and 150°C are interesting, but are the structures developed at these temperatures relevant for those obtained at 37°C?

**Authors:** Examination of the microstructures of these heat-treated alloys with the SEM and TEM would be required to answer this question. The present methodology of using elevated-temperature aging to investigate long-term structural changes that would occur at some relevant lower temperature (37°C for restorative materials *in vivo*) presumes that the mechanisms of the phase transformations do not change at the higher aging temperatures. We have assumed that there is no difference between the microstructures of the Galloy specimens at room temperature and 37°C.

**Z. Cai:** In this study, a new approach to high-temperature heat treatments was applied to accelerate the setting reactions of the gallium alloy specimens. In a clinical situation, however, materials may never be subjected to such temperatures. Can the authors comment on any possible deviation of the setting reaction at elevated temperatures compared to the reactions at mouth temperature, and the effects on the structure and phases of Galloy?

**Authors:** Reynolds (1973) heated both low-copper and high-copper (Dispersalloy) dental amalgams at 70°C for times up to seven weeks and observed transformation of the  $\gamma_1$  phase to the  $\beta_1$  phase. Subsequently, Boyer and Edie (1990) found that the transformation of  $\gamma_1$  to  $\beta_1$  occurred in clinically aged dental amalgam restorations. Under *in vivo* conditions, the maximum transient temperature experienced by a restorative dental alloy is

probably in the range of 60°-70°C. It is likely that a multi-component phase diagram that included all the constituent elements in the gallium restorative alloys would show different phase fields over the temperature range from room temperature to 150°C. However, it must be emphasized that, as is the case for dental amalgams, the microstructures of the Galloy specimens have far from the equilibrium proportions of phases. The change in the microstructures of gallium restorative alloys under aging conditions relevant to the oral environment is an important area for future study.

**Z. Cai:** In Figure 4, the intensities of the  $\text{Ag}_4\text{Sn}$  peak (at about 39.5°C) increased with the heat treatment temperature, as did those for the  $\text{CuGa}_2$  peaks. Can this be related to the setting reaction, or the changes in the alloy particles, as a result of the heat treatment?

**Authors:** We do not have an explanation for the increases in the relative intensity of the major  $\text{Ag}_4\text{Sn}$  peak with heat treatment temperature. The two general suggestions by the reviewer are plausible. Two other possibilities are that the orientation of the  $\text{Ag}_4\text{Sn}$  may be changing during the elevated-temperature reactions, and phase transformation(s) to again produce  $\text{Ag}_4\text{Sn}$  might even be occurring. Further research is necessary to elucidate the detailed mechanism for this observation. Examination of the XRD patterns for the heat treated specimens in Figure 3 shows the same behavior.

**Z. Cai:** Based upon the peak intensity changes in Figure 4, the authors concluded that the  $\text{CuGa}_2$  phase increased substantially after the heat treatment at 150°C for 2 hours, while  $\beta$ -Sn only increased moderately. Could the substantial increase of  $\beta$ -Sn be obscured by the preferred orientation, as noted in Figure 2?

**Authors:** A similar result was observed for two nominally identical specimens, so we concluded that the effect of preferred orientation was not the principal explanation for the observations.

**Z. Cai:** In this study, Galloy specimens were prepared in a well-controlled environment. Clinically, placement of restorations is performed with the possibility of moisture contamination. Can the authors further elaborate on the effects of moisture contamination on the setting reaction, microstructure and properties of Galloy?

**Authors:** We are unable to make any comments about this important area, which should be a subject for further investigation.

**H. Nakajima:** Our previous study (Nakajima *et al.*, 1996) examining the thermal behavior of gallium-based alloys showed that Galloy exhibited a strong endothermic peak around 147°C in a differential scanning calorimetry



(DSC) experiment. The present study heated the gallium alloy to 50°, 100° and 150°C. What is the rationale for selecting these temperatures?

**Authors:** As previously noted, these temperatures were selected with the objective of accelerating any phase transformations that would arise from normal *in vivo* aging of restorations. The maximum heat treatment temperature was simply selected as approximately twice the maximum transient temperature that a restoration might experience during the ingestion of a hot liquid.

**H. Nakajima:** A previous study by Miller *et al.* (1994) reported that the alloy powder in Japanese commercial alloys consists of Ag<sub>4</sub>Sn, while that of Galloy is made from Ag<sub>3</sub>Sn. The XRD results in the present study showed the presence of Ag<sub>4</sub>Sn. How do the authors explain this difference in the original alloy powder phase? This reviewer would suggest presenting the XRD data from the pre-alloy powder prior to the setting reaction.

**Authors:** Careful examination of the XRD pattern for a one-week Galloy specimen obtained at a lower scanning rate of 0.5° per min indicated that peaks for the Ag-Sn phase corresponded better to Ag<sub>4</sub>Sn (ICDD standard 29-1151) than to Ag<sub>3</sub>Sn (ICDD standard 44-1300). There were seven peaks in the XRD pattern covering the 2θ range from 25° to 95° that had positions close to peaks for the ICDD powder standards of both phases. We have subsequently performed XRD examination over a 2θ range of 15°-125° (Cu Kα radiation) on the pre-alloy powder particles, using a high-precision Philips diffractometer system (Brantley *et al.*, 1996), and indexed all of the peaks to Ag<sub>4</sub>Sn and Cu<sub>3</sub>Sn. Interpretation of the XRD pattern is somewhat subtle, because there is a peak for Ag<sub>3</sub>Sn in the ICDD powder standard near each of the peaks observed for Ag<sub>4</sub>Sn. Interpretation of the Ag-Sn phase in the XRD pattern as Ag<sub>4</sub>Sn was based upon two points: (1) The first five peaks for Ag<sub>3</sub>Sn in the ICDD standard were not observed for the Galloy powder. (2) The relative intensities of the peaks from the Ag-Sn phases were a much better match to Ag<sub>4</sub>Sn than Ag<sub>3</sub>Sn. However, the XRD analyses may be complicated by the effects of preferred orientation of the Ag-Sn phase(s) in the pre-alloy powder particles, and it is possible that both Ag<sub>4</sub>Sn and Ag<sub>3</sub>Sn are present.

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