

Pressure-Induced Disappearance of the γ_2 (HgSn₇₋₈) Phase in Dental Amalgam

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 Murray¹ detected the presence of trace concentrations of tin in dentin and enamel, and Brudevold and Steadman² 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

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

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 γ_2 (HgSn₇₋₈) 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 Katz⁴ 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

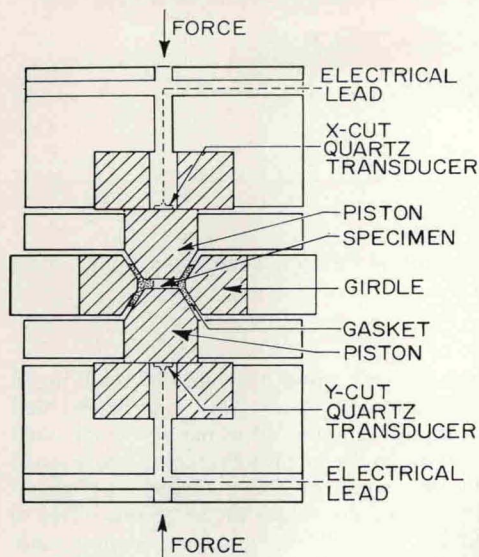


FIG 1.—Pressure vessel: Sample is compressed between two tungsten carbide pistons. Pyrophyllite gaskets and tungsten carbide girdle are used to prevent extrusion of specimen. Apparatus is placed in hydraulic press in which pressures in excess of 50 kb can be obtained.⁵

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 $\gamma_2(\text{HgSn}_{7-8})$ 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 $\gamma_1(\text{Ag}_2\text{Hg}_3)$ and $\gamma_2(\text{HgSn}_{7-8})$ 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 $\gamma(\text{Ag}_3\text{Sn})$.

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 $\eta'\text{Cu}_6\text{Sn}_5$ 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-