

The Elastic Constants of the Constituent Phases of Dental Amalgam*

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Summary

The pressure variations of the elastic constants of the constituent phases of dental amalgam (γ -Ag₃Sn, γ_1 -Ag₂Hg₃, and γ_2 -HgSn₇₋₈) were investigated in the 0-50 kilobar range. The velocities of propagation of longitudinal and transverse ultrasonic waves were measured using an ultrasonic interferometer and a solid media pressure apparatus. Computer analysis yields the pressure dependence of the bulk modulus, shear modulus, Young's modulus, and Poisson's ratio; atmospheric pressure values are obtained by back extrapolation from the high pressure measurements. The values of these elastic constants are related to the crystallographic structures of the individual alloys. The possibility of high pressure first order polymorphic transitions in γ and γ_2 is also discussed.

INTRODUCTION

There have been numerous studies completed on the physical properties of dental amalgam. However, most of these investigations have observed the responses of amalgam to certain physical tests; less effort has been made to explain what is responsible for the

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observed behavior and how physical properties are related to the structure and composition of dental amalgam. In a previous paper,¹ the authors have described the experimental techniques used and the measurements made of the elastic constants of dental amalgams as a function of pressure in the range 0–50 kilobars. In order to develop a model which explains the elastic properties observed, it was necessary to examine the elastic constants of the constituent phases of amalgam as well. This paper presents the results of that investigation of the elastic constants of γ -Ag₃Sn, γ_1 -Ag₂Hg₃, and γ_2 -HgSn₇₋₈. In the final paper of this series,² the authors develop a model of the elastic constants of amalgam based on its composition and structure and on the elastic constants of the constituent alloys.

Materials

Fifty-gram Ag₃Sn samples (74.5 atomic % Ag, 25.5 atomic % Sn) were prepared by melting silver and tin shot under vacuum in vycore tubes; 99.999% pure elements were used. The molten alloys were shaken and slowly cooled to homogenize the samples. The specimens, cut in the form of 1-cm diameter, 2-mm long cylinders, were cold worked and annealed at 450°C for 24 hr. X-ray diffraction patterns verified that the specimens were single phase γ -Ag₃Sn; metallographic examination after polishing and etching showed that the crystallite size was small.

Since the γ_2 phase region of the mercury-tin equilibrium phase diagram is quite broad, HgSn₇₋₈ samples were prepared in the middle of the range—13.4 weight % Hg and 86.6 weight % Sn. The samples were melted in evacuated, sealed vycore tubes and were cooled slowly. Specimens were cut, cold worked, and annealed for 24 hr. X-ray diffraction studies and metallographic examination showed that the specimens were single phase γ_2 .

γ_1 -Ag₂Hg₃ samples were prepared by triturating 200-mesh silver powder with 71 weight % mercury in a Wig-L-Bug for 1 min. The specimens were condensed in a 1-cm cylindrical die and were allowed to set for 10 days. The specimens were shown to be single phase γ_1 by x-ray diffraction.

The velocities of longitudinal and shear ultrasonic waves were measured in each alloy at pressures up to 50 kb. using the technique discussed in the previous paper.¹

Results

The variations of the longitudinal and shear ultrasonic wave velocities with pressure of the three alloys are shown in Figs. 1a and 1b. The wave velocities of all three alloys show linear increases with pressure. Examination of these graphs indicates that the slope of the shear velocity of γ appears to change in the neighborhood of 25 kb.; the slopes of the longitudinal and shear velocities of γ_2 appear to change in the neighborhood of 15–20 kb. The possible causes of these observations will be discussed below. The remaining velocities exhibit linear behavior from 0–50 kb. Table I lists the slopes of these curves and the longitudinal and shear velocities of each alloy at atmospheric pressure; these values were obtained by least squares analysis and back extrapolation. The percent errors shown represent the standard deviation from the least squares line and not the experimental error of the data points; the precision and accuracy of these measurements are as described in the previous paper.¹

The elastic constants of these alloys were calculated from the wave velocities as described in the previous paper.¹ Figures 2, 3, and 4 show the behavior of the bulk, shear, and Young's moduli of γ , γ_1 , and γ_2 as functions of pressure. The values of each elastic constant at atmospheric pressure in Table II were obtained by back extrapolation along the straight lines fitted to the data points by least squares analysis.

TABLE I
Longitudinal Ultrasonic Wave Velocities

Alloy	Pressure range (kb)	Slope ($\times 10^2$ cm/sec/kb)	Velocity at atmospheric pressure ($\times 10^5$ cm/sec)
γ -Ag ₃ Sn	0–50	10.35 \pm 0.64%	3.82 \pm 0.05%
γ_1 -Ag ₂ Hg ₃	0–50	11.52 \pm 1.1%	3.05 \pm 0.12%
γ_2 -HgSn ₇₋₈	0–20	9.55 \pm 1.9%	3.23 \pm 0.08%
	20–50	11.13 \pm 1.2%	
Shear Ultrasonic Wave Velocities			
γ -Ag ₃ Sn	0–25	2.54 \pm 2.7%	1.77 \pm 0.06%
	25–50	3.85 \pm 1.9%	
γ_1 -Ag ₂ Hg ₃	0–50	3.99 \pm 0.93%	1.42 \pm 0.09%
	0–20	3.98 \pm 1.0%	
γ_2 -HgSn ₇₋₈	0–20	3.98 \pm 1.0%	1.54 \pm 0.35%
	20–50	5.31 \pm 1.9%	

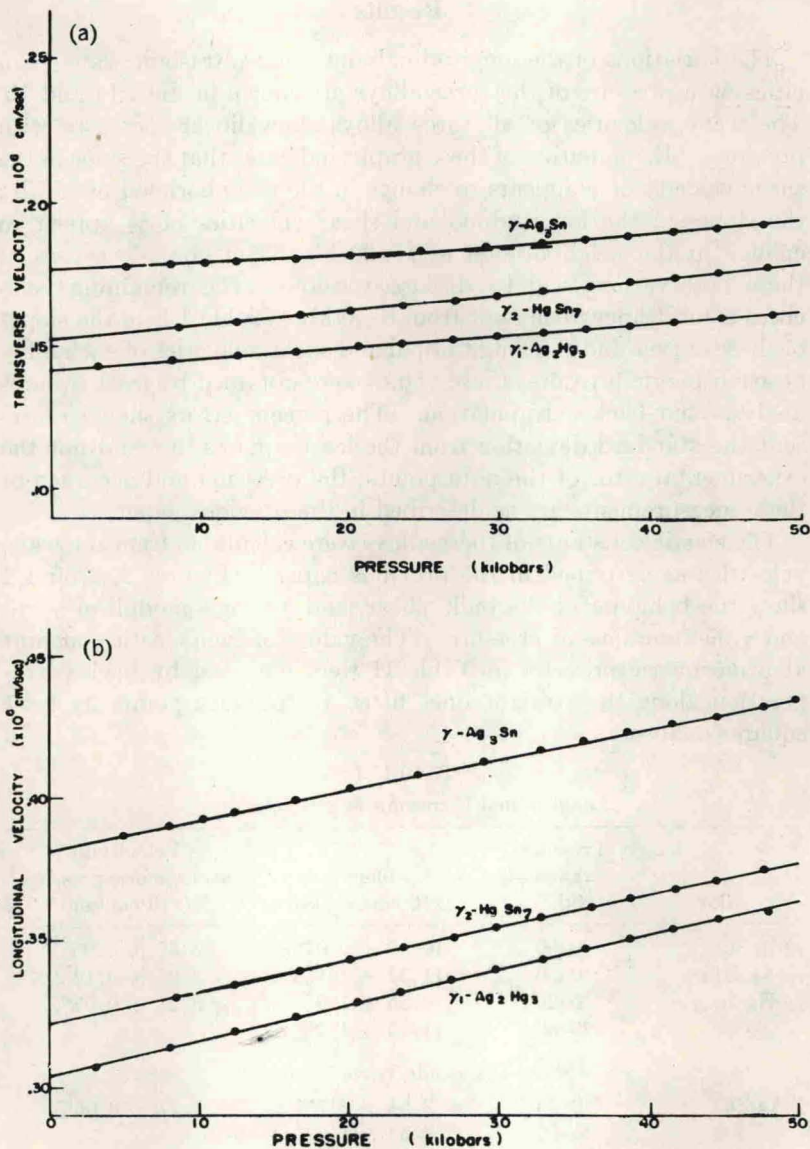


Fig. 1. (a) Velocities of shear ultrasonic waves in the constituent phases of dental amalgam as a function of pressure. (b) Velocities of longitudinal ultrasonic waves in the constituent phases of dental amalgam as a function of pressure.

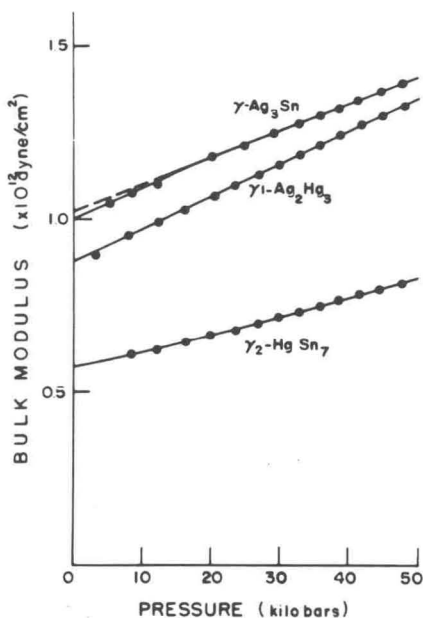


Fig. 2. The bulk moduli of the constituent phases of dental amalgam as functions of pressure.

Discussion

There are many factors, either singly or in combination, which could be responsible for the apparent slope changes observed previously in dental amalgam¹ and also in the γ and γ_2 velocity data (see Table I and Figs. 1a and 1b). Such changes could arise from the experimental configuration; although the pressure calibration is

TABLE II
The Elastic Constants of the Constituent Alloys
of Dental Amalgam at Atmospheric Pressure
(All Moduli in 10^{12} dynes/cm²)

Alloy	Bulk modulus	Shear modulus	Young's modulus	Poisson's ratio
γ -Ag ₃ Sn	1.01	0.307	0.836	.36
γ_1 -Ag ₂ Hg ₃	0.871	0.269	0.731	.36
γ_2 -HgSn ₇₋₈	0.567	0.181	0.491	.35

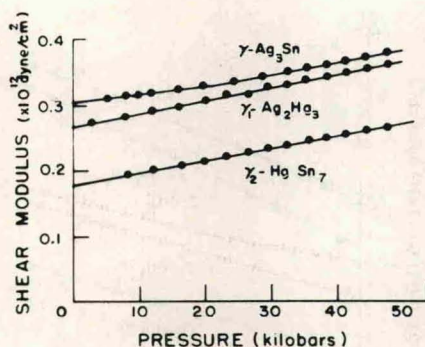


Fig. 3. The shear moduli of the constituent phases of dental amalgam as functions of pressure.

periodically checked, small changes might occur during data runs. Additional changes could arise from the non-hydrostatic geometry of the pressure apparatus and its effect on materials with quite different plastic deformation properties. Another possible factor is the introduction of porosity in the form of microfissures and cracks due to fracturing during stress release.

The analytical calculation itself may be a contributory factor. The analytic computations involve, as part of the boundary conditions, the pressure dependence of the elastic properties of the pyrophyllite gaskets. This input data has been derived from previous experiments.³ However, each data run requires two new pyrophyllite gaskets, and although the gaskets were prepared from a large block of material, small variations in physical properties could occur, thus affecting the calculations.

In addition to these factors, the intrinsic properties of these materials may change due to electronic realignments or phase transformations due to the high pressure. These factors are presently under investigation. Although the changes detected in the slopes of the ultrasonic velocities of γ and γ_2 are not sufficient to determine whether phase transitions are actually occurring at high pressure, such transitions appear possible based on structural considerations and will be discussed later.

The elastic properties of primary importance are those at atmospheric pressure. It is evident from Figs. 2, 3, and 4 and Table II that the elastic constants of γ_2 are considerably less than those of γ

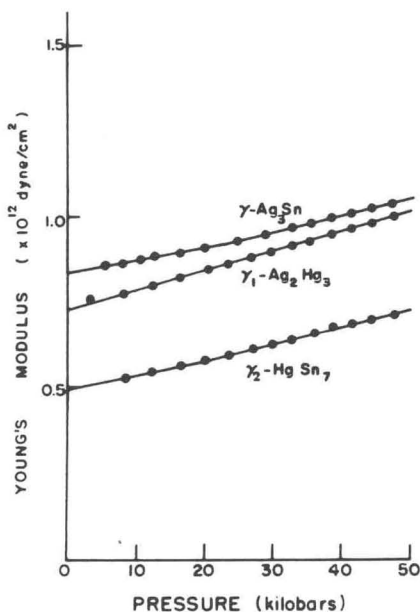


Fig. 4. The Young's moduli of the constituent phases of dental amalgam as functions of pressure.

and γ_1 . The γ_2 phase is a much more compressible material than either γ or γ_1 , and γ_2 is less resistant to shear forces than γ or γ_1 . As a result, the resistance of a mixture of these three phases, i.e., dental amalgam, to externally applied forces will be reduced by the presence of γ_2 .

The differences between the elastic constants of these alloys can be explained on the basis of the differences in their structures.

γ -Ag₃Sn

Ag₃Sn is an intermetallic compound with strong interatomic bonds. Compounds with strong bonding are generally brittle, do not suffer plastic distortion, and are relatively incompressible. Hence, the interatomic bonds in the Ag₃Sn structure give the material relatively high bulk, shear, and Young's moduli.

γ_1 -Ag₂Hg₃

γ_1 belongs to that series of structural types of alloys which occur when particular ratios of valence electrons to atoms are reached, in

this case, 21:13. Hume-Rothery "electron compounds" are found in many alloy systems and, in general, exhibit the same types of phase sequence and physical properties.

The occurrence of the γ_1 structure is explained by the theory of Brillouin Zones developed by Jones⁴ (1934). Jones' theory requires that for an atomic pattern to be stable, all electrons must occupy the lowest energy states when a Brillouin Zone is nearly completely filled. The γ_1 structure is represented by a zone formed by the (411) and (330) planes; these sets of planes have the same interplanar spacing, so the zone is almost spherical in shape; and a maximum number of electrons are packed onto these planes, so that the proper electron to atom ratio is produced. Therefore, if the atomic sites in the structure remain the same, the (411) and (330) planes remain densely populated regardless of how the atoms are distributed among them. As a result, the electron to atom ratio remains 21:13 independent of the precise atomic arrangement, and the structure is highly stable.

Johnson,⁵ in order to explain what he considers to be the "extraordinary stability" of γ_1 in dental amalgam, has proposed that Sn is present in small amounts in the γ_1 phase, as it exists in dental amalgam, rather than located exclusively in the γ_2 phase. He has discussed the γ_1 structure as a three component (Ag-Sn-Hg) Hume-Rothery "electron compound." It would be of interest to study this three component system using the same techniques described here and previously¹ in order to see what effect the addition of small amounts of Sn within the γ_1 structure might have on the elastic properties of this phase.

The variations of the elastic constants of γ_1 -Ag₂Hg₃ with pressure reflect the stability of this structure. Although the atoms in the structure form non-directional metallic linkages, which are generally easily broken and replaced, the stability of the structure produces higher bulk, shear, and Young's moduli than would be expected from this type of bonding. It is probably for this reason that the elastic constants of γ_1 are quite close to those of the intermetallic compound γ .

γ_2 -HgSn₇₋₈

γ_2 has the form of a solid solution of mercury in tin; however, the structure is simple hexagonal rather than the tetragonal cell found in pure tin. This structure is formed by weak interatomic, metallic

linkages. Since metallic bonds are non-directional, slip processes occur easily in the directions of closest atomic packing; planes of high atomic density slide past each other under the application of small shearing forces. The interatomic metallic linkages reform as easily as they are broken. Hence, γ_2 has considerably lower bulk, shear and Young's moduli than the other two alloys.

Possible Phase Transitions

Many materials are able to transform from one crystalline form to another when hydrostatic pressures are applied. These transformations, when they occur, always occur with the structure changing to one of higher density with increase in pressure.

γ -Ag₃Sn

The slope changes in the elastic constants and the ultrasonic velocities of Ag₃Sn may imply that some type of pressure dependent volume change may be occurring in the range of 20-30 kb. Since the gasket and frictional effects take up most of the applied force, a considerable increase in force is required to compress the gaskets when the sample undergoes a discontinuous volume change. This effect spreads the volume transition over a range of applied force or apparent pressure. For this reason, it is not possible to determine the exact transition pressure with this apparatus. An examination of the structure of Ag₃Sn using a high pressure x-ray diffraction apparatus is planned to see whether a phase transition is actually occurring.

Bridgman⁶ (1935) has examined the compressibilities of several intermetallic compounds as a function of pressure. The striking characteristic in his data is the large number of volume discontinuities detected and the observance of such irregularities as creep and hysteresis. This behavior is expected since intermetallic compounds are not strict chemical compounds. Often large superstructures are formed since the interatomic linkages are not as strong as true chemical bonds. Since γ -Ag₃Sn has an orthorhombic superlattice, formed from a slightly deformed hexagonal close packed structure, there is a possibility that the structure returns to the hexagonal close packed lattice at high pressures. A detailed x-ray determination of structure at high pressures will be necessary to fully determine the characteristics of the transition if a structure change is taking place.

There is also a possibility that the transition reflects an electronic rearrangement. Murphy⁷ reported that γ -Ag₃Sn undergoes a transformation at about 60°C at atmospheric pressure and that the nature of the transformation was not known. Preston⁸ showed by x-ray diffraction methods that the lattice did not change during this transition.

γ_2 -HgSn₇₋₈

The transformation suggested in the γ_2 data appears to occur in the range 15–20 kb. Although an x-ray diffraction study of the structure at high pressures is necessary to determine whether the structure actually changes, structural transitions can be suggested from the work of Raynor and Lee.⁹

γ_2 is a tin-rich solid solution. Raynor and Lee have shown how the simple hexagonal lattice of γ_2 could be formed from the body-centered tetragonal lattice of tin when solute atoms of very similar diameter are added. The structure can be derived by drawing the hexagonal structure in terms of an orthorhombic cell and by stacking three such unit cells on top of each other. The atoms of this structure lie on two inter-penetrating, body-centered, orthorhombic sublattices. If one sublattice is moved in the direction of the "a" axis by an amount "a"/4, a contraction along the "c" axis can occur, resulting in the tin type of structure. During this transformation, the (01.1) and (10.1) planes of the hexagonal structure become the (220) and (121) planes of the tetragonal structure. Since the Brillouin Zone of white tin is formed by the (220) and (121) planes,¹⁰ the formation of γ_2 may be due to the tendency of these (220) and (121) planes to equalize their interplanar spacings when mercury is added, resulting in a decrease in the electron: atom ratio. At high pressure, further change may occur.

Conclusion

Measurement of the elastic constants of the constituent alloys of dental amalgam has shown that the bulk, shear and Young's moduli of the γ_2 -HgSn₇₋₈ phase are considerably lower than the elastic moduli of γ -Ag₃Sn and γ_1 -Ag₂Hg₃. Consequently, the elastic response of dental amalgam to applied forces will be influenced by the presence of the γ_2 phase. These lower elastic moduli are produced by the weak intermetallic forces bonding the mercury and tin

together contrasted to the stronger bonds formed in the γ and γ_1 structures.

The ultrasonic data suggests the possibility of high pressure, first order polymorphic transitions in γ and γ_2 . These proposed transitions should be examined using high pressure x-ray diffraction techniques.

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References

1. D. E. Grenoble and J. L. Katz, *J. Biomed. Mater. Res.*, **5**, 489 (1971).
2. J. L. Katz and D. E. Grenoble, *J. Biomed. Mater. Res.*, **5**, 515 (1971).
3. R. S. Gilmore, "The Elastic Constants of Fifteen Materials as Functions of Pressure and Their Equations of State," Ph.D. Thesis, Rensselaer Polytechnic Institute (1968).
4. H. Jones, *Proc. Roy. Soc., (A)*, **144**, 225 (1934).
5. L. B. Johnson, Jr., *J. Biomed. Mater. Res.*, **4**, 269 (1970).
6. P. W. Bridgman, "Solids Under Pressure," McGraw-Hill, New York (1963).
7. A. J. Murphy, *J. Inst. Met.*, **35**, 107 (1926).
8. G. D. Preston, Appendix to A. J. Murphy, *J. Inst. Met.*, **35**, 107 (1926).
9. G. V. Raynor and A. Lee, *Acta Met.*, **2**, 616 (1954).
10. K. Z. Schubert, *Metallkunde*, **41**, 423 (1950).

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