Pressure-Induced Disappearance of the γ_2 ($HgSn_{7-8}$) Phase in Dental Amalgam

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DALE E. GRENOBLE and J. LAWRENCE KATZ*

Laboratory for Crystallographic Research, Department of Physics, Rensselaer Polytechnic Institute, Troy, New York 12181, USA

Examination of the crystalline structure of dental amalgam during an investigation that involved high pressures led to the detection of the disappearance of the γ_2 phase after high pressure treatment. This phase disappearance was detected during periodic X-ray diffraction measurements made several months to a year after the samples had been subjected to pressures of up to 50 kilobars (750,000 psi) by use of a solid medium pressure apparatus. No new phases were detected during the process.

Lowater and Murray[1] detected the presence of trace concentrations of tin in dentin and enamel, and Brudevold and Steadman[2] have shown that the tin concentrations of enamel in teeth that contain amalgam restorations are greater than tin concentrations of normal teeth. Studies of the application of stannous fluoride to the surfaces of teeth have shown that tin penetrates the enamel surface to depths of 5 to 20 micrometers (μm).[3] Since trace concentrations of various elements can have significant effects on the physical and chemical properties of hard tissues, it is important to know from where these trace concentrations are derived.

Dental amalgam is subjected to large stresses and rapid thermal fluctuations in the oral environment. This study shows that amalgam samples subjected to severe cold working in the laboratory exhibit the gradual disappearance of the $\gamma_2(HgSn_{7-8})$ phase. The tin present in this phase becomes free to diffuse through the amalgam sample and, presumably, when the restoration is in a tooth, is available to diffuse into the surrounding hard tissue.

Materials and Methods

Amalgam samples were prepared from commercial dental alloys by triturating for 15 seconds in a Wig-L-Bug; ratios of 8:5 and 5:5 of mercury to alloy were used. The samples were condensed in a cylindrical steel die at various condensation pressures from 1,000 to 15,000 psi and then were allowed to set at room temperature for seven days.

A continually increasing pressure of up to 50 kilobars (kb) was applied to each sample two or three times by compressing the sample between two tungsten carbide anvils in a high pressure apparatus designed by Ahrens and Katz[4] and Gilmore.[5] Each sample was jacketed by two pyrophyllite gaskets to prevent extrusion of the specimen as force was applied, and a tungsten carbide girdle was used to restrain lateral expansion of the sample and to reduce radial pressure gradients (Fig 1). The applied force was measured by strain gauges in a load cell, and the pressure on the sample was determined from the force-pressure calibration curve of the apparatus.[6] Each sample was kept under pressure from one hour to 24 hours. After pressure cycling, samples were removed from the apparatus and stored at room temperature.

X-ray diffraction patterns of each sample

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* Present address: Department of Dental Materials, School of Dentistry, University of Southern California, Los Angeles, Calif.

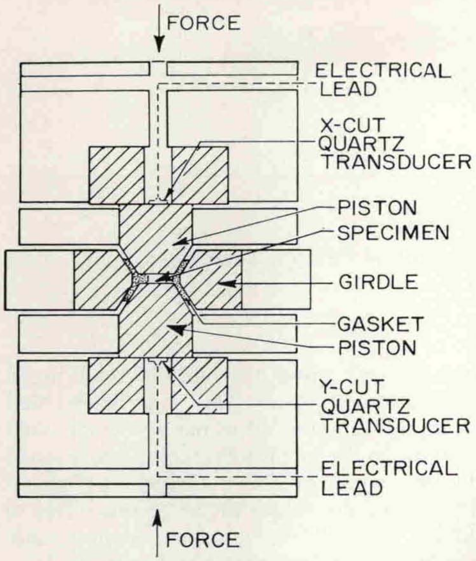

FIG 1.—Pressure vessel: Sample is compressed between two tungsten carbide pistons. Pyrophyllite gaskets and tungsten carbide girdle are used to prevent extrusion of specimen. Apparatus is placed in hydraulic press in which pressures in excess of 50 kb can be obtained.[5]

were recorded before and after the application of pressure by use of a recording diffractometer; nickel-filtered copper radiation was used. Samples were scanned at 2° (2θ)/minute from 20 to 100° (2θ), and high resolution diffraction patterns were obtained by step scanning in 0.01° (2θ) intervals. Particular attention was paid to the regions corresponding to the locations of $\gamma_2(HgSn_{7-8})$ diffraction peaks. This procedure was repeated several times during the two years after the samples were subjected to high pressures.

Results

Figure 2, *top,* shows the X-ray diffraction pattern of an amalgam sample before the application of pressure. The surfaces of the sample were polished off under cold water by use of successively finer grit papers and alumina powder; thus, the phases represented in the diffraction pattern correspond to the internal structure of the sample. The diffraction peaks that correspond to the $\gamma_1(Ag_2Hg_3)$ and $\gamma_2(HgSn_{7-8})$ alloys are labeled. Since this sample was prepared with an 8:5 mercury-to-alloy ratio and little mercury was expressed during condensation, no diffraction peaks are present in the diffraction pattern from unreacted alloy $\gamma(Ag_3Sn)$.

The unlabeled peaks at 43° (2θ) correspond to the copper-tin phase present in this alloy; another copper-tin diffraction peak is present beneath the $\gamma_2(001)$ peak at 30.2°. High resolution, step-scanned, diffraction patterns have shown that these peaks correspond to the $\eta' Cu_6Sn_5$ structure.

The small peak at 34.2° is the copper K_β radiation reflection from the (330), (411) planes of γ_1.

Figure 2, *bottom,* shows the X-ray diffraction pattern of the same specimen immediately after it had been cycled twice to 50 kb. The large increase in intensity in the $\gamma_2(001)$ reflection signifies that a preferred orientation or recrystallization of the γ_2 crystallites takes place under pressure; each crystal tends to align the *c* axis of its unit cell with the direction of the applied pressure in an effort to reduce the stress within the crystal.

This checking procedure, using X-ray diffraction techniques to study the amalgam composition, was repeated at several time intervals, as long as two years after the samples were subjected to pressure. The diffraction peaks corresponding to the γ_2 phase were missing in many samples after a period of several months and no new diffraction peaks appeared. Figure 3 shows the diffraction patterns of a sample in which this phenomenon occurs. The sample was prepared from a zinc-containing alloy with an 8:5 mercury-to-alloy ratio. It is clear from a comparison of the diffraction patterns taken before (*top*) and after (*bottom*) the application of pressure that the diffraction peaks that correspond to γ_2 are missing after the sample has been subjected to high pressure and allowed to sit for a period of time. The mercury and tin in this sample no longer exist in the crystalline form of γ_2. Because the diffraction pattern after pressure was taken with a cross-section of the sample exposed to the X-ray beam, the pattern corresponds to the internal structure, not just the surface composition.

The same behavior is demonstrated in Figure 4. This nonzinc amalgam was prepared with a 5:5 mercury-to-alloy ratio, and unreacted alloy peaks are seen at 37.7 and 39.7° in Figure 4, *bottom*. Figure 4, *top,* is a diffraction pattern of the unpolished sur-

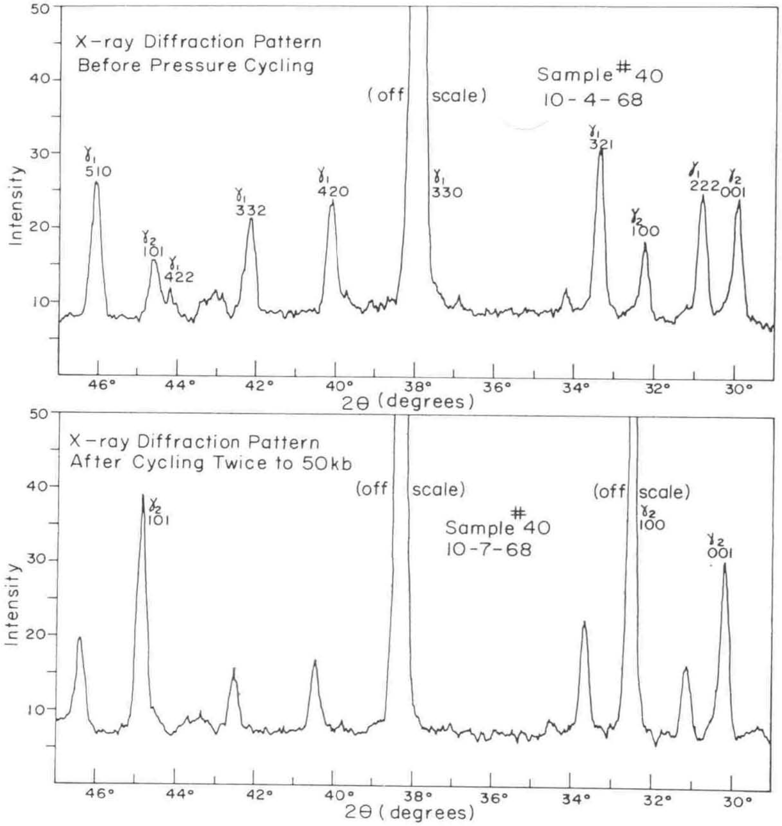

FIG 2.—*Top,* X-ray diffraction pattern of dental amalgam before application of pressure. Diffraction peaks corresponding to $\gamma_1(Ag_2Hg_3)$ and $\gamma_2(HgSn_{7-8})$ are labeled. *Bottom,* X-ray diffraction pattern of the same amalgam immediately after the application of 50 kb pressure shows an increase in intensities of γ_2 peaks, which corresponds to reorientation or recrystallization of γ_2 crystals. Surfaces of sample were removed by grinding; thus, X-ray diffraction patterns correspond to internal amalgam structure.

face of the sample. Since the surface of dental amalgam usually has a higher mercury content from the action of condensation, unreacted alloy is seldom seen there. Also, since this alloy does not contain zinc, the phase disappearance is not catalyzed by the presence of small amounts of zinc.

Further investigation of this phase disappearance was performed using optical and scanning electron microscopy. Samples were polished slowly under cold water down to 0.05 μm alumina and were etched according to Wing's[7] procedure. Photographs were taken with a Jeolco scanning electron microscope. Figure 5 (*top left and right; bottom left*) shows the grain structure of one sample; Figure 5, *bottom right,* shows the structure of the matrix of another sample after pressure had been applied.

Three distinct crystal types can be seen in Figure 5, *top left* (orig mag ×2,100, on a 4 × 5 inch negative): (1) an unreacted alloy particle, $\gamma(Ag_3Sn)$; (2) a $\gamma_2(HgSn_{7-8})$ crystal growing in the grain boundary between two γ grains; (3) $\gamma_1(Ag_2Hg_3)$ crystals that belong to the matrix. The identification of these phases was made by holding the electron beam fixed in the middle of each crystal and using nondispersive techniques to obtain the energy spectrum of the scattered

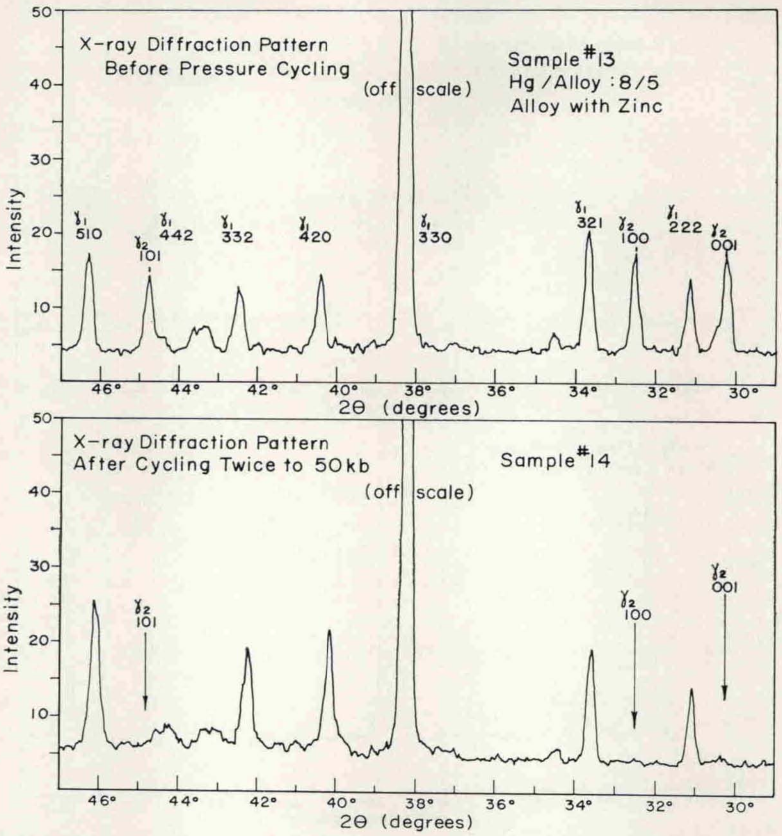

FIG 3.—*Top,* X-ray diffraction pattern of amalgam before application of pressure. Sample contained mercury-to-alloy ratio of 8:5, alloy contained zinc. *Bottom,* X-ray diffraction pattern of identical sample shows γ_2 peaks have disappeared six months after cycling twice to 50 kb. There is no evidence of formation of new phase.

X rays. This identification is considered tentative until additional microprobe analyses can be performed.

Figure 5, *top right, s*hows the region that contains $\gamma(Ag_3Sn)$ and $\gamma_2(HgSn_{7-8})$ at orig mag ×8,000; the crystal boundaries, shapes, and textures can be clearly seen. No similar γ_2 crystals were found in the samples that had been subjected to high pressure. Figure 5, *bottom left,* presents the grain structure of $\gamma_1(Ag_2Hg_3)$ in the matrix between unreacted alloy particles. Comparison with Figure 5, *bottom right,* shows that the application of high pressures fractures, severely cold works and plastically deforms the crystals in the sample.

Discussion

Although a pressure-induced phase transformation could occur in γ_2, new diffraction peaks would be detected in the X-ray traces if the transformation were irreversible. Since the γ_2 phase disappears in some of these samples after several months to a year, this phase disappearance is probably a diffusion dependent phenomenon rather than a pressure induced phase transformation. Solid state reactions are often accelerated by cold working and plastic deformation. The activation energy for atomic diffusion may be lowered in plastically deformed regions, yielding an increase in the diffusion rate. Also, the process of deformation may produce a large temporary increase in the num-

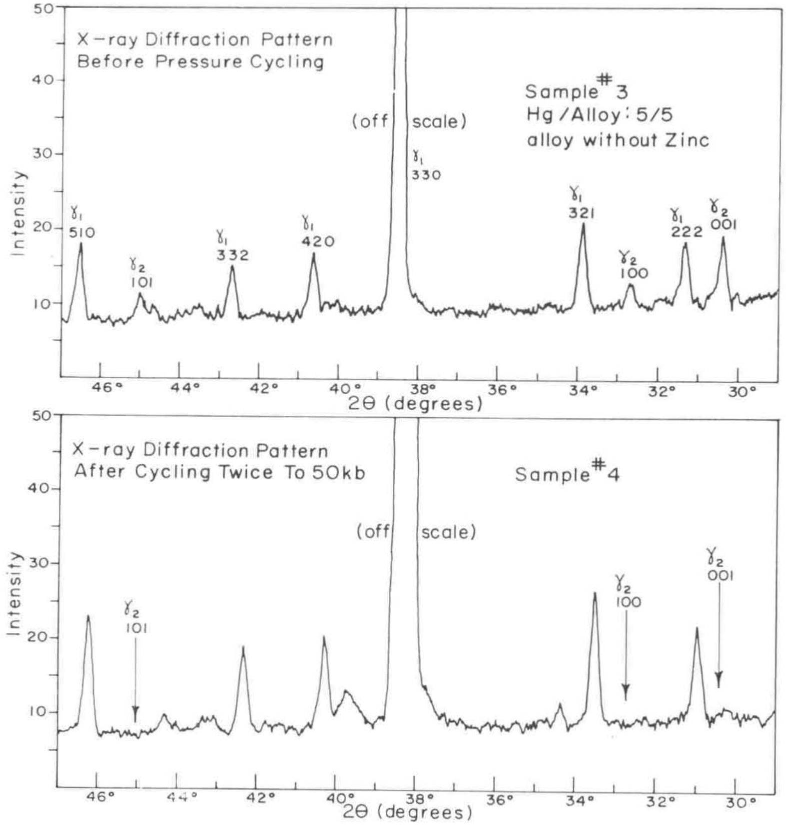

FIG 4.—*Top,* X-ray diffraction pattern of amalgam surface before application of pressure. Amalgam contained 5:5 mercury-to-alloy ratio, alloy was zinc free. *Bottom,* X-ray diffraction pattern of identical sample shows γ_2 peaks missing six months after application of high pressures. Since surface of this specimen was ground off, pattern corresponds to internal structure; unlabeled peaks correspond to unreacted alloy (Ag_3Sn) in sample.

ber of vacant lattice sites that results in a temporary increase in the diffusion rate.

If tin diffusion is activated by cold working and plastic deformation, then free tin would be available in amalgam to recombine with free silver, if present, to form Ag_3Sn. This process was not detected in the diffraction patterns, and it is unlikely that there is sufficient free silver available to form enough Ag_3Sn to be detected by X-ray diffraction. The temperature-induced phase transition from $\gamma_1 \rightarrow \beta_1$[8] also does not appear to be caused by high pressures. It is more likely that some of the tin atoms diffuse into γ_1 crystals, forming the Ag-Sn-Hg phase described by Johnson.[9] Additional microprobe studies should aid in locating where the remaining tin is diffusing in the specimens.

This proposed acceleration of the diffusion rate of tin in dental amalgam may have clinical importance, since amalgam restorations are subjected to large deforming forces during mastication and during rapid temperature changes. Since there is more tin present in amalgam than can diffuse into the γ_1 phase, this excess tin can diffuse into the surrounding hard tissues. Domagala, Van Thyne, and Lenke[10] and Jeolco, Inc.,[11] have demonstrated tin diffusion from amalgam restorations into hard tissues.

This evidence of tin diffusion into hard tissue may be associated with the phase disappearance detected in amalgam. γ_2-($HgSn_{7-8}$)

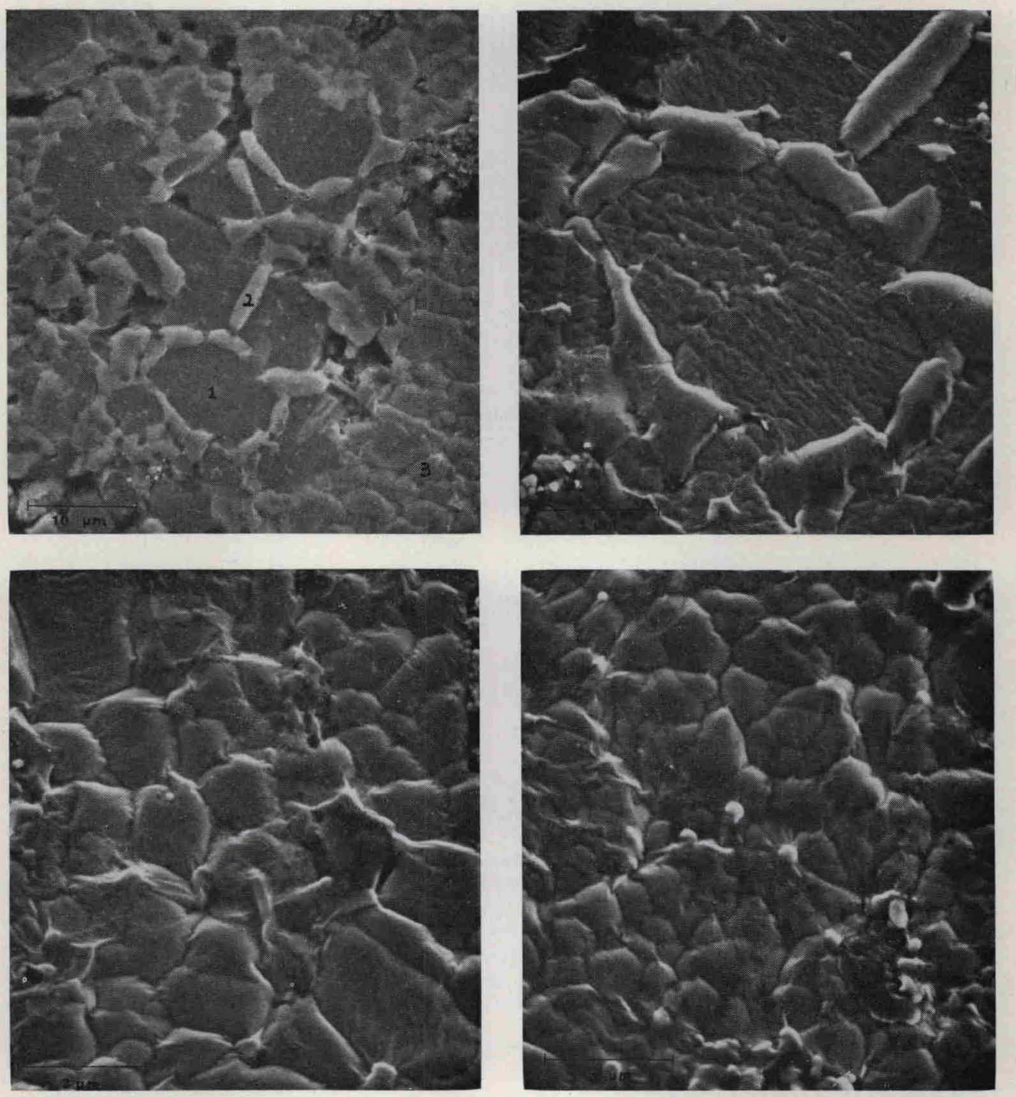

FIG 5.—*Top left,* Structure of dental amalgam before application of high pressure; sample has been polished and etched. Area photographed is 45 × 49 µm. *1,* unreacted alloy (Ag_3Sn) particle; *2,* $\gamma_2(HgSn_{7-8})$ crystal; *3,* crystal of $\gamma_1(Ag_2Hg_3)$ (orig mag ×2,100; reproduced at 41%).

Top right, Region containing *1* and *2* at higher magnification; area photographed is 11 × 13 µm. No γ_2 crystals such as these were found in specimens six months after application of 50 kb (orig mag ×8,000; reproduced at 41%).

Bottom left, Grain structure of $\gamma_1(Ag_2Hg_3)$ crystals before application of high pressure. Area photographed is 11 × 13 µm.

Bottom right, Area similar to that of Figure 5, *left,* shows effects of high pressures on γ_1 crystals. Sample has been subjected to severe cold working and plastic deformation.

is the phase in amalgam with the lowest modulus of stiffness (Grenoble and Katz)[12] and is most susceptible to cold working and plastic deformation. In addition, Wing[13] has reported that γ_2 crystallites tend to form along the surfaces and in the neighborhood of the voids present in amalgam. Since voids tend to act as stress concentrators, ie, concentrate the stress in the material between the voids, these γ_2 crystallites are probably subjected to some of the highest stresses formed within the amalgam. The constant cold working experienced by amalgam in the oral environment may activate the diffusion of free tin in the amalgam and tin diffusion into the adjacent hard tissues. Also, since the γ_2 phase is the phase in amalgam most susceptible to corrosion,[14] some of this tin may be carried to the hard tissue as a corrosion product.

Further study of this phenomenon should be conducted to determine the rate of diffusion of tin into hard tissue, as well as the effects of tin on hard tissue.

Conclusions

The disappearance of the $\gamma_2(HgSn_{7-8})$ phase has been detected in dental amalgam samples that were subjected to pressures up to 50 kb. X-ray diffraction studies have shown that this disappearance occurs over several months to a year in different samples. Since each sample acted differently, and not all samples showed significant change in one year, the diffusion rate could not be estimated. It does appear that the mercury-to-alloy ratio and the presence of zinc and copper in the alloy have no effect.

The activation of tin diffusion is caused by the severe cold working and plastic deformation that the samples experience at high pressures; the phase disappearance does not occur in samples not exposed to pressure. Some of the free tin probably diffuses into the γ_1 phase and stabilizes the structure, as discussed by Johnson[9]; tin atoms also diffuse into the surrounding hard tissues.

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