

In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institution shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the Dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.

DIFFUSION OF MERCURY INTO SILVER-TIN DENTAL ALLOY (Ag_3Sn)
INCLUDING THE EFFECT OF ULTRASONIC ENERGY

A THESIS

Presented to

The Faculty of the Graduate Division

by

Stephen Weil Freiman

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Metallurgy

Georgia Institute of Technology

June, 1965

Approved:

Chairman

Date approved by Chairman: 6/28/65

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to his thesis advisor, Dr. R. F. Hochman, who suggested this research project, and who contributed much invaluable aid to the work.

Great appreciation is also extended to Dr. E. A. Starke, Jr., for his great help in obtaining much of the data in this work and to Dr. Niels Engel for the time spent in review of this research and his many helpful suggestions on the evaluation of the data.

This research was sponsored by a National Institutes of Health Dental Research Grant which made available the funds for the equipment and facilities and the author's personal support on an NIDR traineeship.

Thanks are also extended to Dr. O. D. Harvey and other members of the staff of the Emory University School of Dentistry for their instruction in the use of dental materials.

Thanks are given to Mr. Dean Kimmel of the L. D. Caulk Company for his contribution of materials.

In addition, gratitude is given to Mr. J. W. Johnson and Mr. J. L. Hubbard for their fine efforts in electron and optical microscopy.

To Mr. J. W. Koger, who contributed much helpful aid and advice to this research, is extended the author's thanks.

Finally, special thanks are given to my wife, Adele, for her help, encouragement and understanding.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	iv
LIST OF FIGURES	v
SUMMARY	viii
Chapter	
I. INTRODUCTION	1
Formation of Dental Amalgam	
Mercury Diffusion in Tin and Silver	
Influence of Ultrasonic Energy	
II. PROCEDURE	17
Materials	
Sample Preparation	
Experimental Arrangement	
Analysis	
III. RESULTS	22
Incomplete Reaction of Amalgam	
Grain Boundary Diffusion	
Rate of Diffusion	
Error Analysis	
IV. CONCLUSIONS AND RECOMMENDATIONS	42
Recommendations for Further Research	
APPENDICES	
A. SAMPLE CALCULATIONS	45
B. EXPERIMENTAL RESULTS	48
BIBLIOGRAPHY	71

LIST OF TABLES

Table		Page
1.	Diffusivities of Both Non-Ultrasonic and Ultrasonically Activated Samples.	35
2.	Activation Energies and Frequency Factors for Both Ultrasonic and Non-Ultrasonic Samples.	36
B-1.	Results Obtained from Hg Conc. vs. Depth of Penetration Curves for all Diffusion Runs	48

LIST OF FIGURES

Figure		Page
1.	Silver-Tin Phase Diagram.	3
2.	Silver-Mercury Phase Diagram.	4
3.	Tin-Mercury Phase Diagram	5
4.	Diffusion Penetration Curve of Mercury in Tin, Obtained by Taylor.	10
5.	Experimental Arrangement for the Application of Ultrasonic Energy During Mercury Diffusion.	19
6.	Electron Micrograph of Microtomed Amalgam, Showing Unreacted Ag_3Sn Particles	23
7.	Electron Micrograph of Microtomed Amalgam, Showing Unreacted Ag_3Sn Particles	24
8.	Actual Penetration Curve of Mercury Concentration in Ag_3Sn , Obtained on Electron Probe Microanalyzer	26
9.	Surface of Cross-Section of Reacted Ag_3Sn Showing Grain Boundary Attack	27
10.	Mercury Distribution in Cross-Section of Reacted Ag_3Sn . . .	27
11.	Cross-Section of Reacted Ag_3Sn Showing Mercury Attack at the Grain Boundaries.	30
12.	Cross-Section of Reacted Ag_3Sn Showing Mercury Attack at the Grain Boundaries.	31
13.	Reacted Cross-Section of Ag_3Sn Showing Widmanstätten Type Structure.	32
14.	Unreacted Cross-Section of Ag Cast Ag_3Sn Showing Widmanstätten Type Structure.	33
15.	Electron Micrograph of Unreacted Annealed Ag_3Sn Showing Widmanstätten Type Structure.	34
16.	An Arrhenius Plot of Log Diffusivity Versus $1/T$ for Non-Ultrasonic and Ultrasonically Activated Samples	37

Figure		Page
B-1	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 5.45 Hours at 40°C.	53
B-2	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 1.94 Hours at 60°C.	54
B-3	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 3.63 Hours at 60°C.	55
B-4	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 2.00 Hours at 80°C.	56
B-5	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for 1.57 Hours at 40°C	57
B-6	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for 1.65 Hours at 40°C	58
B-7	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 3.18 Hours at 40°C.	59
B-8	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 2.08 Hours at 110°C	60
B-9	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 5.27 Hours at 110°C	61
B-10	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 2.00 Hours at 40°C.	62
B-11	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 2.00 Hours at 80°C.	63
B-12	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for .78 Hours at 60°C.	64

Figure		Page
B-13	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for .83 Hours at 60°C.	65
B-14	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for 1.23 Hours at 80°C	66
B-15	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for 1.43 Hours at 80°C	67
B-16	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for .67 Hours at 40°C.	68
B-17	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for .75 Hours at 60°C.	69
B-18	Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for .67 Hours at 80°C.	70

SUMMARY

Since there is some indication that the diffusion rate of mercury is a large factor in determining the rate of reaction of dental amalgam, this study was undertaken to cast some light on the diffusion of mercury into Ag_3Sn dental alloy. The diffusivities at different temperatures were determined, the mechanism was investigated, and the effect of ultrasonic energy on the diffusivity was measured.

After mercury was allowed to diffuse into the Ag_3Sn at the different temperatures, either with or without the presence of ultrasonic energy, the concentration of mercury at several depths in the sample was measured through the use of x-ray fluorescence analysis. Mercury concentration versus depth of penetration curves, from which the diffusivities were calculated, were then plotted for each sample. The Norelco Electron Probe Microanalyzer and various metallographic techniques were employed to study the mechanism of the diffusion.

The results showed that a large percentage of the diffusion occurred in the grain boundaries of the Ag_3Sn . It was also shown that ultrasonic energy greatly increased the diffusivity of mercury in Ag_3Sn at each temperature. A needle-like structure was found in both reacted and unreacted Ag_3Sn , but further investigation will be necessary before any conclusions can be drawn as to its constitution or the reason for its existence.

CHAPTER I

INTRODUCTION

Formation of Dental Amalgam

Interest in the diffusion rate of mercury in an alloy of Ag_3Sn stems from the use of this alloy in the production of amalgam for dental restorations. The actual dental alloy consists of approximately 75 per cent silver, 25 per cent tin, and small amounts of copper and zinc. Silver and tin are the primary ingredients which undergo reaction with the mercury. These two metals are chosen because of the ease with which they react with mercury and also because the amalgam formed from this alloy expands very slightly during the reaction. This slight expansion fills the cavity and helps prevent further decay at the margins of the restoration. The copper replaces some of the silver in the reaction and adds strength to the amalgam. The zinc acts as a scavenger and reacts with any impurities in the amalgam. Because of the presence of zinc, it is necessary to prevent the amalgam from coming into contact with any moisture before setting has occurred.

The blending of the constituent metals in the alloy is accomplished by melting them together in their proper proportions. Only pure materials are used and these are melted under controlled conditions, free from oxygen and other contaminants.

The alloy is cast into bars and cut into fillings, which are often ball milled. Because segregation occurs when the bar is cast,

particles from the outside of the bar have different properties from those of the center. For this reason, the bar is annealed at about 425°C for 24 hours before cutting. After cutting and ball milling the particles are given a stress relief anneal.

Because particle size affects the properties of the amalgam, it is necessary to size the particles into coarse, medium, and fine cut. This is achieved by setting the depth of cut during machining and using a suitable sizing and separation procedure to attain the final particle distribution. Finally, the alloy is chemically cleaned to remove any oxide coating. This leaves the surface ready to combine with the mercury.

The alloy and mercury are triturerated together, either by hand with mortar and pestle, or in a mechanical amalgamator. This plastic mass is then pressed into the cavity in small pieces. The amalgam is then condensed in the cavity. During condensation, which consists of removing the excess mercury from the mix, the mercury goes into solution in the Ag_3Sn .

The essential component of the silver-tin system which enters into the reaction with mercury is the Ag_3Sn phase. Any β solid solution which may be present only enhances the reaction. These phases are shown in the Ag-Sn diagram in Figure 1.

When the alloy is mixed with mercury during trituration, the Ag_3Sn dissolves or absorbs mercury, and two crystalline phases result, which are known as γ_1 and γ_2 .



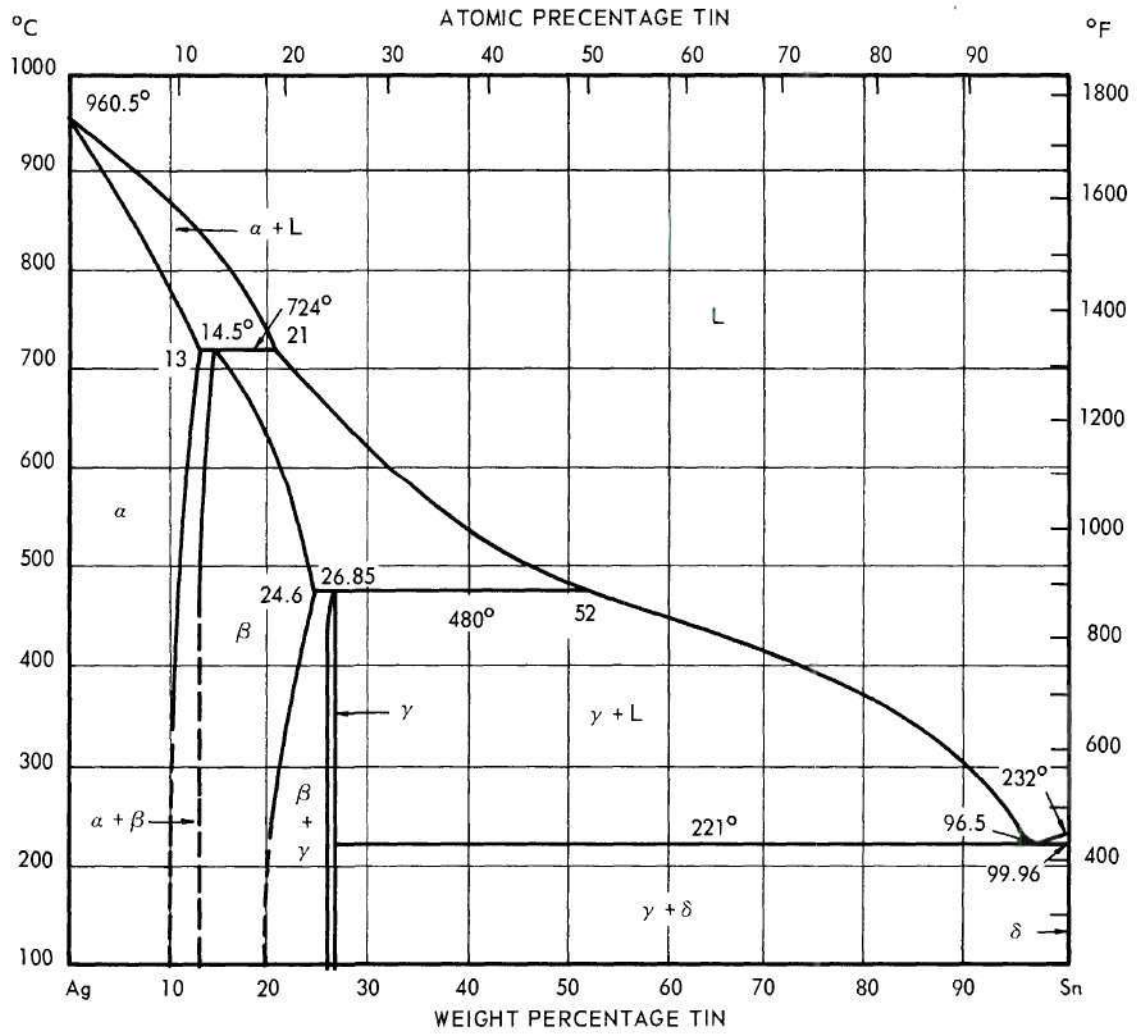


Figure 1. Silver-Tin Phase Diagram.

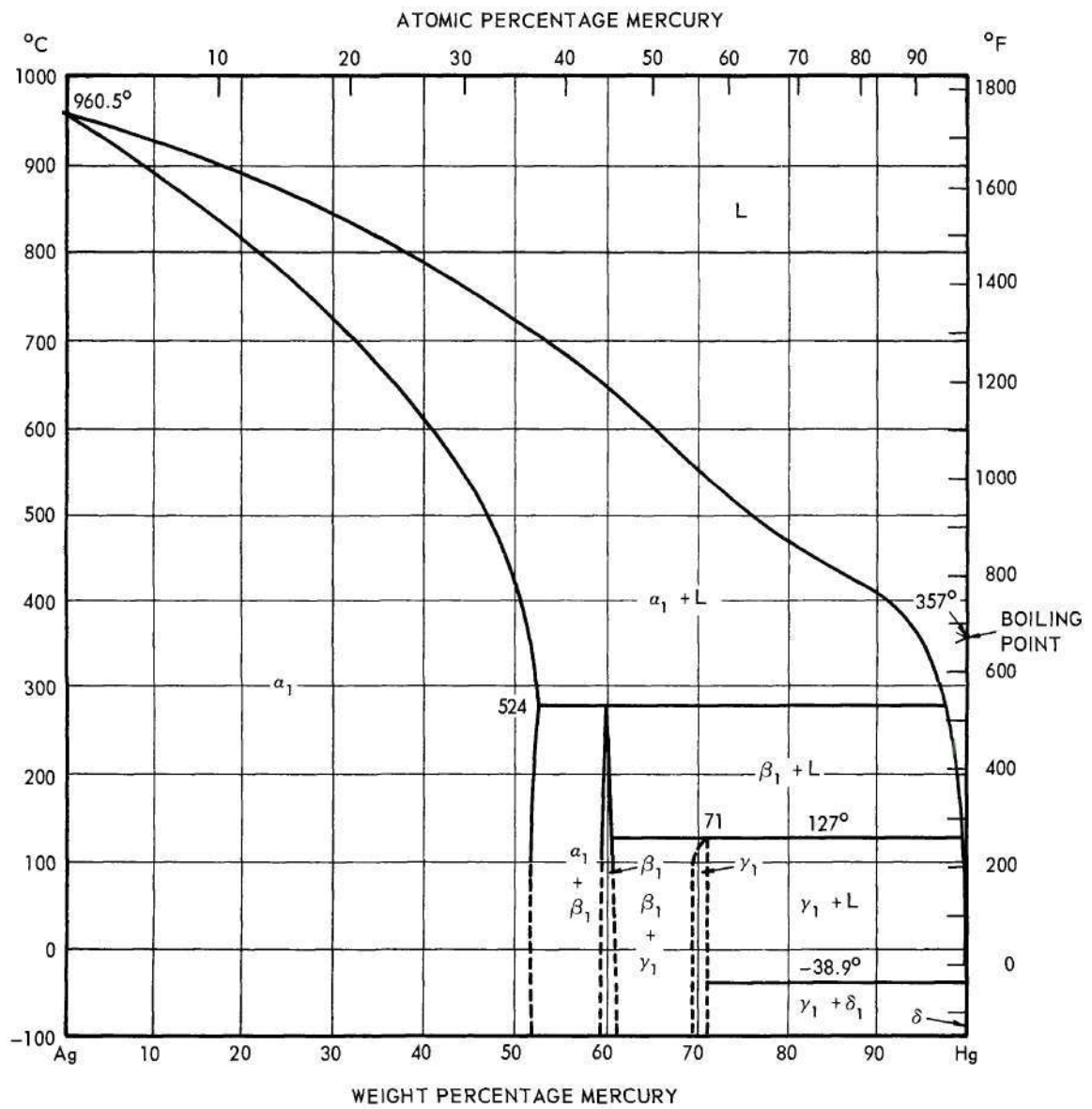


Figure 2. Silver-Mercury Phase Diagram.

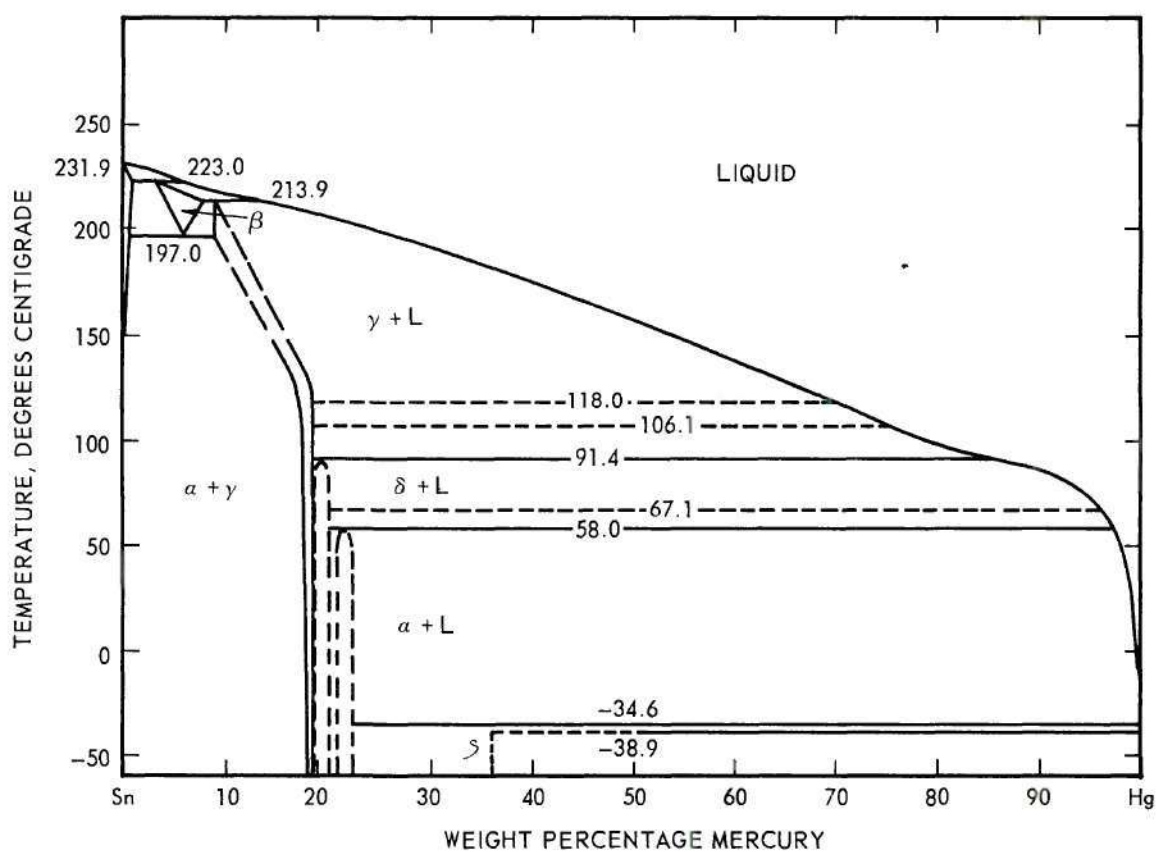


Figure 3. Tin-Mercury Phase Diagram.

where γ_1 is the γ phase in the Ag-Hg system, and γ_2 is the γ phase in the Sn-Hg system. These phase diagrams are shown in Figures 2 and 3.

The γ_1 begins to precipitate first. It has been identified as an intermetallic compound with the formula Ag_2Hg_3 . Although the crystals of the γ_2 phase appear a short time after those of the γ_1 , their rate of growth is more rapid. This phase consists of tin and mercury combined in a hexagonal lattice.² According to some authorities,¹ its composition is Sn_8Hg . Actually the amount of precipitation of both phases will depend upon the amount of mercury present. A reduction in the amount of mercury available for the reactions causes a greater decrease in the formation of the γ_2 phase than the γ_1 phase.³

As the precipitation of the γ_1 and γ_2 phases proceeds, more of the mercury is dissolved by the Ag_3Sn . Presumably, as the γ_1 and γ_2 phases form around the alloy particles, they are rubbed off by the trituration process, and further solution of the mercury by the Ag_3Sn phase occurs, and so on. Eventually, there may be insufficient mercury present for the reaction to proceed further, and the precipitation of the γ_1 and γ_2 phases terminates. A certain amount of free mercury may remain but more likely a solid solution of mercury in the Ag_3Sn occurs. It is thought that a third phase may form by a reaction between the solution phase and the remaining Ag_3Sn . This new phase is known as β_1 .⁴ Koger,¹ however, has shown no evidence of a β_1 phase in reacted amalgam.

The period when the greatest dimensional changes occur in the amalgamation coincides with the disappearance of the uncombined mercury.⁵ X-ray diffraction studies fail to reveal any uncombined mercury in hardened amalgam below a temperature of 149°F after this period.⁶ The mer-

cury is apparently completely in combination with the other phases present at this stage. These observations as well as the determination of the phases formed are also substantiated with measurements of the electrical conductivity during the hardening of the amalgam.⁷ The conductivity is markedly influenced by the alloy composition and by the residual mercury content.

Complete equilibrium is never attained in practice unless an extremely small particle size of alloy is used. Usually the core of the alloy particles will remain dispersed in the alloy. The undissolved particles are surrounded by a matrix which according to the theory presented consists of γ_1 , γ_2 , and possibly some β_1 .

Mercury Diffusion in Tin and Silver

Because the diffusion of Hg into the alloy particles is one of the important steps in the formation of dental amalgam, the mechanism by which it occurs is of interest.

Although no previous work has been done on Hg diffusion in Ag_3Sn , investigations have been carried out on mercury diffusion into pure Ag and pure Sn.

Gunther and Jehmlich⁸ investigated the diffusion of Hg into Sn. Because the two components absorb x-rays differently, x-ray radiography was utilized. A series of radiographs was made, and from the degree of darkening of the film, the amount of mercury present was calculated. The curves of intensity versus distance yielded a staircase type of diffusion. This type of diffusion could not be reconciled with Fick's Law. For calculation of the diffusion coefficient, therefore, the

curves were smoothed. A diffusion coefficient, $D_k = 4 \times 10^{-8} \text{ cm}^2 \text{ per sec.}$ was determined at room temperature. The relatively high diffusion coefficient is explained by the fact that the mercury is present as a liquid.

The staircase type of curves implies a formation of threshold values of concentration; i.e., the diffusion does not proceed continuously and a concentration gradient must always be present before the diffusion process is possible. This would mean that the diffusion practically comes to a standstill when the concentration regresses to the particular position beneath this threshold.

C. V. Simon⁷ established, in an investigation of the lattice structure of tin rich alloys, that tetragonal β tin crystals are first formed from pure tin. A second crystal type with simple hexagonal lattice occurs in addition to tetragonal β tin. The Sn crystals completely vanish at about 11 to 13 per cent Hg.

X-ray analysis carried out by S. Steenbech¹⁰ was able to confirm the previous results in that an intermediate phase of hexagonal structure was found between 6 and 10 per cent Hg. With a somewhat higher mercury content a second phase is present whose structure can be derived from the first phase, by means of slight deformation (degradation of the symmetry from hexagonal to rhombic). X-ray analysis has shed no light on whether these two lattices belong to the same or to different phases.

On the basis of these findings, the concentration threshold could perhaps be explained: Each of these phases which are traversed during the diffusion process is bound to a definite concentration as

well as an individual diffusion rate. Therefore the individual phases will first attempt to fill themselves. If one phase is saturated first as the concentration rises, a concentration gradient is created which is sufficient to permit the diffusion process to occur.

Taylor¹¹ also investigated the diffusion of mercury into tin. His specimens were exposed to mercury by immersion in saturated mercury solutions at constant temperatures of 37°C, 60°C, 85°C, and 110°C. Saturated solutions of tin in mercury were used at each temperature in order to prevent excessive initial dissolution of the specimens.

After varying periods of immersion, the specimens were removed from the mercury and the excess liquid was blown from the surface with an air blast. This treatment did not remove all the liquid, but did reduce the quantity to a thin film adhering to the surface. Some of the specimens were then sectioned immediately while others were returned to the oven for an additional annealing period.

The specimens were turned down in a lathe. A series of samples was then taken from the mercury containing layer. Mercury analysis was performed by a modification of the technique of Crawford and Larson.¹² When the specimens were removed from the liquid and blown as dry as possible, their surfaces normally exhibited a fine roughness which appeared to resemble cobblestones. In some specimens, flat platelike crystals appeared.

Figure 4 shows the results of the analyses of one of Taylor's specimens. Each point represents the analysis of one entire sample.

The curve as drawn through the experimental points, shows, as expected, a continual decrease of mercury content with depth. It also

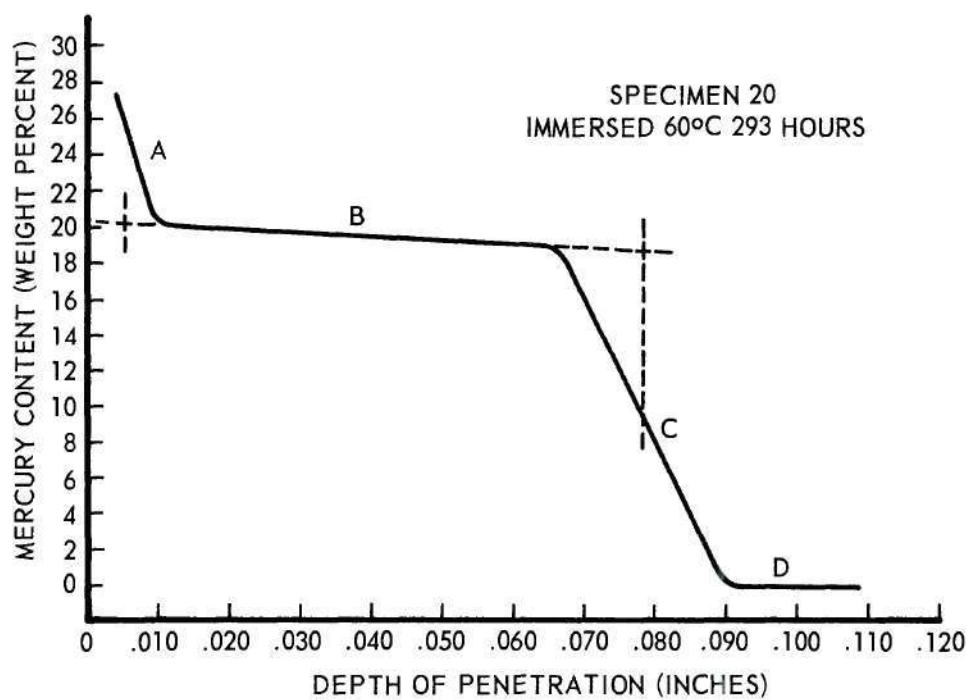


Figure 4. Diffusion Penetration Curve of Mercury in Tin Obtained by Taylor.

appears to consist of four distinct sections lettered A through D.

Section A indicates a surface layer of high, but rapidly decreasing mercury content. It is readily interpreted as a mixture of the equilibrium surface phase with the adherent mercury film. Section B indicates a thick layer of very slowly decreasing mercury content. Such steps in diffusion curves are commonly taken as indicating a one phase layer and the composition at each boundary is represented by the minimum and maximum solubility of the phase. Section C indicating a layer of rapidly decreasing mercury content probably represents a mixture of the phase of Section B with that of Section D. A mixture of phases, however, is known to be impossible under these conditions. Section D which here consists only of portions of zero mercury content, normally will include the unreacted core material and also the solid solution region of the same structure.

The curve as a whole seems to show the presence of only one intermediate tin-mercury phase. The composition limits were estimated to be between 18.8 and 20.3 per cent mercury.

Since Gunther and Jehmlich demonstrated that the initial penetration of mercury into tin is intergranular, it is possible that the mercury content of Section B is too high. The possibility also exists that there might be one or more undetected solid phases in Section C, which remained undetected because a low diffusivity or narrow composition limits kept the layer thickness too small to be detected by the sectioning technique employed.

Other curves obtained by annealing further after the mercury source had been removed indicated the existence of more than one phase.

In discussing the results obtained from all diffusion curves, Taylor concluded that three intermediate tin-mercury phases were present. These are referred to as the "first," "second," and "third," in order of their depth in the specimen.

The "third" phase appears to correspond to the gamma phase of existing diagrams. The "second" phase appears to correspond to the delta phase reported by Gayler.⁴ The "first" phase was previously unreported but is here tentatively designated epsilon.

Some work was also done on diffusion of mercury into silver. However, the results were unsatisfactory and inconclusive. With the immersion times and temperatures employed, the total depth of diffusion was much smaller than in the tin specimens. As a result, the section thickness needed to maintain accuracy was too large relative to the thickness of the mercury containing layer, to permit valid conclusions to be drawn. In addition, these specimens showed considerable local irregularity in depth of penetration, which could be explained by grain boundary diffusion. The samples, consequently, tended to contain mixtures of phases rather than single phases.

Winterlager and Schlosser¹³ showed that Hg diffuses into Sn mostly along the grain boundaries. They also determined that this diffusion was fairly rapid. In mercury diffusion in an 80 per cent gold-20 per cent tin alloy, an x-ray investigation showed only AuHg_2 and no compound of Sn-Hg.

Bykhouski¹⁴ found that a grayish film of Hg-Sn amalgam forms on an Sn sample during the mercury diffusion reaction. A change in electrical resistance was measured as the amalgam, which had a crystal lat-

tice different from Sn, was formed. Bykhouski also found that if the limiting link of the diffusion process is the entering of the diffusion zone, a linear law holds instead of a parabolic one. At low temperature, nevertheless, the parabolic law is obeyed. The activation energy of the velocity of Hg atoms in the diffusion zone was 10.2 kcal per mole. The activation energy of mercury diffusion was found to be 8.8 kcal per mole.

Sawatzky and Jaumat¹⁵ measured the diffusion of mercury vapor into silver over a temperature range of 650-900°C. They found $D_0 = .079 \text{ cm}^2$ per sec. and $Q = 38.1$ kcal per mole.

Influence of Ultrasonic Energy

Ultrasonic energy has been used for many purposes such as the mixing of liquids, the cleaning of small parts, nondestructive testing, welding, refining, crystallization, and grain size. However, very little work has been accomplished on the effect of ultrasonic vibrations on diffusion. Also, the little work that has been done was primarily in the diffusion of liquids into one another.

In 1950, Baumgartl¹⁶ showed that the diffusion of a 5 per cent NaCl solution through cellophane was increased by a factor of two under the influence of ultrasonics, whether the ultrasonic waves were in the direction of, or opposite the direction of the diffusion.

In 1951, however, Hagen, Rust, and Lewonsky¹⁷ measured the effect of ultrasonics on the osmosis of H_2O through a copper foil to CuSO_4 solution. Only a negligible effect was shown.

Dolgoplov, Fridman, and Karavev,¹⁸ nevertheless, showed a large increase in diffusion rate under the influence of ultrasonics. They

measured the diffusion rate of CuSO_4 in 5 per cent gelatin and the diffusion of $\text{Na}_2\text{S}_2\text{O}_3$ through swollen gelatin film, both with and without ultrasonics. In the first case the diffusion rate constant was increased from $.51 \times 10^{-4}$ to $.8 \times 10^{-4} \text{ cm}^2$ per sec. when ultrasonic energy was employed. In the second case the constant was increased from 2.6×10^{-4} to $11.7 \times 10^{-4} \text{ cm}^2$ per sec.

Rozanski¹⁹ did work in the solid state diffusion of carbon in steel, and showed that the diffusion rate was increased by ultrasonics, especially at the grain boundaries.

Other evidence of the increase in diffusion rates under ultrasonic energy is contained in Rhines' work in ultrasonic welding techniques and age hardening. Rhines²⁰ demonstrated that ultrasonic waves of a frequency of 15,000 cps can be used as a substitute for the thermal energy in bonding two pieces together at a weld. He also showed that the rate of aging in an age hardened material is increased by ultrasonic energy. It is his theory that the ultrasonic waves are absorbed by the atoms in the material so that their energy is increased. This in turn means that the diffusivity of the material is increased. He also postulated that the concentration of vacancies in a material is possibly increased under ultrasonic energy.

Gucer²¹ described an experimental setup for measuring and controlling the vibrational energy input into a liquid solid mixture. He also proposed a method of calculation of the energy transmitted through the interface between transmission bar and liquid sintering specimen and of the dynamic variables inside the specimen.

Parkhutik²² showed that ultrasonic vibrations decreased the artificial aging time of aluminum alloys by a factor of ten.

Meyer and others²³ found that the amount of nitrogen diffusion into steel, and its diffusion rate were increased by sonic treatment. However, no considerable increase in depth of penetration was discovered.

Matroux²⁴ showed that in the nitriding of steel, ultrasonic energy increased the hardness of the steel and also increased the strength and depth of the nitrided case.

One of the important experiments which prompted the work in this thesis was undertaken by Skinner and Mizera.²⁵ They investigated the effect of ultrasonics on the condensation of dental amalgam. They showed that the amalgams hardened faster when condensed with ultrasonic energy.

The ultrasonic energy was supplied by an ultrasonic generator which delivered the energy to a handpiece at 29,000 cps. The experimenters were able to vary the relative output energy of the generator from 50 to 90.

An alloy-mercury ratio of 5/8 was employed in the study. A mechanical amalgamator was used to triturate the amalgam. The mass was squeezed as free from mercury as possible and rapidly placed under the condensor point. The time of condensation was about 1/2 of that required by hand. The condensation pressure was much less than that employed in hand condensation. Intermittent application of pressure was found to be preferable to a continuous application.

Compressive tests were made after one hour and seven days. Cylindrical specimens 4 by 8 mm were employed. It was found that the compressive strengths of the amalgams after one hour were greatly in-

creased over that of amalgams condensed by hand. The strengths after seven days were about the same as those found with hand condensation. It was also found that the optimum output setting was 70 or 80 on a relative scale.

The values for dimensional change and flow observed with the ultrasonic technique were not significantly different from those obtained with manual condensation.

Because it was seen that various diffusion controlled processes were enhanced through the use of ultrasonic energy it was decided to investigate the effect of ultrasonics on the diffusion of mercury into Ag_3Sn . The diffusion will be allowed to occur at various temperatures both with and without the use of ultrasonics. In this way, the frequency factor (D_0) and the activation energy (Q) for diffusion can be determined for each case.

CHAPTER II

PROCEDURE

Materials

The Ag_3Sn used in this study was furnished by the L. D. Caulk Co. as cast cylindrical bars, one inch in diameter, and was of commercial purity. The composition was approximately 73.15 wt. per cent silver and 26.85 wt. per cent tin.

The mercury used was spectrographically pure and was the same type as that employed by the dentist.

Sample Preparation

The Ag_3Sn bars were annealed in vacuum at 400°C for 72 hours, after which the surface was turned off on a lathe until the diameter was $7/8$ of an inch. Specimens $1/16$ of an inch thick were cut from the bar. One side of the specimen was polished on water lubricated SiC papers, while the other side and edges were covered with micro-mask to insure that diffusion would occur in only one direction.

After the completion of each diffusion run, each sample was cut in half with a jeweler's saw. One half was mounted in cross-section in a one inch diameter mold in acrylic mounting material which would not increase the temperature of the specimen as it hardened. Small steel balls were mounted with the specimen to increase the hardness of the mount and to prevent rounding of the specimen edges. It was necessary to polish the specimens carefully so that smearing of the mercury would

not take place. The samples were first ground on 240 through 600 grit, water lubricated, SiC papers. They were then polished on a nylon cloth using one micron diamond dust with an extender of lapping oil. The samples were then placed in a dessicator to prevent any surface oxidation. In some instances, a vacuum was pulled on the sample at this point in order to bring any free mercury to the surface. The other half of each reacted sample was mounted in acrylic so that the surface could be analyzed. The mount was then placed on a lathe and the back was machined parallel to the other side so that the thickness could be measured.

Experimental Arrangement

For the portion of the experiment in which no ultrasonic energy was used, the apparatus consisted of a glass tube with a heating tape wrapped around it that was connected to a thermistor type temperature controller accurate to $\pm 1^\circ\text{C}$. Before the diffusion was allowed to begin, the thermistor probe was placed in the mercury, the required temperature was set by means of an external dial on the thermistor, and the temperature of the sample was allowed to come to equilibrium. Temperatures of 40, 60, 80 and 110°C were employed. The diffusion couple was set up by placing the sample, polished side down, atop mercury in the tube. Times of reaction ranged from about 40 minutes to 6 hours.

The experimental arrangement for the case in which ultrasonic energy was applied during diffusion is shown in Figure 5. The glass tube containing the mercury and Ag_3Sn specimen was placed at the focal point of a concave transducer utilizing water coupling and operated by a Brush

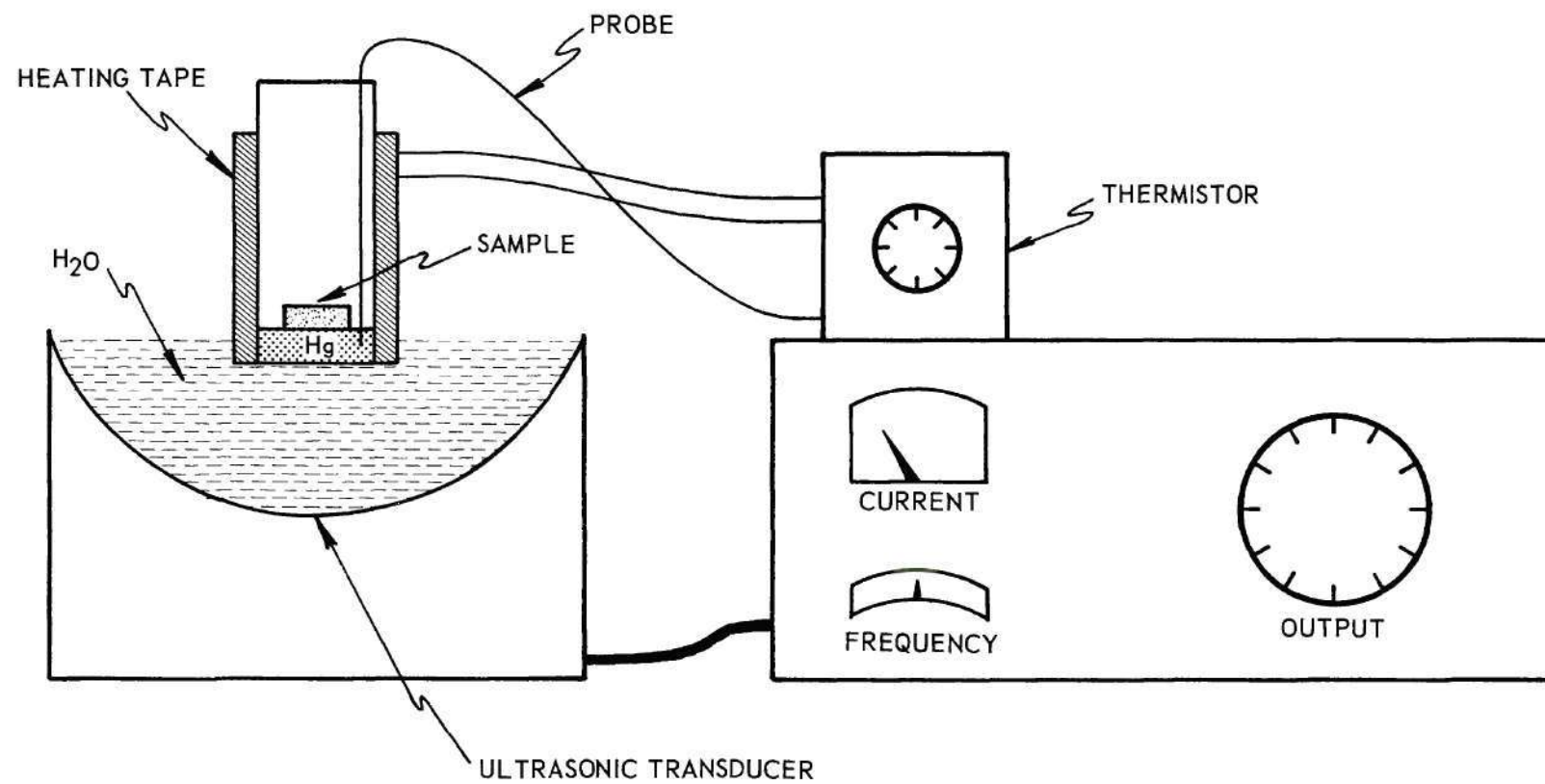


Figure 5. Experimental Arrangement for the Application of Ultrasonic Energy During Mercury Diffusion.

Co. ultrasonic generator. The frequency of the ultrasonic waves was adjusted so that resonance, seen by a peak in the output current, occurred. This frequency was about 400 Kcps. The amplitude of the waves was set by a dial graduated from 0 to 120 on the relative scale of the instrument to a reading of 90. The actual energy of the ultrasound reaching the specimen could not be accurately determined but was less than 1200 watts at the focal point and less than 250 watts in other places.

After removal from the mercury, the surfaces of the specimens were scraped as free from liquid mercury as possible. A thin film of mercury, nevertheless, still clung to the surface. The specimens were then placed in a mixture of acetone and dry ice to lower the temperature sufficiently to prevent further diffusion. The samples were kept in the dry ice mixture for three to four days.

Analysis

Analysis of the cross-sections was carried out using a Norelco Electron Probe Microanalyzer with a Beams scanner attachment. Diffusion profiles were obtained with the stage drive by driving the sample at 125 microns per minute through the electron beam. Studies of the surfaces of the mercury rich portions of the sections along with investigations of the mercury distribution were made using the Beams scanner attachment.

A mercury diffusion profile was obtained on the samples mounted as surfaces through the use of x-ray fluorescence analysis. A Phillips Spectrometer with a gas flow proportional counter was employed for this

purpose. A series of standards was run before the diffusion specimens in order to obtain a plot of the intensity (counts per sec) of mercury radiation versus mercury concentration (wt. per cent) in Ag_3Sn . The experimental curves were obtained by measuring the intensity (counts per second) of mercury radiation, polishing off part of the sample using No. 3 SiC paper, determining the new thickness of the mounted sample with a micrometer, and remeasuring the mercury concentration. In this way, a plot of mercury concentration versus depth of penetration was obtained. The diffusivity of mercury at the various temperatures was then calculated using the procedure outlined in Appendix A.

Various metallographic techniques were employed to investigate the unreacted Ag_3Sn , the reacted samples, and normal dental amalgams. These techniques included the use of both the light and electron microscope. The specimens for the electron microscope were prepared by both replicating and microtoming. The Leitz Ultramicrotome was employed in the latter case.

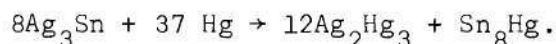
CHAPTER III

RESULTS

Incomplete Reaction of Amalgams

Electron-micrographs of the microtomed dental amalgams are shown in Figures 6 and 7. The presence of the large particles of Ag_3Sn indicates that the reactions between the mercury and the Ag_3Sn alloy particles never reached completion. This incomplete reaction might have one of two possible explanations: either there was insufficient mercury to react with the Ag_3Sn or the rate of diffusion is such that this free mercury does not come into contact with all of the Ag_3Sn .

Looking at the first possibility, we see that the chemical equation for total reaction of the Ag_3Sn is:



This equation indicates that 68 weight per cent mercury is the minimum necessary for complete reaction of the Ag_3Sn . However, when a mercury concentration as large as this was employed, particles of the Ag_3Sn could still be detected in the amalgam. Therefore, the second possibility, that the diffusion rate was too low to permit homogeneity, seems more plausible.

By calculating the diffusion rate of mercury in Ag_3Sn at room temperature, it is seen that it is unlikely that the diffusion of



Figure 6. Electron Micrograph of Microtomed Amalgam Showing Unreacted Ag_3Sn Particles X 42,000.



Figure 7. Electron Micrograph of Microtomed Amalgam Showing Unreacted Ag_3Sn Particles X 21,200.

mercury into the Ag_3Sn would allow 100 per cent reaction of the particles.

If the average particle diameter of a commercial alloy = 1.1×10^{-3} cm. Diffusivity (D) at 25 C = $.7 \times 10^{-10}$ cm^2/sec from the plot of D vs. $1/T$ for non-ultrasonic specimens in Figure 16.

In order to use Fick's Law, it is necessary to assume a surface concentration and a concentration at the center of the particles.

C_s is assumed to be 60 per cent which is the greatest surface concentration found during this work.

C , at the center of the particle, is assumed to be 17.5 per cent, the concentration of mercury in Sn_8Hg .

The time of diffusion is then calculated from the equation:

$$\frac{C - C_o}{C_s - C_o} = 1 - \text{erf} \frac{x}{\sqrt{2Dt}}$$

as shown in the sample calculations to be 129 min. During this period a great percentage of the reaction occurs, and the free mercury becomes tied up in the silver and tin compounds. This reduces the diffusion rate to such an extent that the particle core remains unreacted.

Grain Boundary Diffusion

One of the strip charts from a scan of the Electron Probe Micro-analyzer is shown in Figure 8. Although the curve obtained was not smooth enough to calculate the diffusivity, it nevertheless yielded useful information in regard to the mechanism of the diffusion.

Large peaks can be seen at regular intervals as the beam passes

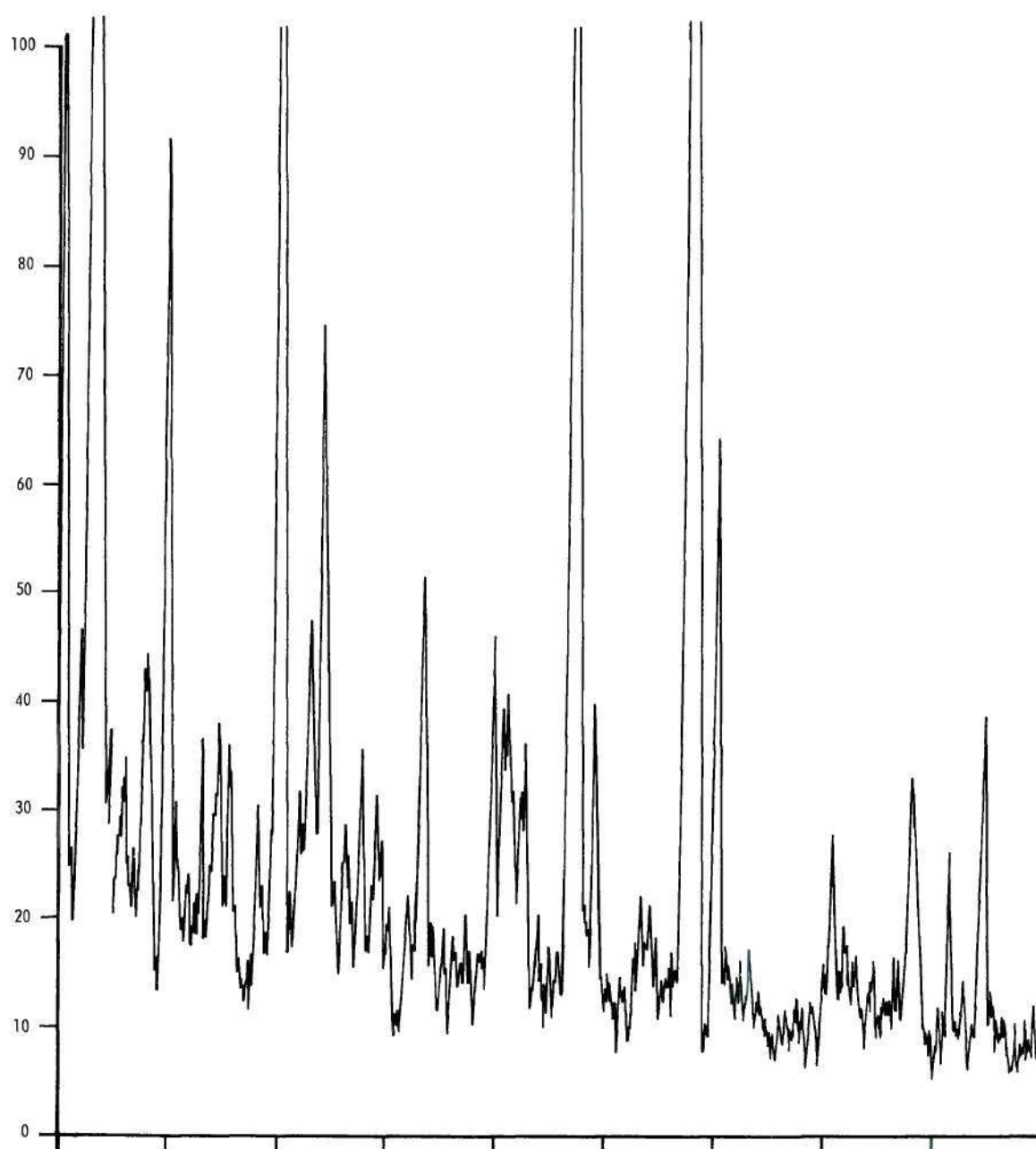


Figure 8. Actual Penetration Curve of Mercury Concentration in Ag_3Sn Obtained on Electron Probe Microanalyzer. Large Peaks Correspond to Grain Boundaries.

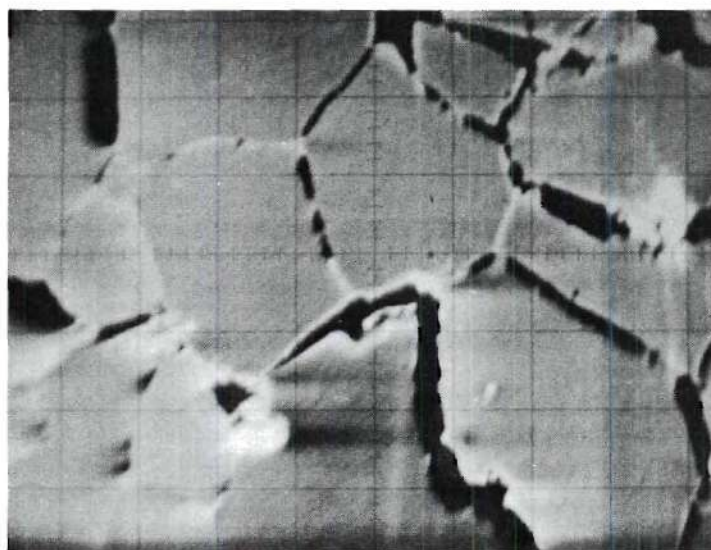


Figure 9. Surface of Cross-Section of Reacted Ag_3Sn Showing Grain Boundary Attack Made on Beam Scanner Attachment of Electron Probe Microanalyzer Using Sample Current X 400; Unetched.



Figure 10. Mercury Distribution in Cross-Section of Reacted Ag_3Sn Made on Beam Scanner Using L α Mercury Radiation X 400.

from one edge of the specimen to the other. These peaks occurred whenever the beam crossed a grain boundary in the Ag_3Sn . This is an indication that a large percentage of the diffused mercury is contained in the grain boundaries. This was not entirely unexpected since Günther and Jehmlich⁸ showed that the diffusion of mercury in tin occurred predominantly at the grain boundaries. This hypothesis of grain boundary diffusion is further substantiated in Figures 9 and 10. In Figure 9, which is a micrograph of the surface of the reacted Ag_3Sn taken on the Beams scanner attachment of the Electron Microprobe, the grains and grain boundaries are very thick and seem to contain some type of precipitate. Figure 10 was made on the Beams scanner using the characteristic x-rays of the $\text{L}\alpha_1$ peak of mercury. This was accomplished by setting the goniometer on the Electron Microprobe at the required angle and adjusting the Pulse Analysis Discriminator to receive only the x-rays of mercury. The white portions of the photograph are the areas of high mercury content. Since this picture was made over the same area as Figure 9, it is easily seen that the regions of high mercury concentration correspond to the grain boundaries in the Ag_3Sn .

Further evidence of this grain boundary diffusion is shown in Figures 11 and 12. These are photomicrographs of a reacted Ag_3Sn sample which has been etched with 2 per cent HF. They clearly show the grain boundaries in which the mercury diffusion has occurred. The grains which have been pulled out of the specimen indicate that the grain boundaries are much weaker than the grains themselves. This could be the explanation for the low strength of the dental amalgam during the period right after condensation. Also, if grain boundary diffusion pre-

dominates in the mercury- Ag_3Sn system, the grain size of the Ag_3Sn will have a large effect on the diffusion rate and therefore the reaction rates in dental amalgam. Both optical and electron micrographs, as given in Figures 13, 14 and 15, of the etched reacted specimen and an unreacted sample, reveal another interesting phenomenon. Some type of structure is seen which resembles a Widmanstätten Structure. Since the same type of structure was found in unreacted Ag_3Sn , it cannot be a result of reaction with mercury. If the silver concentration in the specimens was greater than the limits of the gamma phase in the silver-tin system, then the structure could be some beta phase which has formed along with the Ag_3Sn . Further investigation will be necessary before any conclusive statement can be made about the constitution of this structure or the reason for its existence.

Rate of Diffusion

The major portion of the work in this thesis is concerned with measuring the diffusion rate of mercury in Ag_3Sn .

The penetration curves, from which the diffusivities of mercury in Ag_3Sn were calculated, are given in Appendix B. Most of these plots are unusual in that they show an increase in mercury concentration with depth during the initial part of the curve. After a maximum concentration is reached, the plots resemble normal diffusion curves. In order to determine the exact reason for this phenomenon it will be necessary to investigate the diffusion of Ag and Sn as well as mercury. One explanation, however, is that the curve is due to the formation of the Sn-Hg phase (Sn_8Hg) on the surface of the reacted sample and a

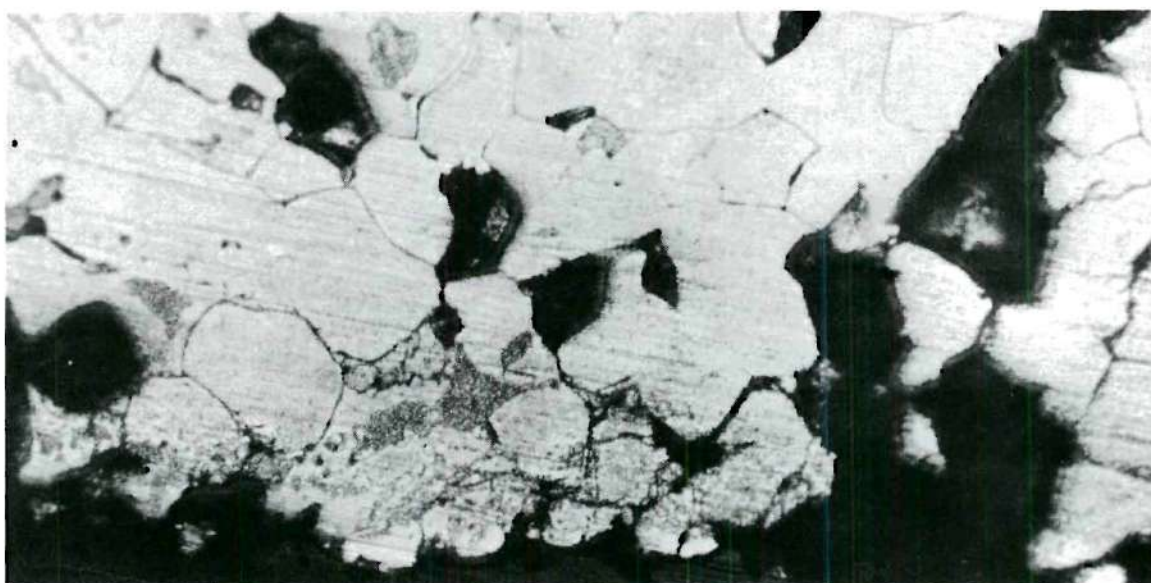


Figure 11. Cross-Section of Reacted Ag_3Sn Showing Mercury Attack at the Grain Boundaries X 225; 2% HF Etch.

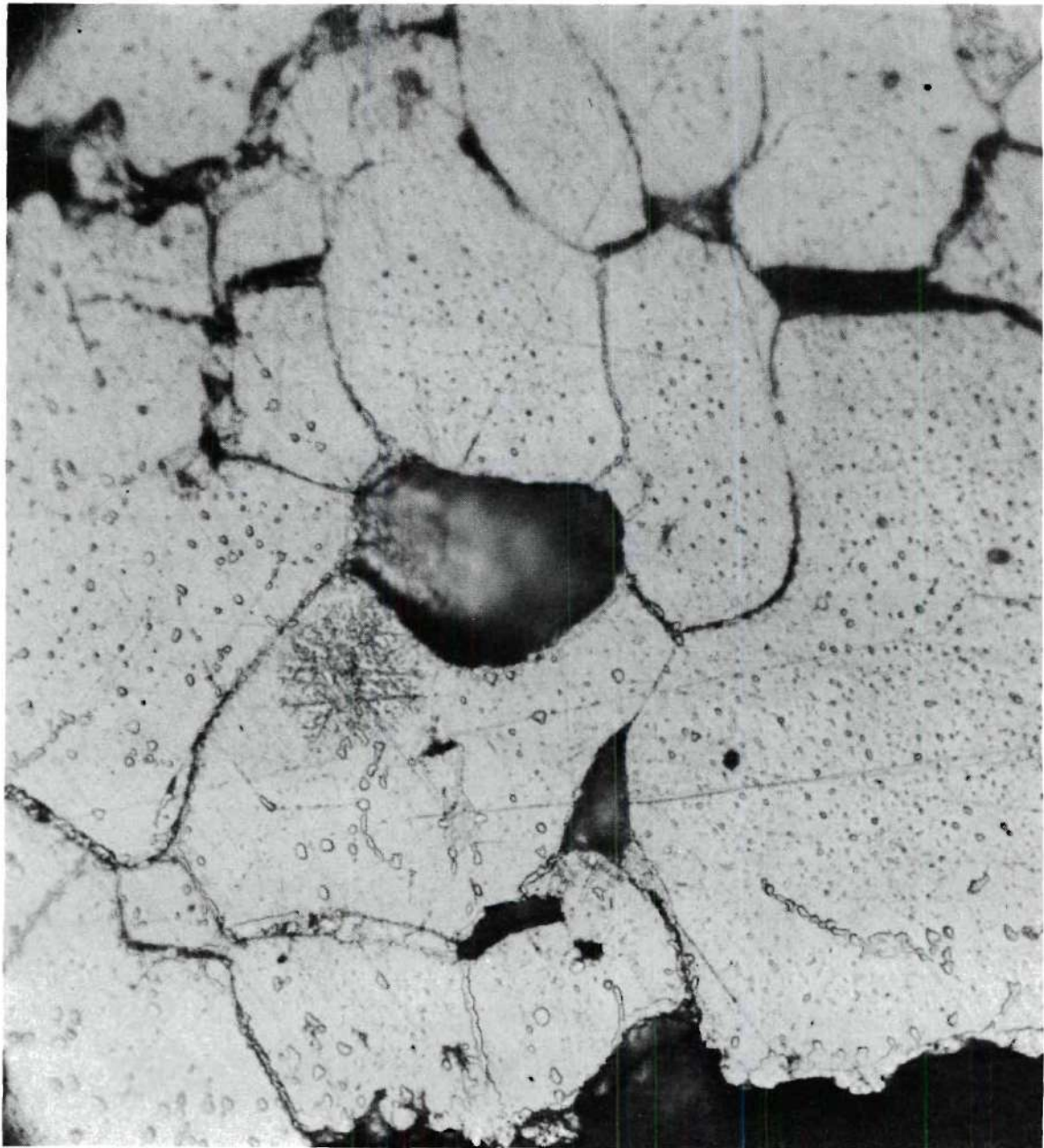


Figure 12. Cross-Section of Reacted Ag_3Sn Showing Mercury Attack at the Grain Boundries X 720; 2% HF Etch.

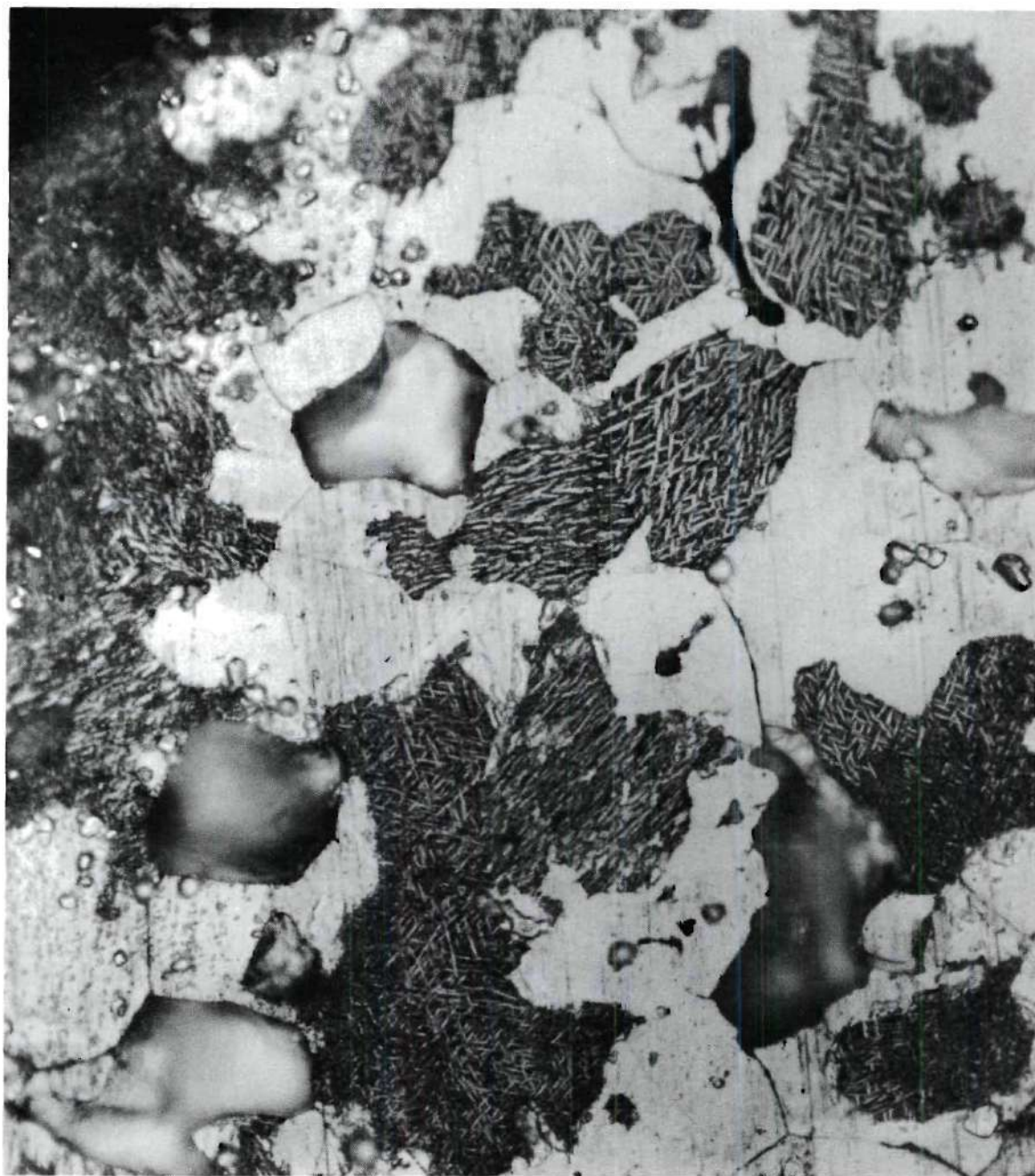


Figure 13. Reacted Cross-Section of Ag₃Sn Showing Widmanstätten Type Structure X 720; 2% HF Etch.



Figure 14. Unreacted Cross-Section of As Cast Ag_3Sn Showing Widmanstätten Type Structure X 720; 2% HF Etch.

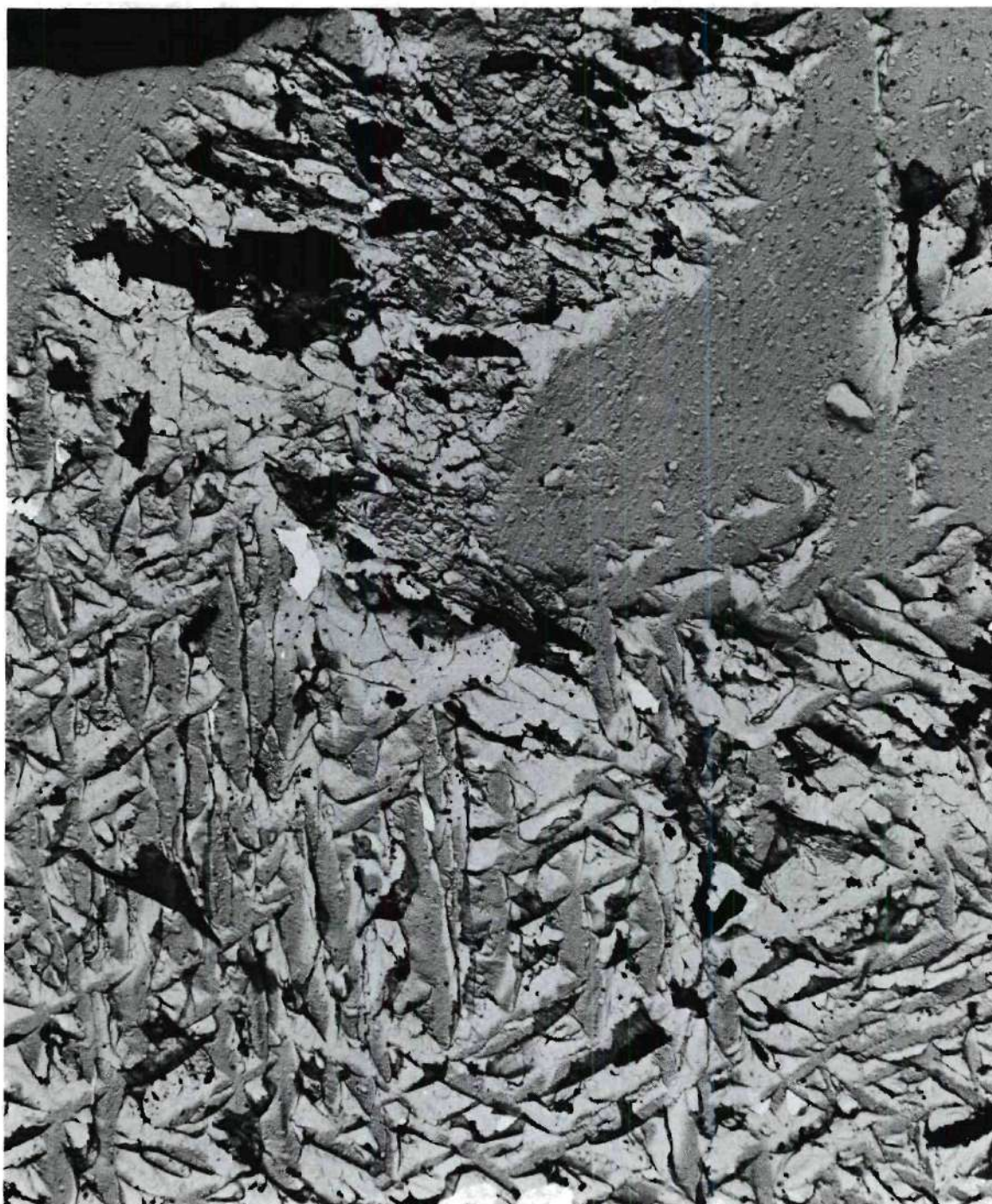


Figure 15. Electron Micrograph of Unreacted Annealed Ag_3Sn Showing Widmanstätten Type Structure X 3,800; 2% HF Etch.

Table 1. Diffusivities of Both Non-Ultrasonic and Ultrasonically Activated Samples

<u>Non-Ultrasonic</u>		
D (cm ² /sec)	Temperature (° C)	Time of Reaction (Hours)
.83 x 10 ⁻¹⁰	40	5.45
1.28 x 10 ⁻¹⁰	40	3.18
1.36 x 10 ⁻¹⁰	40	2.00
1.70 x 10 ⁻¹⁰	60	1.94
1.68 x 10 ⁻¹⁰	60	3.63
1.85 x 10 ⁻¹⁰	80	5.92
3.24 x 10 ⁻¹⁰	80	2.00
4.13 x 10 ⁻¹⁰	110	2.08
6.02 x 10 ⁻¹⁰	110	5.27

<u>Ultrasonic</u>		
D(cm ² /sec)	Temperature (° C)	Time of Reaction (Hours)
9.76 x 10 ⁻¹⁰	40	1.57
3.24 x 10 ⁻¹⁰	40	1.65
12.70 x 10 ⁻¹⁰	40	.67
31.10 x 10 ⁻¹⁰	60	.83
4.05 x 10 ⁻¹⁰	60	.75
22.8 x 10 ⁻¹⁰	60	.78
23.60 x 10 ⁻¹⁰	80	1.23
7.89 x 10 ⁻¹⁰	80	1.43
11.10 x 10 ⁻¹⁰	80	.67

solution of Hg in Ag below this. Evidence to support this theory has been shown by the fact that the x-ray diffraction peak of the Sn_8Hg is much larger right on the surface than just below it.

The diffusivities of mercury in Ag_3Sn were calculated as explained in Appendix A and are listed in Table 1. The activation energies (Q) and the frequency factors (D_0) for both non-ultrasonic and ultrasonically activated samples are given in Table 2.

Table 2. Activation Energies and Frequency Factors for Both Ultrasonic and Non-Ultrasonic Samples

	Q cal/mole	D_0 cm^2/sec
Non-Ultrasonic	5150	4.22×10^{-7}
Ultrasonic (Unfocused)	7410	1.45×10^{-5}
Ultrasonic (Focused)	7580	4.36×10^{-4}

Figure 16 shows the plot of $\log D$ versus $1/T$. The lower curve represents the data from the non-ultrasonic specimens. The upper and middle curves represent samples which were in the focal point of the ultrasonic generator and those which are considered to have been outside this focal point. It is easily seen that those samples that were in the focal point have a much greater diffusivity at any given temperature than those which had no ultrasonic energy or those which were not in the focal point during the application of ultrasonic energy. This indicates that the

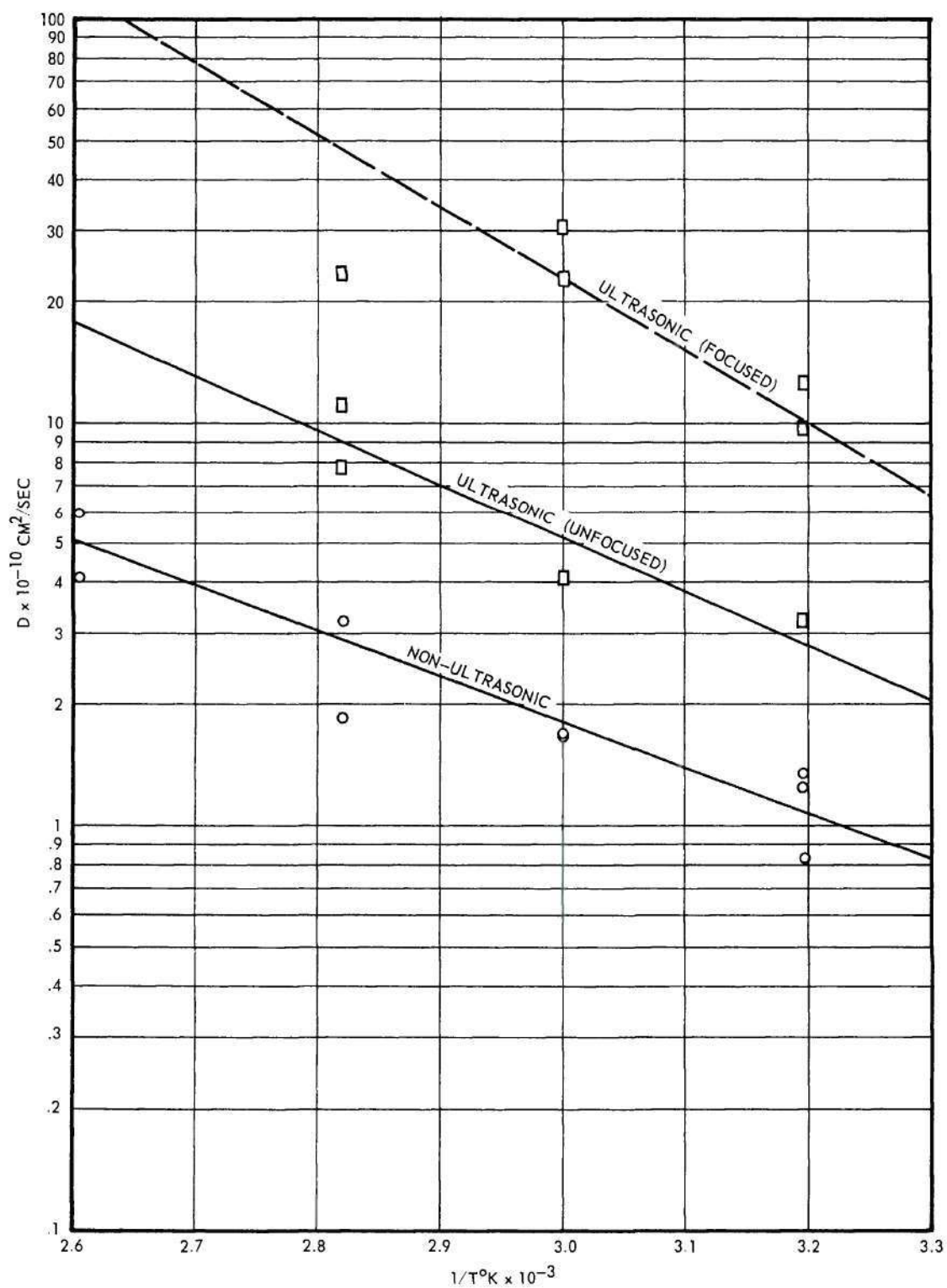


Figure 16. An Arrhenius Plot of Log Diffusivity Versus $1/T$ for Non-Ultrasonic and Ultrasonically Activated Samples.

ultrasonic energy increased the diffusivity.

Reed-Hill²⁶ gives the equation for diffusion by a vacancy mechanism in a pure metal as:

$$D = \sigma \alpha^2 Z \gamma e^{(\Delta S_m + \Delta S_f)/R} e^{-(Q_m + Q_f)/RT}$$

where $D_0 = \sigma \alpha^2 Z \gamma e^{(\Delta S_m + \Delta S_f)/R}$

$$Q = Q_f + Q_m$$

so that we have $D = D_0 e^{-Q/RT}$ which is the equation of the straight lines in Figure 16. Defining the individual terms in the equation:

σ = Dimensionless constant depending on the structure.

α = Lattice constant.

Z = Lattice coordination number.

γ = Lattice vibration frequency.

ΔS_m = Entropy change per mole resulting from the strain of the lattice during the jumps.

ΔS_f = Increase in entropy of the lattice due to the introduction of a mole of vacancies.

$e^{-Q_m/RT}$ = Probability that an atom will have sufficient energy to make a jump.

$e^{-Q_f/RT}$ = Concentration of vacancies in the lattice.

Some of these factors are increased by the ultrasonic energy, while others are unaffected.

Since σ , α , and Z are dependent only on the structure of the material, they are necessarily unchanged during ultrasonic diffusion.

γ , the lattice vibration frequency, is of the order of 10^{12} cycles

per second at room temperature. Because the frequency of the ultrasonic waves was 4×10^5 cycles per sec, it is unlikely that the ultrasonic waves affected the vibrational frequency of the atoms to any great extent. At lower temperatures and at higher ultrasonic frequencies, there is more likelihood of resonance absorption by the atoms in the lattice.

Rhines²⁰ suggests that ultrasonic energy increased the vacancy concentration in a metal. The increase, however, would have to be quite marked to be large enough to increase the diffusivity. Increase in the terms in the equation which depend on the vacancy concentration (ΔS_f and $e^{-Q_f/RT}$) may therefore be of minor importance in interpretation of the effect of ultrasonic energy on diffusion. Also, an increase in $e^{-Q_f/RT}$ would mean a decrease in Q_f . This is not shown in the results.

The remaining terms are those involving the probability of an atom having enough energy to make a jump and the increase in entropy due to strain in the lattice during a jump. Both of these could be increased by ultrasonic waves. The added energy should increase the amplitude of the atomic vibrations, thereby increasing the probability that an atom will have sufficient energy to make a jump. This would mean that Q_m would have to decrease. Although this is not shown in this work, the increase in Q during ultrasonic diffusion is fairly small, and could be due to experimental error. By adding additional strains to the lattice, the ultrasonic vibrations should also increase the entropy of the material.

The results seem to show that the increase in the diffusivity during ultrasonic diffusion is due primarily to an increase in D_0 . This indicates an appreciable increase in the entropy term, ΔS_m . The ultra-

sonic energy appears to have a relatively minor effect on the activation energy, Q .

Another possible explanation for the increase in the diffusion of mercury in Ag_3Sn under the influence of ultrasonic energy is that the action of the ultrasonic waves in the mercury continually creates a fresh surface on the Ag_3Sn by removing the reaction product.

Error Analysis

The principal error incurred in the calculation of the diffusivities of mercury occurred in the measurement of the depth of penetrations. The greatest degree of accuracy that can be obtained with the micrometer is 10^{-5} inches = 2.54×10^{-5} cm. However, this is not the only error present in this measurement. Since it was impossible to make both sides of the mount exactly parallel, the thickness of the mount varied from point to point. Although an attempt was made to take each measurement at the same place on the sample, some error was bound to occur.

Further error in the calculation of the diffusivity occurred in plotting the curves of per cent mercury versus depth of penetration, because it was necessary to draw the best curve possible through the experimental points. Examples of Fick's law curves drawn from the average diffusivities of the samples are given with the experimental curves in Figures 31 and 35. These show that although the experimental curves do not follow the theoretical, they are close enough so that little error occurs.

The results of the ultrasonically activated samples are further defective due to two reasons. One was the difficulty of placing the

sample directly in the focal point of the ultrasonic waves. The other was the fact that at a temperature of 80°C, the water around the sample tube is evaporating at such a rate that the action of the ultrasonic waves is interferred with. This tends to lower the values of the diffusivity at this temperature.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

From this research work it was concluded that:

1. Reaction of all the Ag_3Sn during amalgamation is impossible due to the low diffusion rate of mercury.
2. Diffusion of mercury into Ag_3Sn occurs primarily at the grain boundaries.
3. Ultrasonic energy greatly increases the diffusion rate of mercury in Ag_3Sn .
4. A needle-like microstructure resembling a Widmanstätten structure was found in both unreacted and reacted Ag_3Sn .

Recommendations for Further Research

It is recommended that:

1. An investigation of ternary diffusion in the Ag-Sn-Hg system be carried out.
2. The initial portion of the mercury concentration versus depth of penetration plot be studied in order to determine the reason for the increase in concentration with depth.
3. A study be carried out to determine the actual mechanism by which ultrasonic energy increases the diffusivity.
4. Further investigation of the phases in the dental amalgam be carried out using the Electron Probe Microanalyzer.

5. The constitution of the needle-like structure be studied.
6. The effect of the power and frequency of the ultrasonic waves on diffusion be investigated.

APPENDICES

APPENDIX A

SAMPLE CALCULATIONS

The diffusivity of mercury in Ag_3Sn was calculated from the per cent Hg vs. depth of penetration curves at each temperature using Grube's method.²⁷

In order to calculate the diffusivities using this method, it was necessary to assume that the diffusion was governed by Fick's Law. This could be done only if the diffusion was unaffected by the reaction between the mercury and the Ag_3Sn and that no intermediate carry rounds were formed during diffusion. It was also assumed that the diffusivity was independent of concentration.

It was first necessary to assume a starting point and a surface concentration in each curve. It was decided that the initial point (0 depth) would be in most cases the point at which the normal penetration curve crossed the line increasing Hg concentration. In cases where no increase in mercury concentration with depth was observed, the original surface was taken to be the Zero point. The mercury concentration at these points were taken to be C_s and were assumed constant throughout the run.

Fick's second law states:

$$\frac{C - C_o}{C_s - C_o} = 1 - \exp \frac{-x^2}{4Dt}$$

where C = concentration at desired depth.

C_s = surface concentration.

C_o = initial Hg concentration in sample.

x = depth of penetration.

D = diffusivity of Hg.

t = time of run.

For Sample 11 80°C

$$C_o = 0$$

$$C_s = 42.0\%$$

$$\text{Time of run} = 7200 \text{ seconds}$$

(1) At $x = 1 \times 10^{-3}$ cm.,

$$\frac{C}{C_s} = \frac{25.6}{42.0} = .61$$

28

Interpolating from Table 18-1 in Darken and Gurry

$$\frac{x}{Dt} = .7226$$

$$\begin{aligned} D &= \frac{x^2}{(.7226)^2 t} \\ &= \frac{1 \times 10^{-6} \text{ cm}^2}{.522 \times .72 \times 10^4 \text{ sec.}} \\ &= 2.91 \times 10^{-10} \text{ cm}^2/\text{sec.} \end{aligned}$$

(2) At $x = 2 \times 10^{-3}$ cm.,

$$D = 3.11 \times 10^{-10} \text{ cm}^2/\text{sec.}$$

(3) At $x = 4 \times 10^{-3}$ cm.,

$$D = 3.70 \times 10^{-10} \text{ cm}^2/\text{sec.}$$

These values were averaged to give

$$D = 3.24 \times 10^{-10} \text{ cm}^2/\text{sec.}$$

Log D was plotted against $1/T$ ok. This gave a straight line, whose slope is $-\frac{Q}{2.3R}$, and whose intercept at $1/T = 0$ is D_0 .

APPENDIX B

EXPERIMENTAL RESULTS

Table B-1. Results Obtained from Hg Conc vs. Depth of Penetration Curves for all Diffusion Runs

	Depth of Penetration - $\text{cm} \times 10^{-3}$	Hg Conc - Wt %
<u>Sample 1</u>		
Non-Ultrasonic	1	18.5
40°C	2	10.0
5.45 Hr.	4	4.5
$C_s = 46.6\%$		
<u>Sample 2</u>		
Non-Ultrasonic	1	17.0
60°C	2	8.35
1.94 Hr.	4	0.50
$C_s = 37.0\%$		
<u>Sample 3</u>		
Non-Ultrasonic	1	32.5
60°C	2	18.7
3.63 Hr.	4	3.20
$C_s = 52.5\%$		
<u>Sample 4</u>		
Non-Ultrasonic	1	29.5

Table B-1. Results Obtained from Hg Conc vs. Depth of Penetration Curves for all Diffusion Runs
(Continued)

	Depth of Penetration - $\text{cm} \times 10^{-3}$	Hg Conc - Wt %
<u>Sample 4 Continued</u>		
80° C	2	19.5
5.92 Hr.	4	9.02
$C_s = 42.5\%$		
<u>Sample 5</u>		
Ultrasonic	1	22.1
40° C	2	15.5
1.57 Hr.	4	5.15
$C_s = 28.3\%$		
<u>Sample 6</u>		
Ultrasonic	1	22.0
40° C	2	12.5
1.65 Hr.	4	2.00
$C_s = 36.5\%$		
<u>Sample 7</u>		
Non-Ultrasonic	1	22.0
40° C	2	12.2
3.18 Hr.	4	4.30
$C_s = 58.5\%$		

Table B-1. Results Obtained from Hg Conc vs. Depth of Penetration Curves for all Diffusion Runs
(Continued)

	Depth of Penetration - $\text{cm} \times 10^{-3}$	Hg Conc - Wt %
<u>Sample 8</u>		
Non-Ultrasonic	1	30.5
110° C	2	20.0
2.08 Hr.	4	6.18
$C_s = 46.4\%$		
<u>Sample 9</u>		
Non-Ultrasonic	1	31.0
110° C	2	25.2
5.27 Hr.	4	16.7
$C_s = 38.7\%$		
<u>Sample 10</u>		
Non-Ultrasonic	1	6.00
40° C	2	2.09
2.00 Hr.	4	.60
$C_s = 19.0\%$		
<u>Sample 11</u>		
Non-Ultrasonic	1	25.6
80° C	2	14.5
2.00 Hr.	4	3.50
$C_s = 42.0\%$		

Table B-1. Results Obtained from Hg Conc vs. Depth of Penetration Curves for all Diffusion Runs
(Continued)

	Depth of Penetration - $\text{cm} \times 10^{-3}$	Hg Conc - Wt %
<u>Sample 12</u>		
Ultrasonic	1	20.0
60° C	2	14.5
.78 Hr.	4	5.10
$C_s = 25.0\%$		
<u>Sample 13</u>		
Ultrasonic	1	20.2
60° C	2	16.5
.83 Hr.	4	8.14
$C_s = 24.5\%$		
<u>Sample 14</u>		
Ultrasonic	1	21.5
80° C	2	17.5
1.23 Hr.	4	9.02
$C_s = 26.0\%$		
<u>Sample 15</u>		
Ultrasonic	1	30.5
80° C	2	22.0
1.43 Hr.	4	10.5
$C_s = 45.5\%$		

Table B-1. Results Obtained from Hg Conc vs. Depth of Penetration Curves for all Diffusion Runs
(Continued)

Depth of Penetration - $\text{cm} \times 10^{-3}$		Hg Conc - Wt %
<u>Sample 16</u>		
Ultrasonic	1	31.0
40° C	2	19.4
.67 Hr.	4	1.50
$C_s = 43.0\%$		
<u>Sample 17</u>		
Ultrasonic	1	15.0
60° C	2	6.40
.75 Hr.	3	1.00
$C_s = 30.5\%$		
<u>Sample 18</u>		
Ultrasonic	1	14.4
80° C	2	9.21
.67 Hr.	3	4.41
$C_s = 18.9\%$		

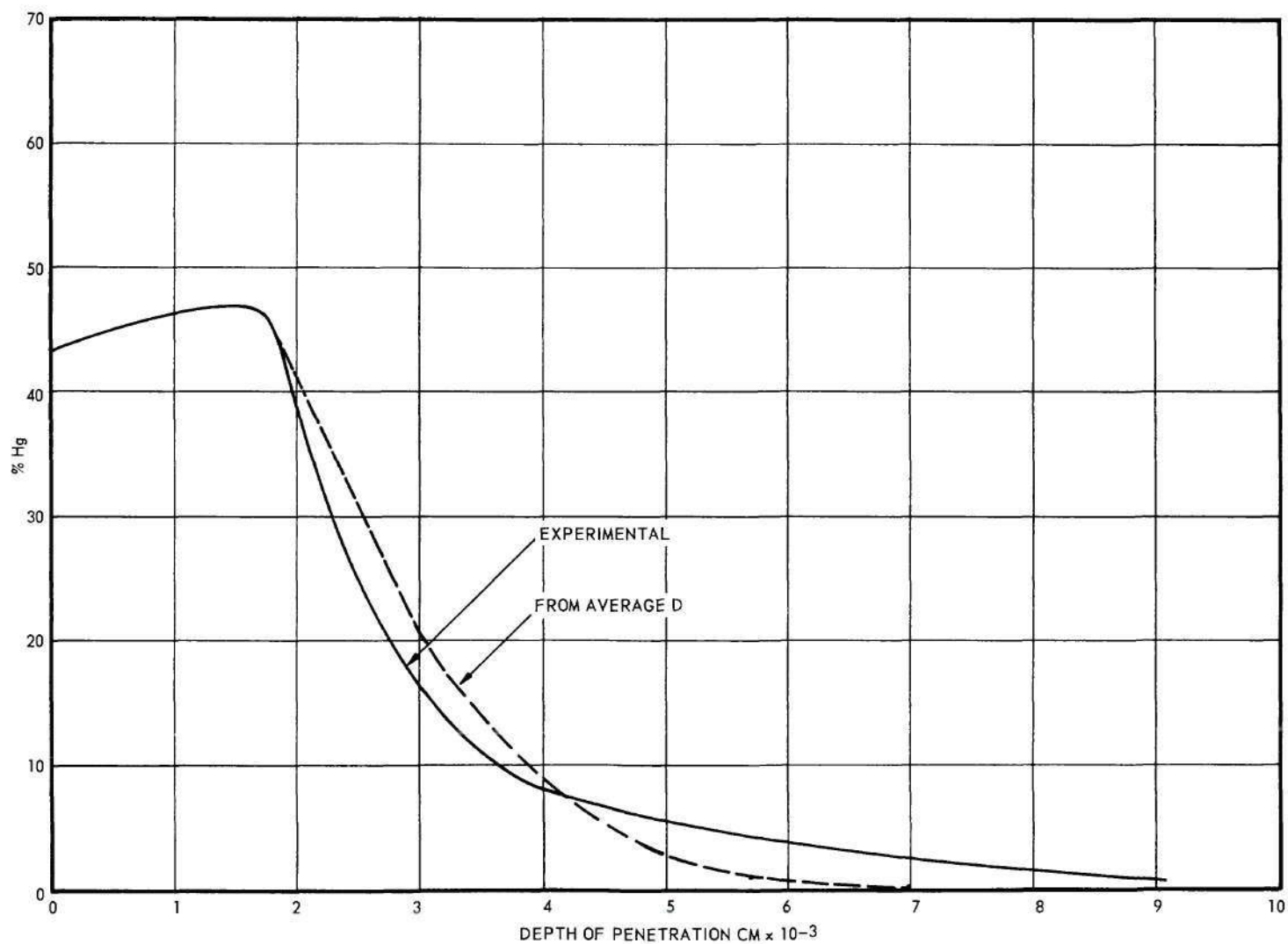


Figure B-1. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 5.45 Hours at 40°C.

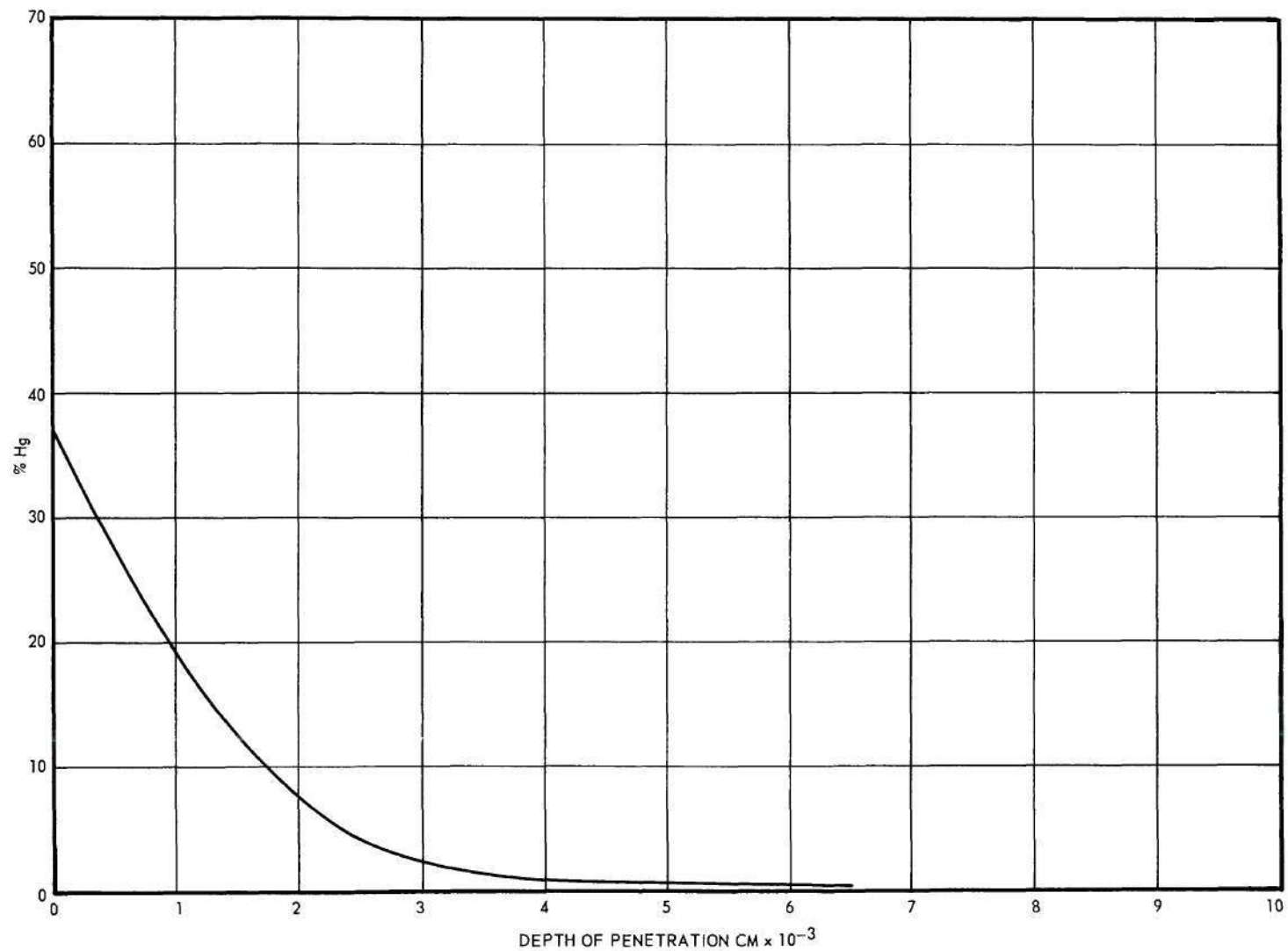


Figure B-2. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non/Ultrasonic Environment for 1.94 Hours at 60°C.

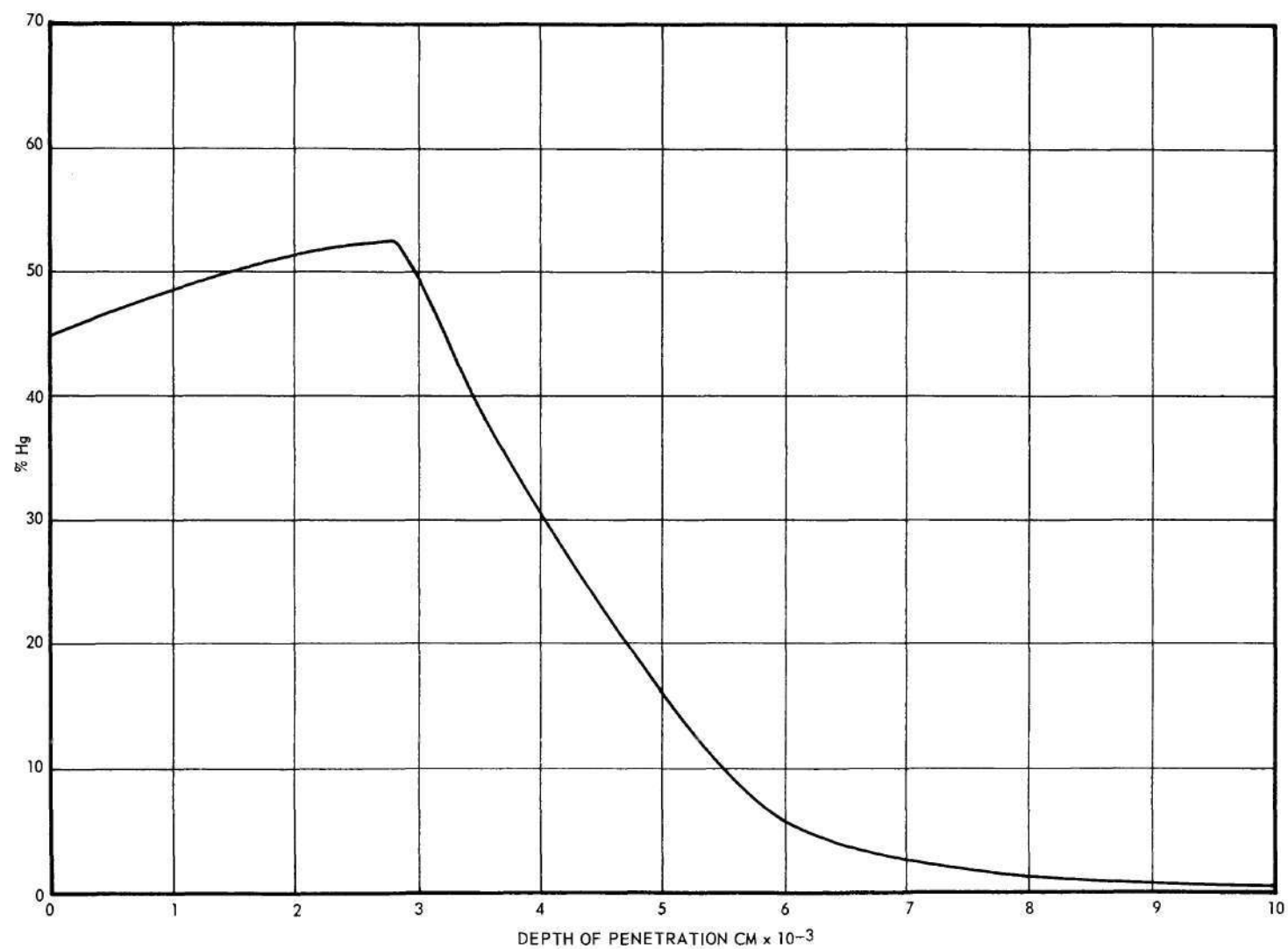


Figure B-3. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 3.63 Hours at 60°C.

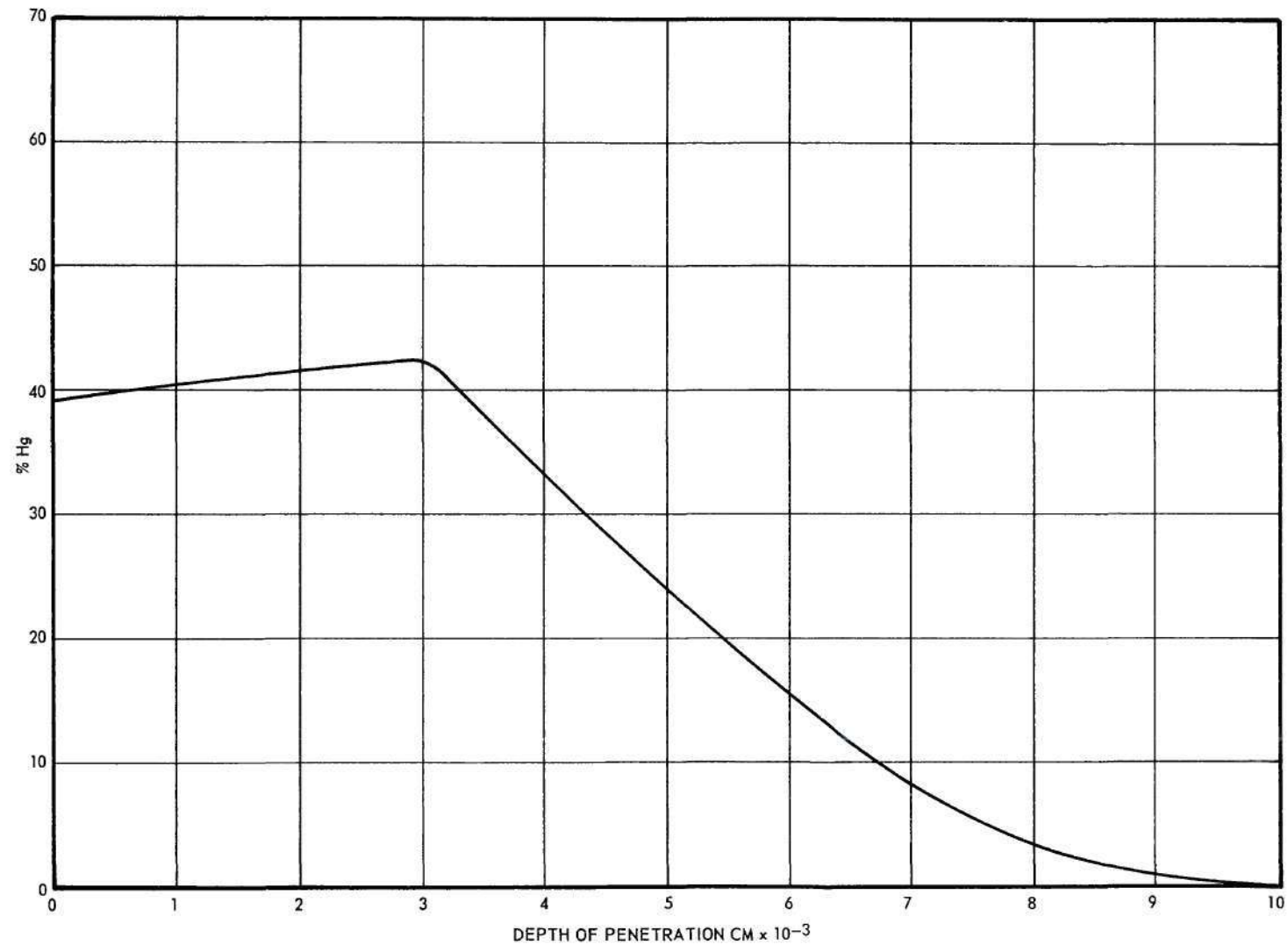


Figure B-4. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 2.00 Hours at 80°C.

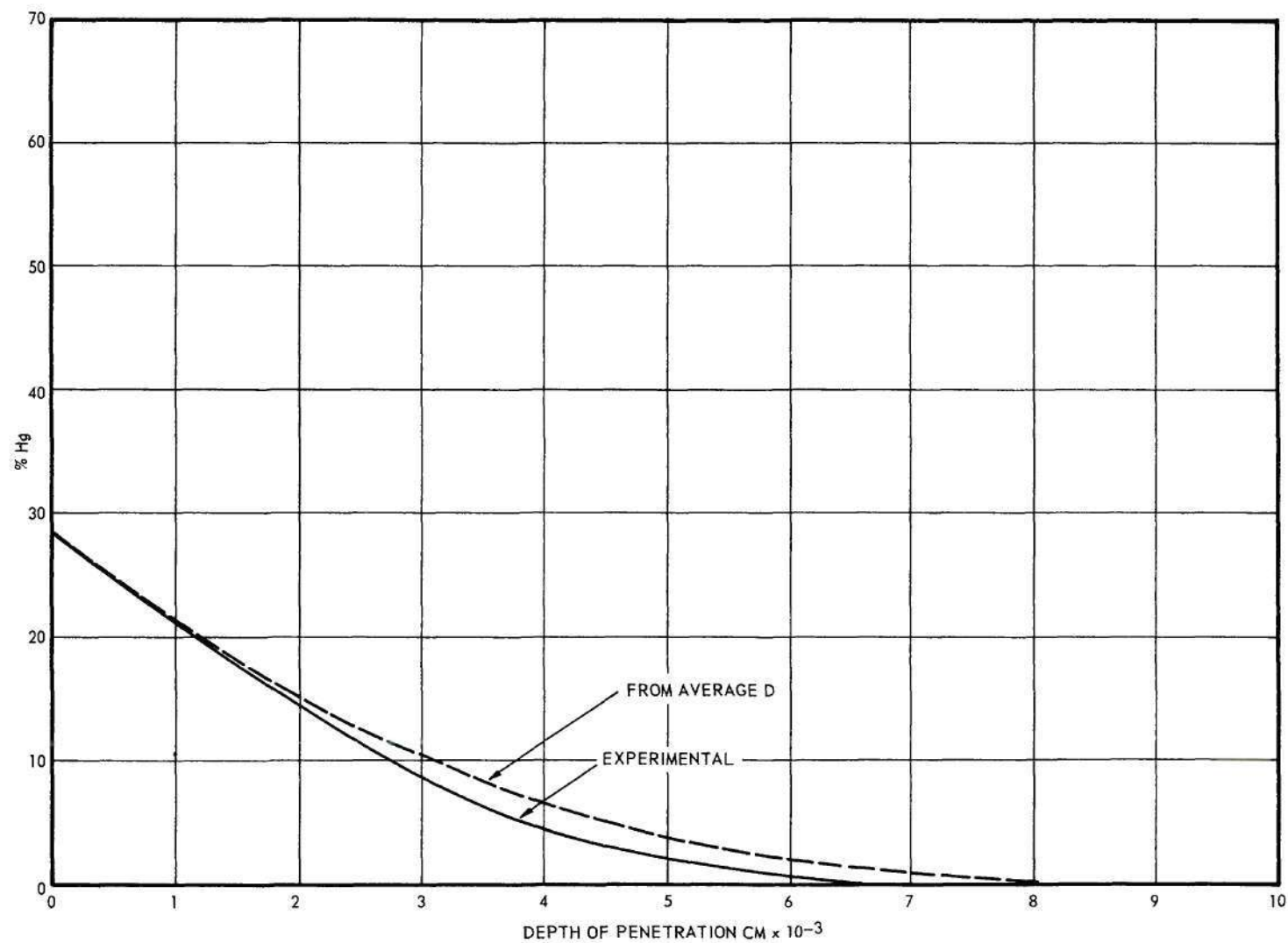


Figure B-5. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for 1.57 Hours at 40°C.

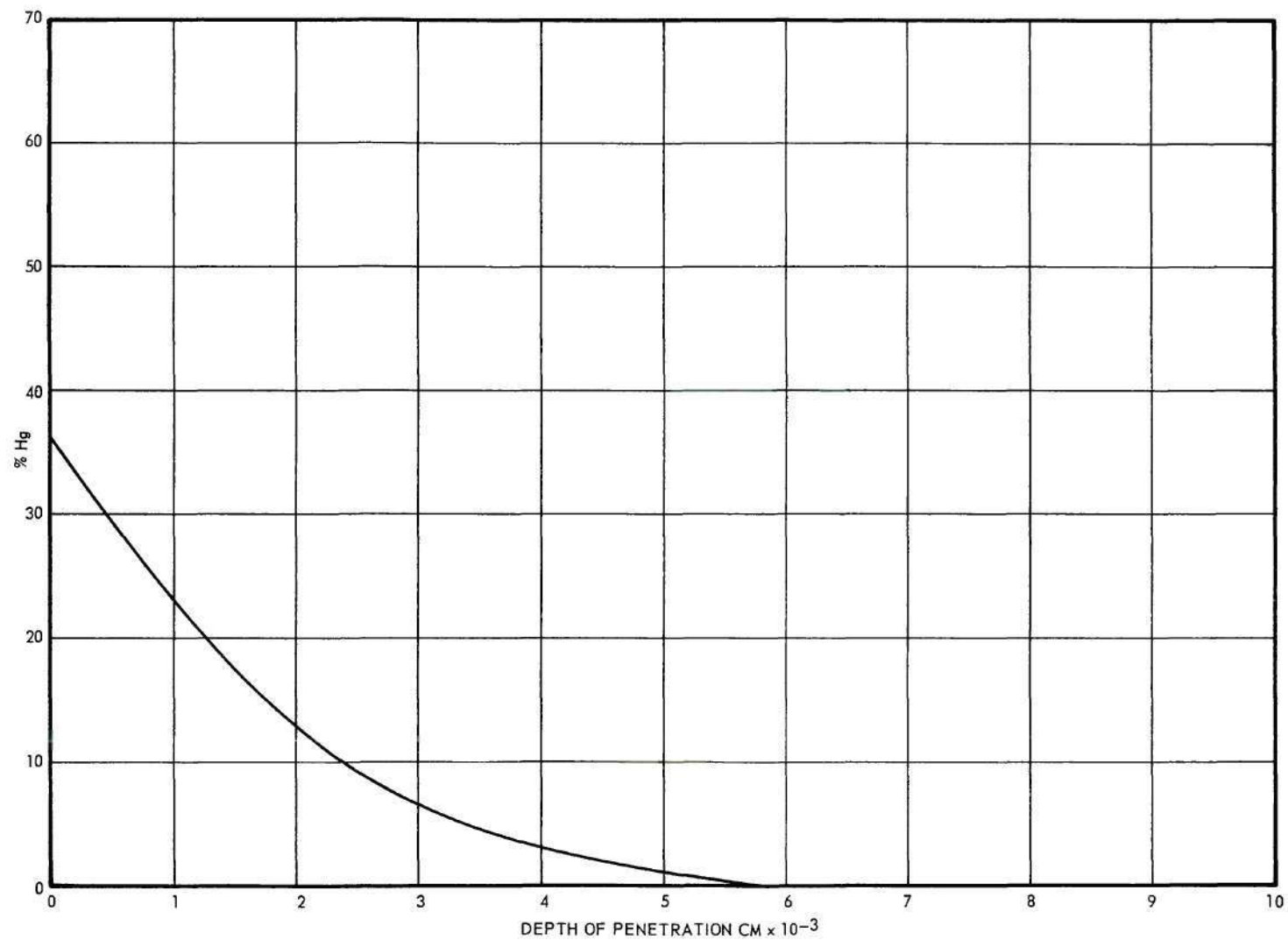


Figure B-6. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for 1.65 Hours at 40°C.

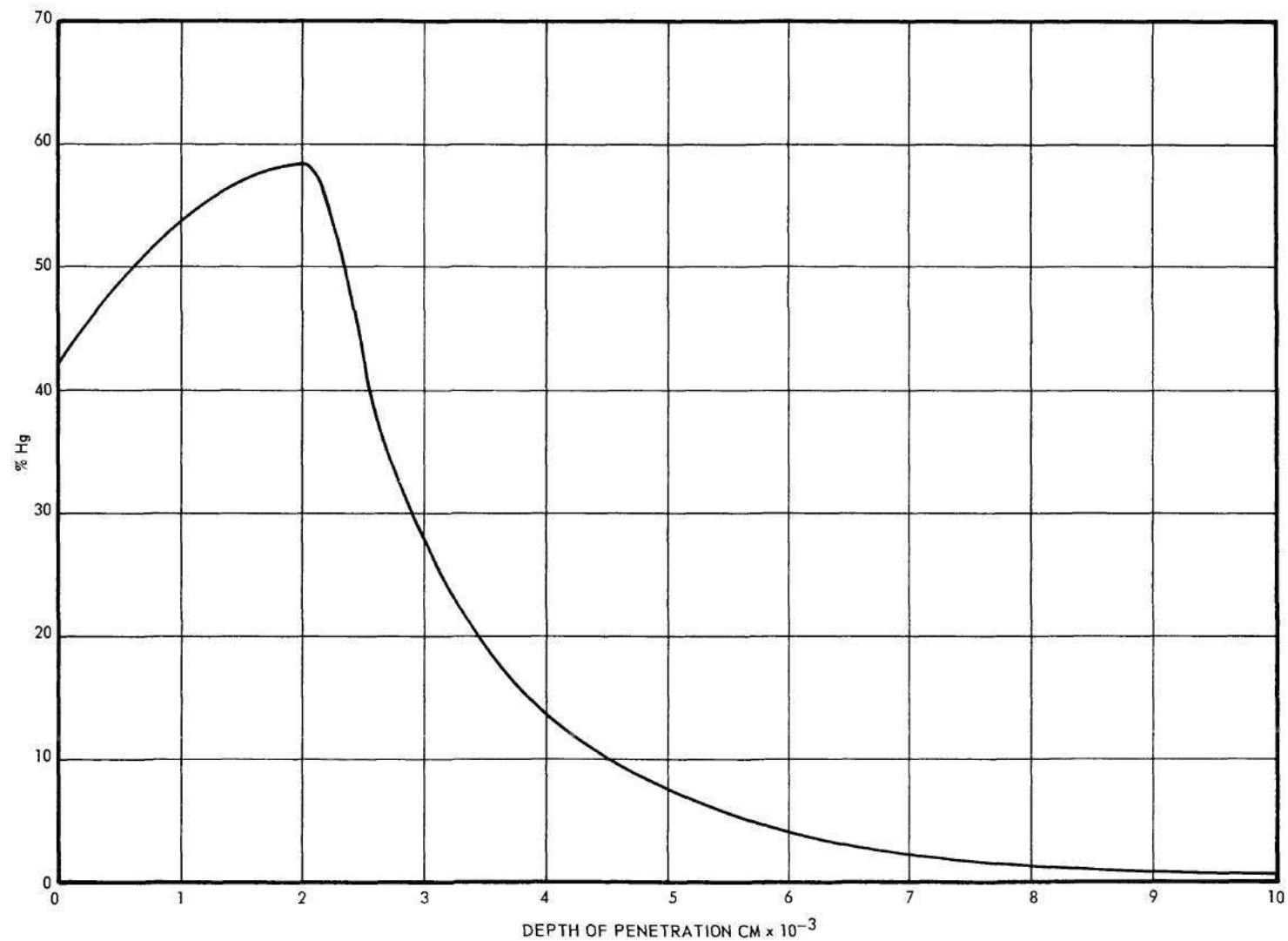


Figure B-7. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 3.18 Hours at 40°C.

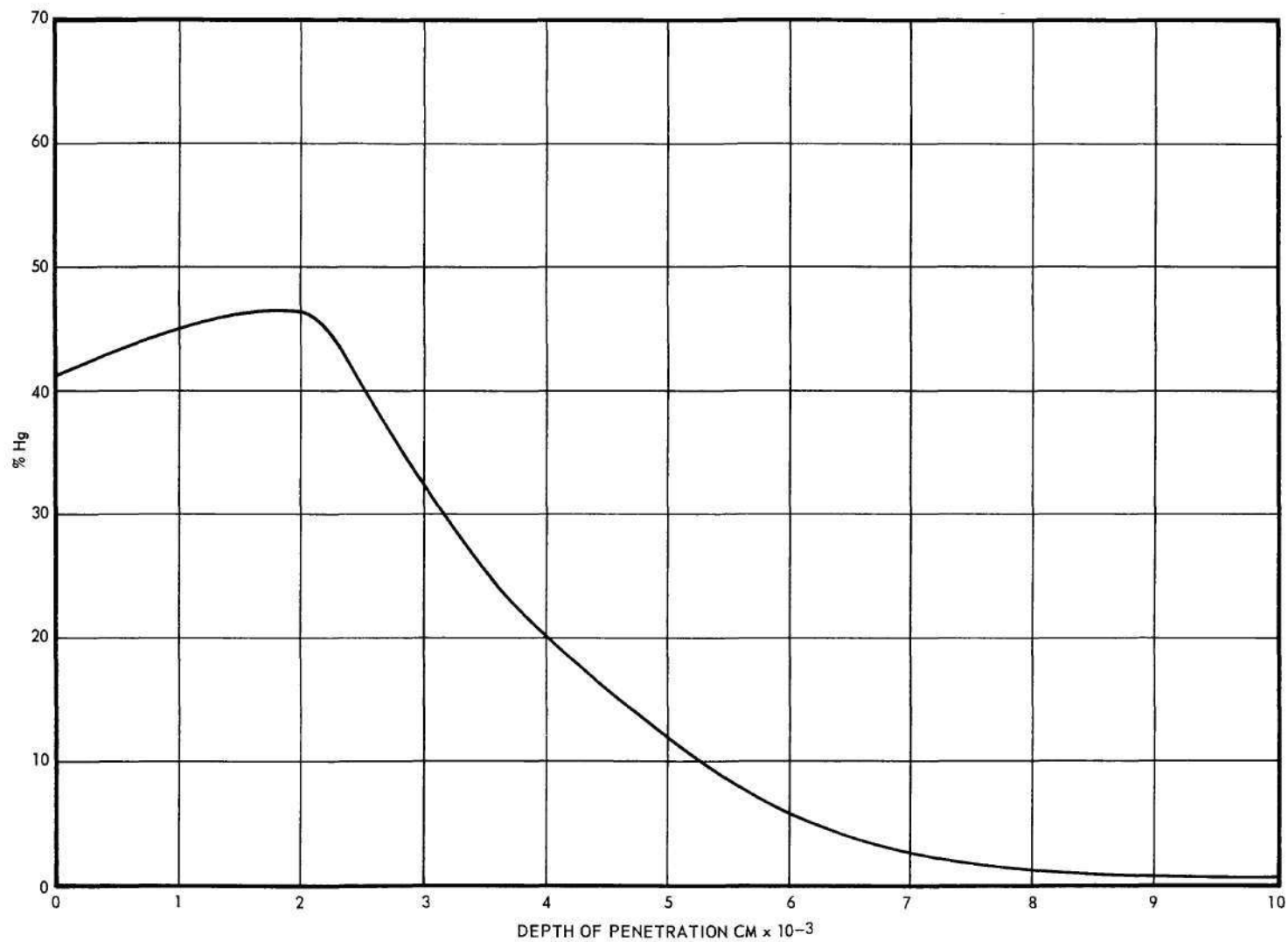


Figure B-8. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 2.08 Hours at 110°C.

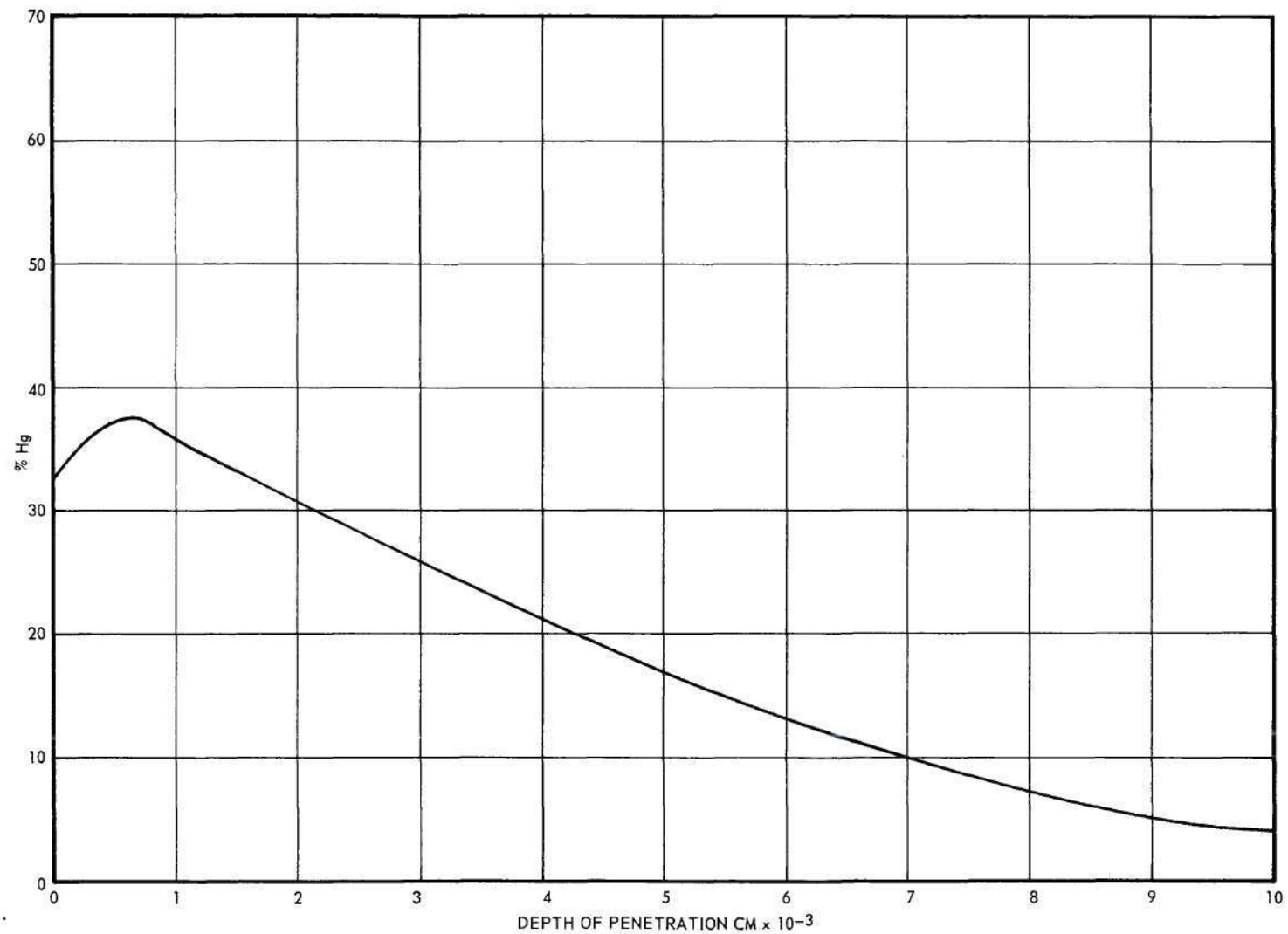


Figure B-9. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 5.27 Hours at 110°C.

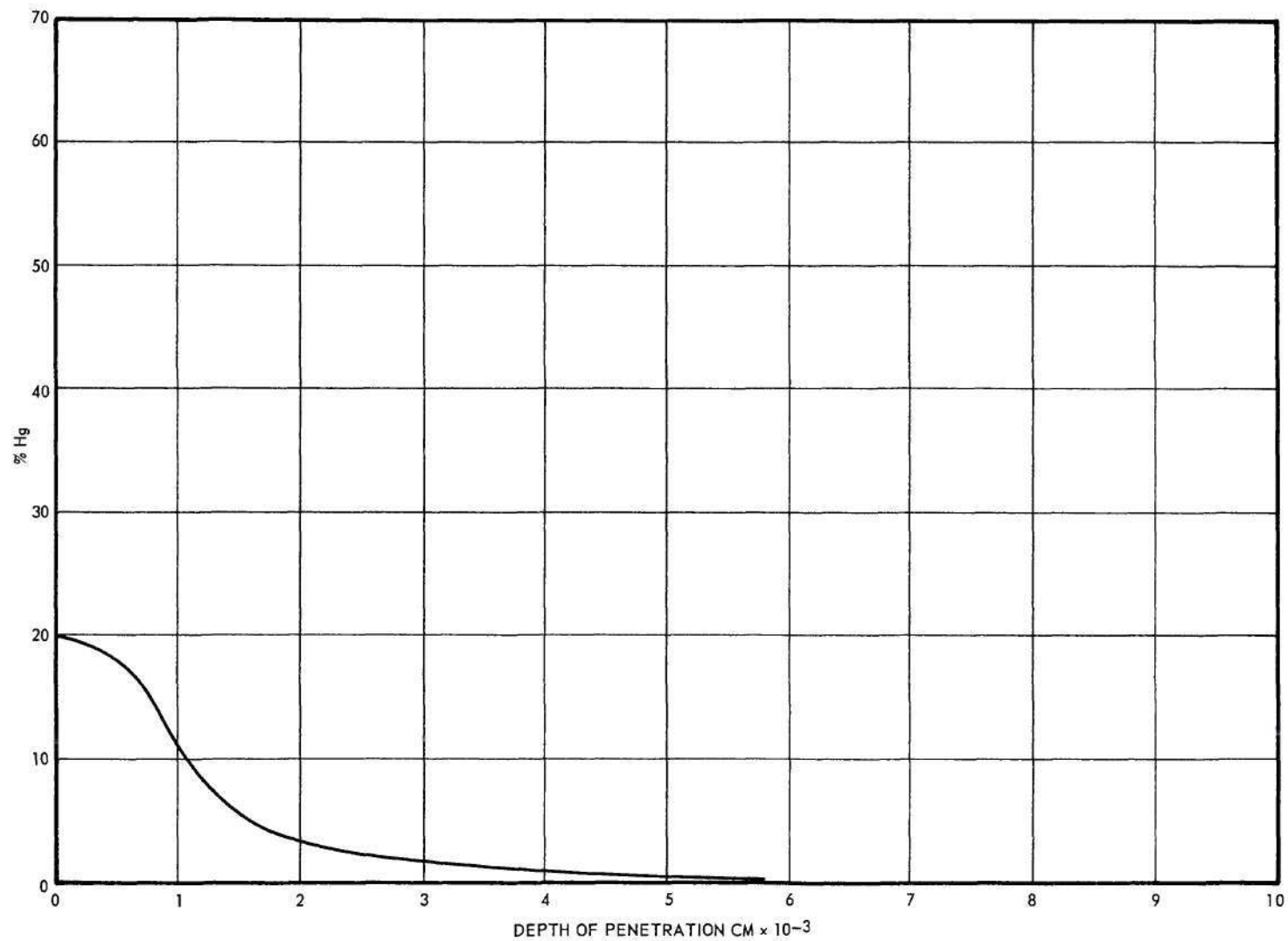


Figure B-10. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 2.00 Hours at 40°C.

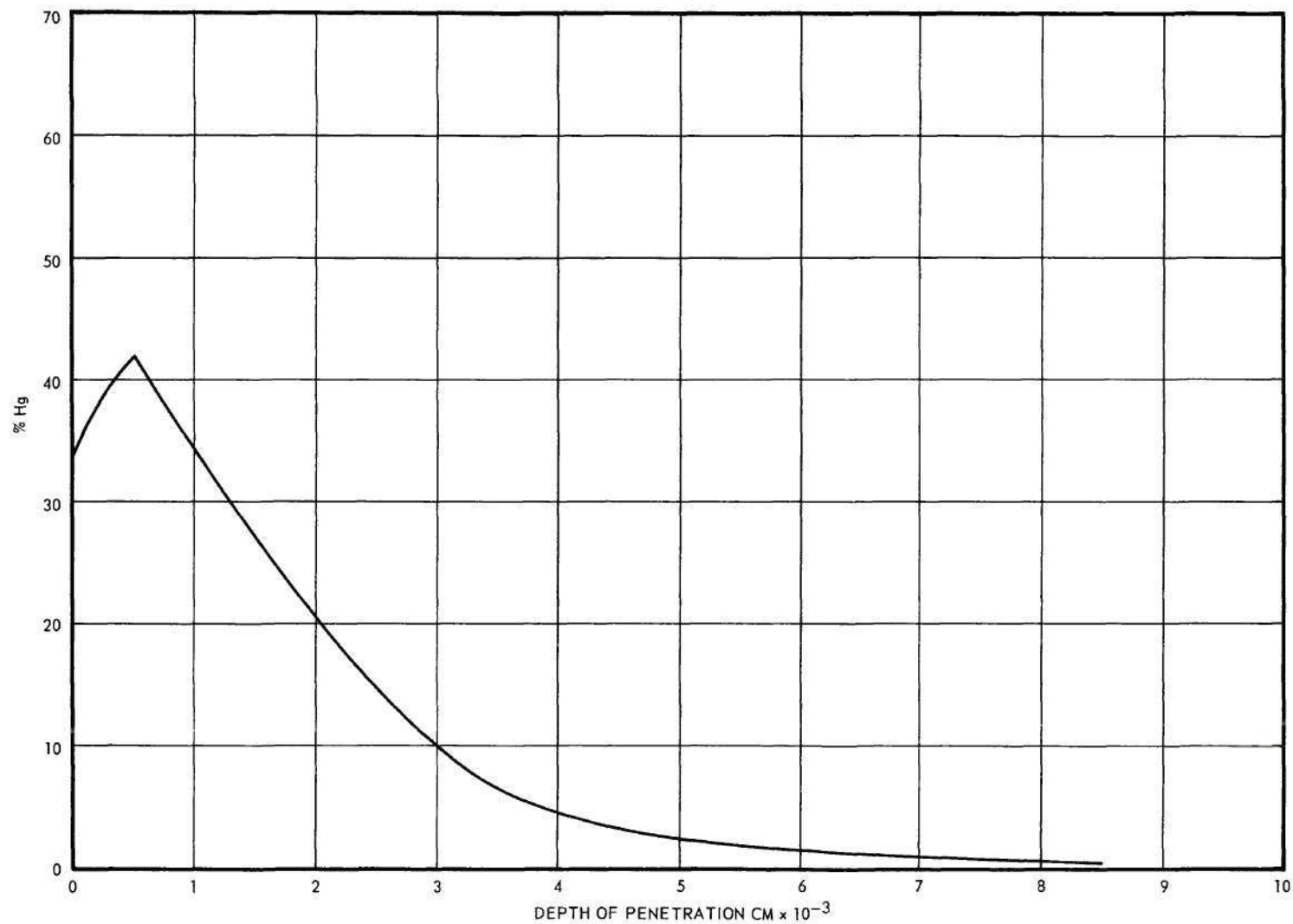


Figure B-11. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, in Non-Ultrasonic Environment for 2.00 Hours at 80°C.

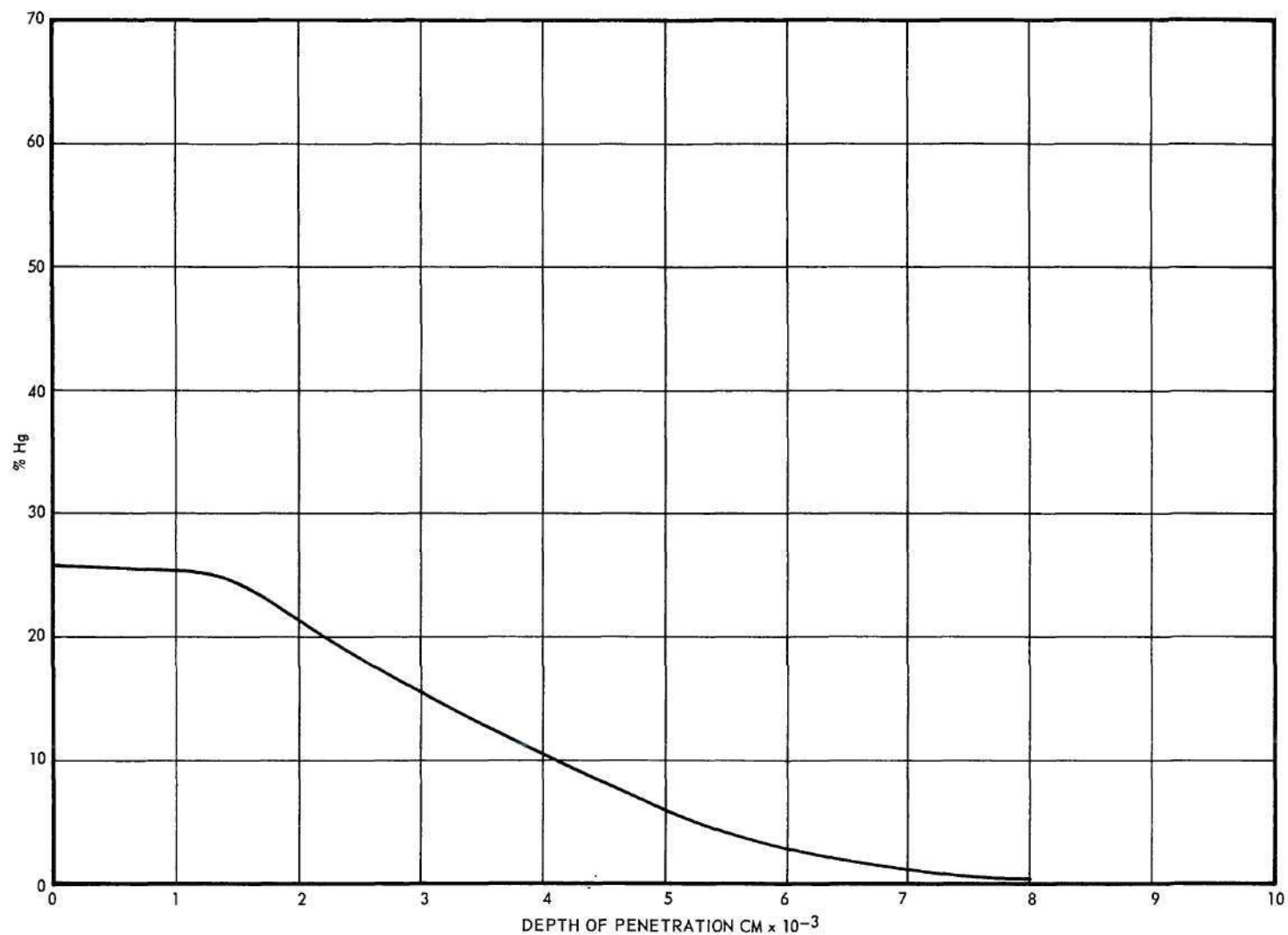


Figure B-12. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for .78 Hours at 60°C.

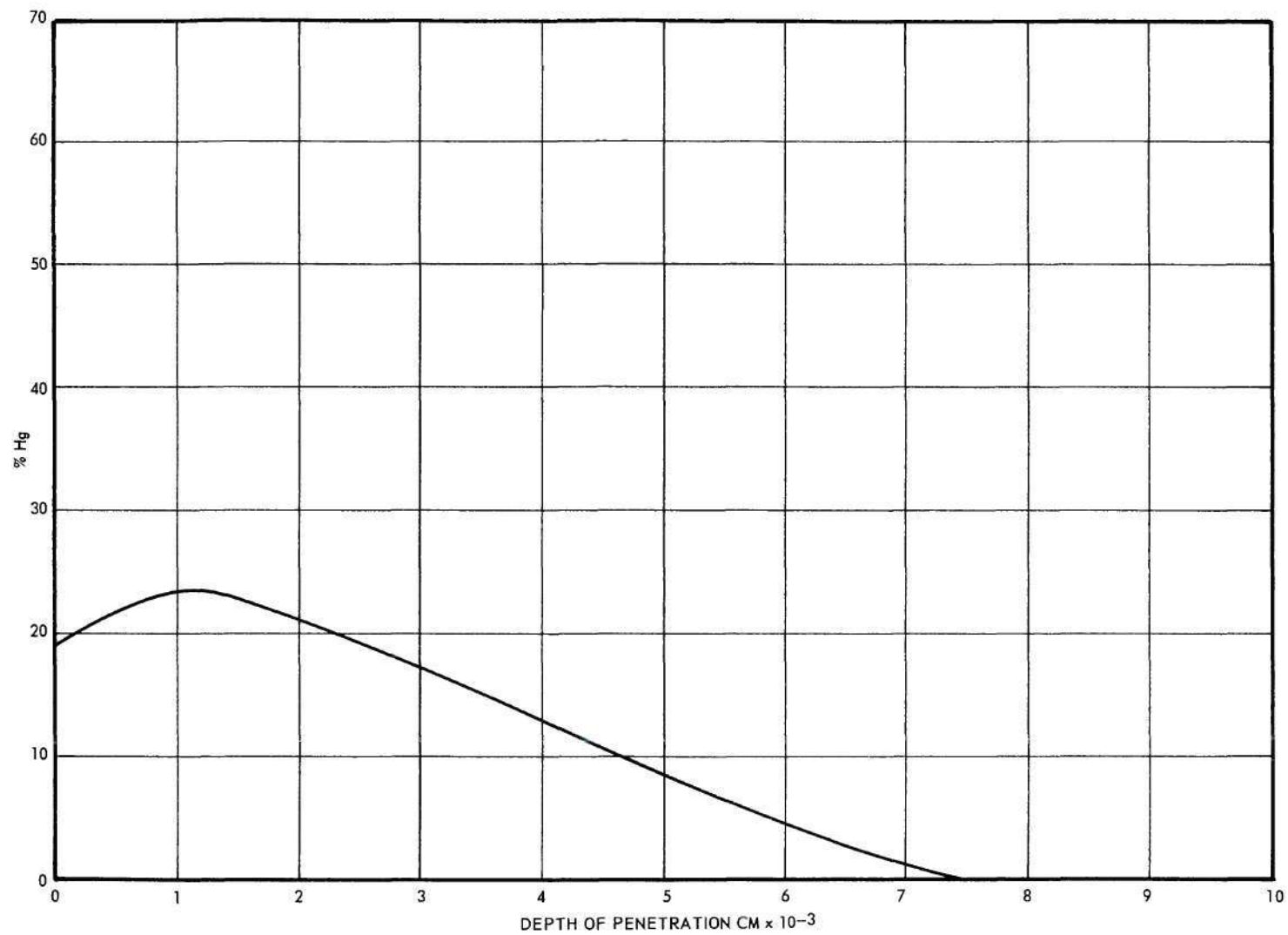


Figure B-13. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for .83 Hours at 60°C.

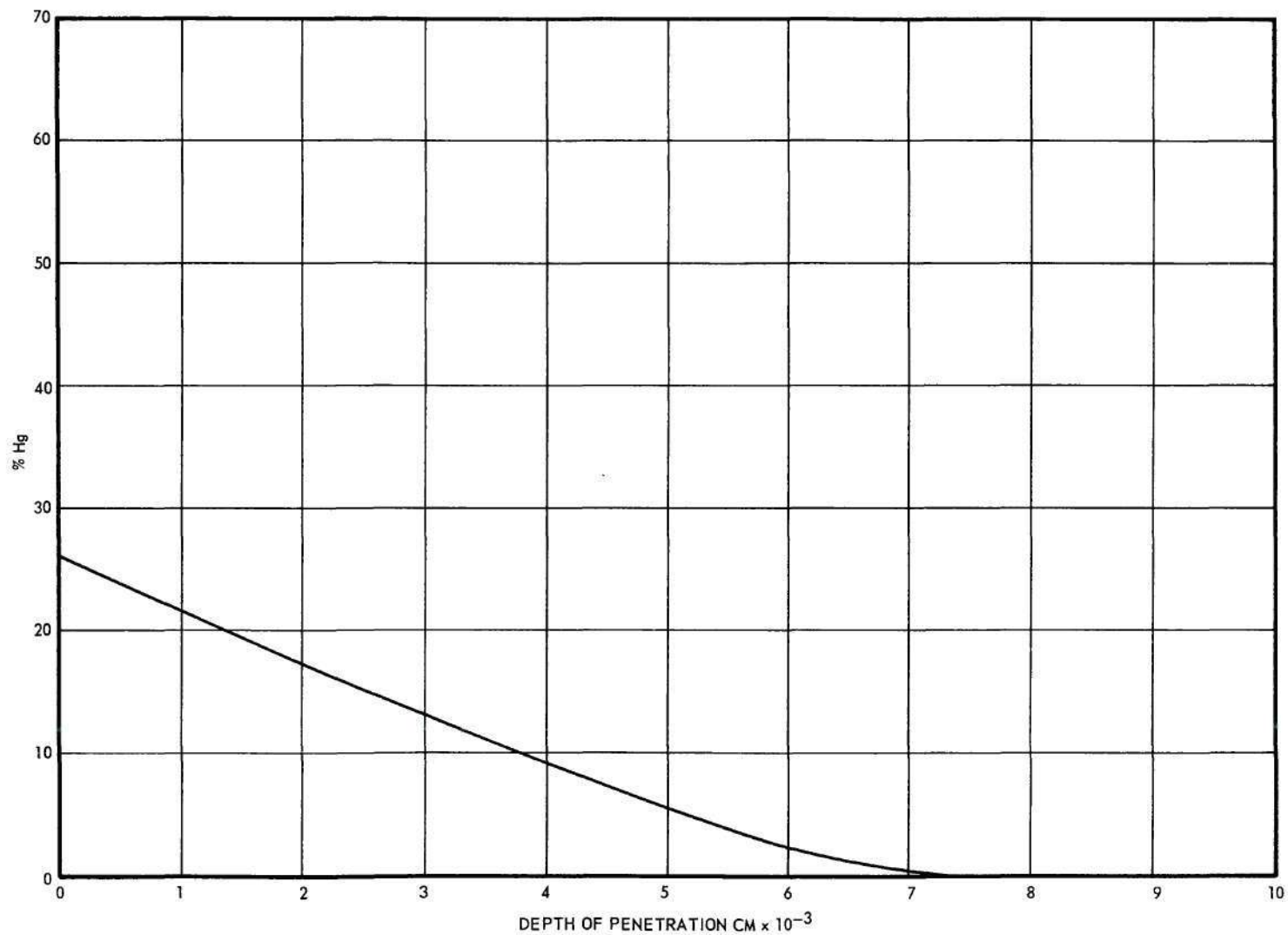


Figure B-14. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for 1.23 Hours at 80°C.

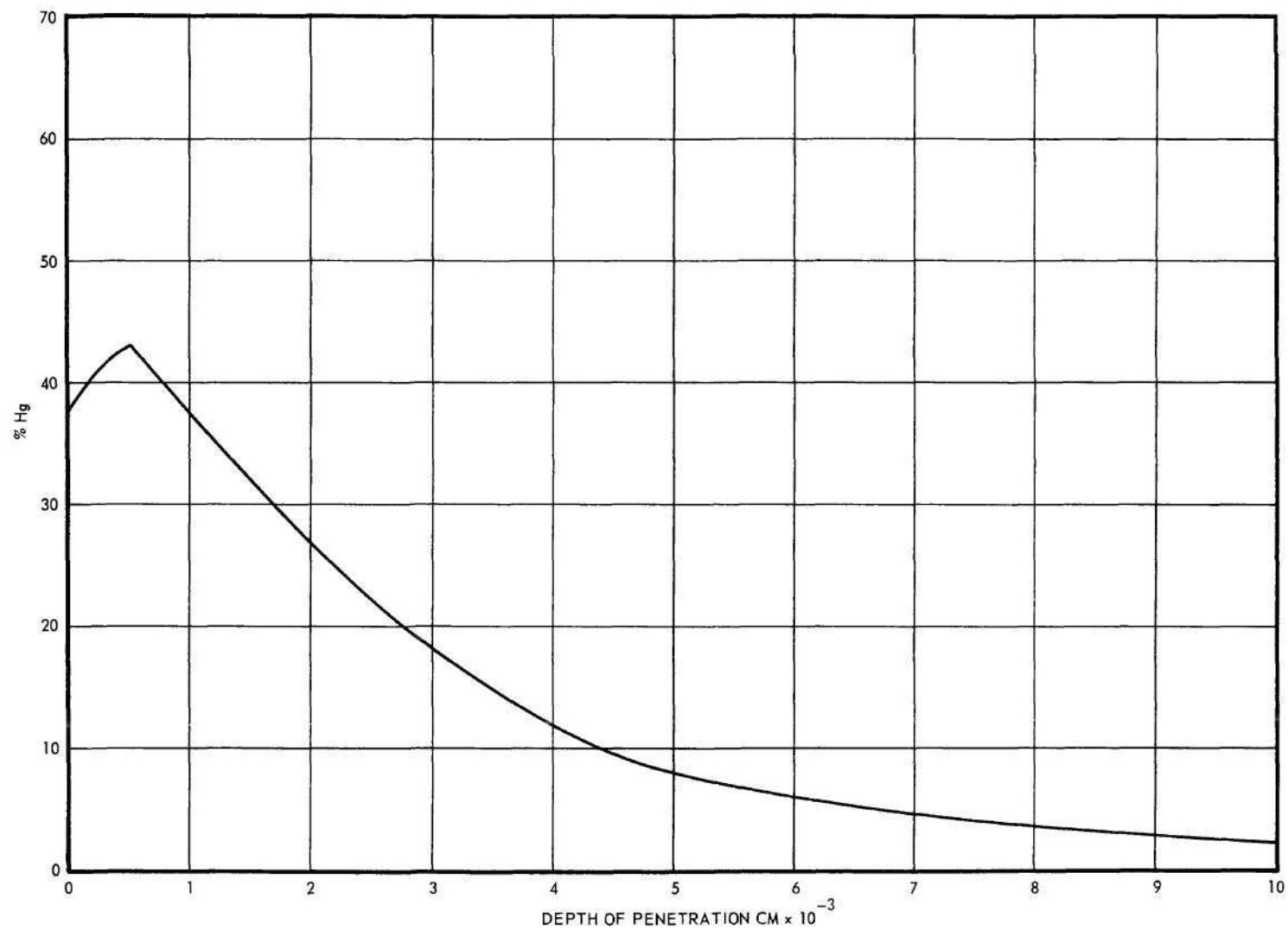


Figure B-15. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for 1.43 Hours at 80°C.

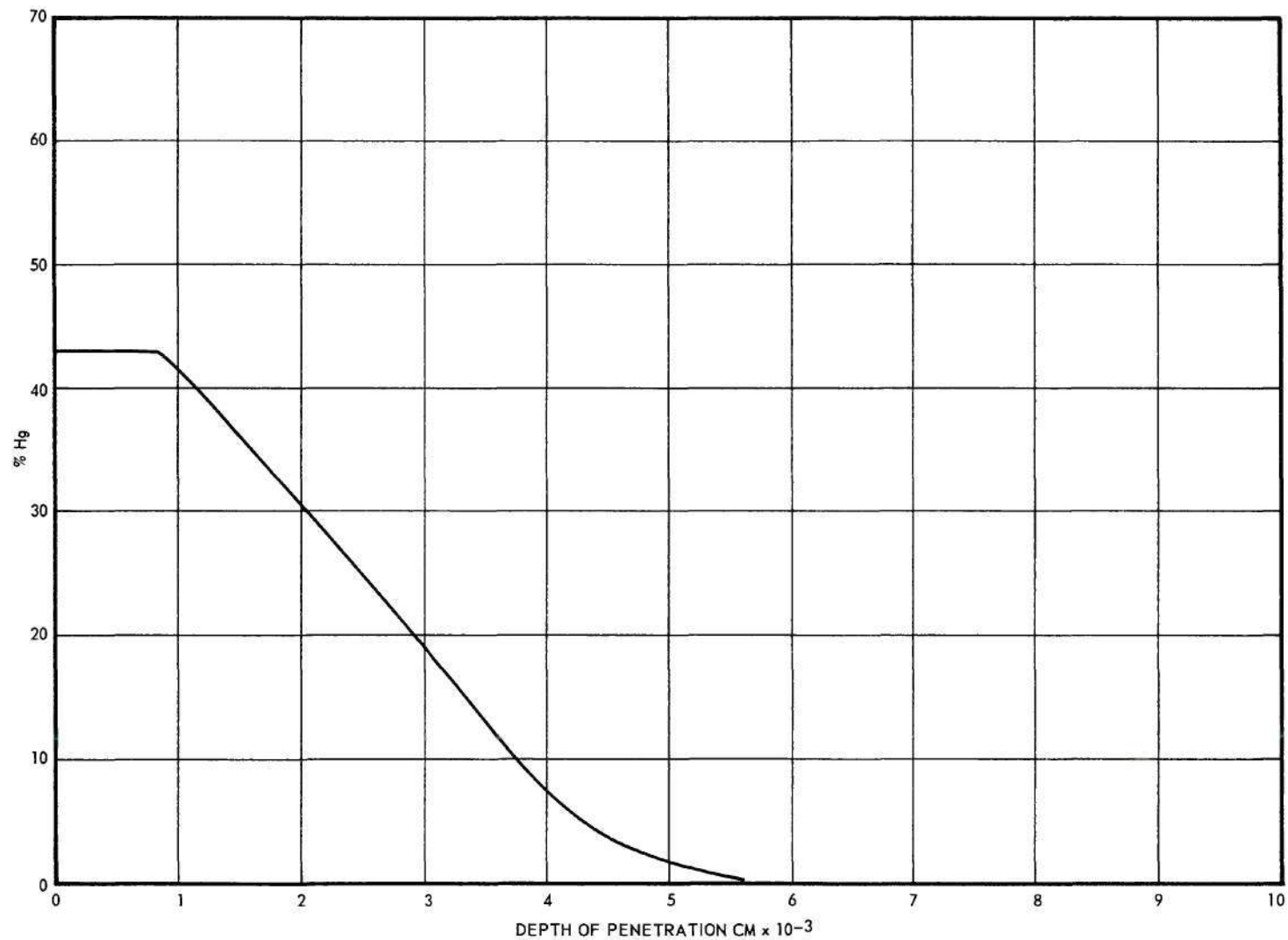


Figure B-16. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for .67 Hours at 40°C.

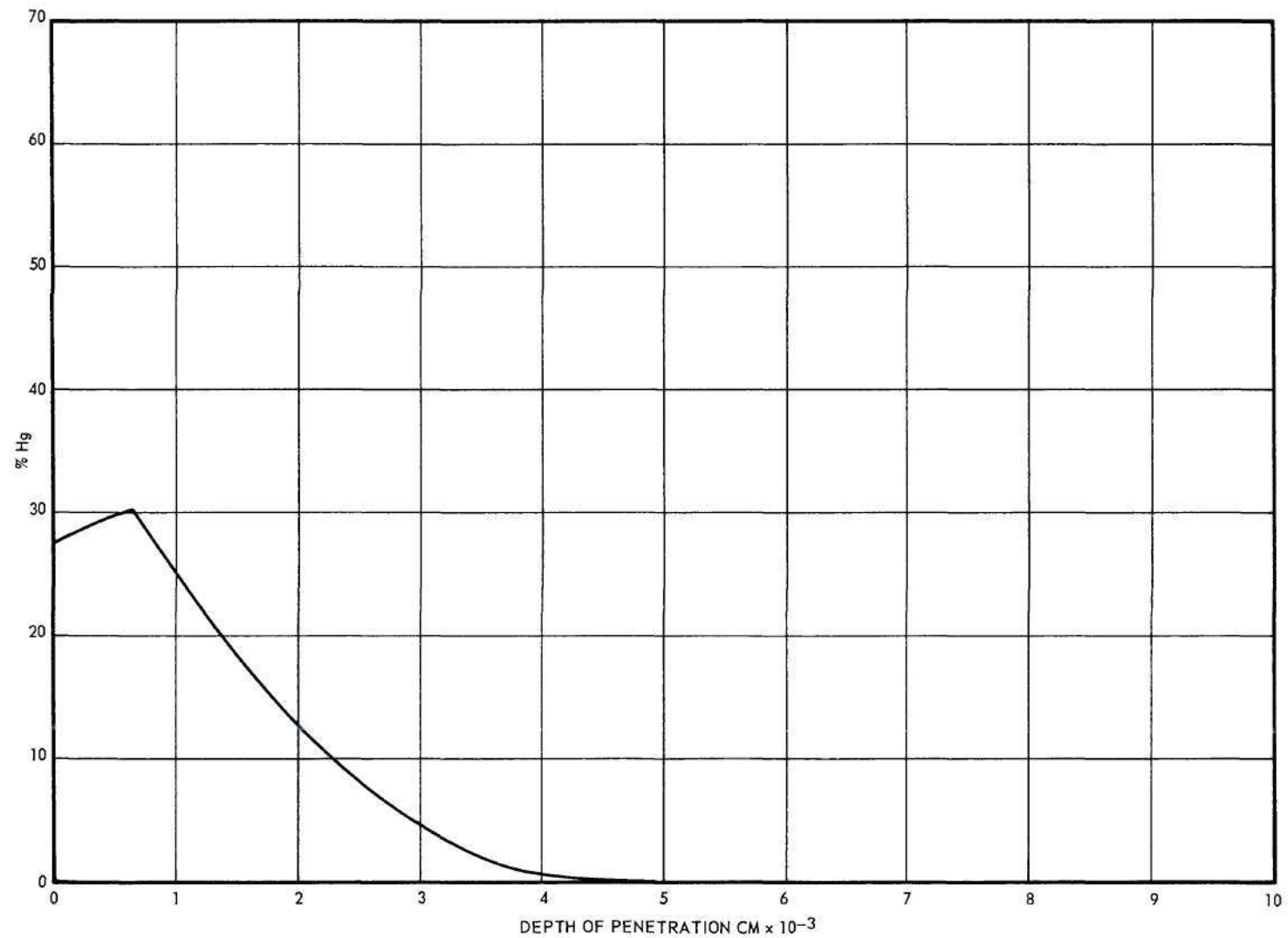


Figure B-17. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for .75 Hours at 60°C.

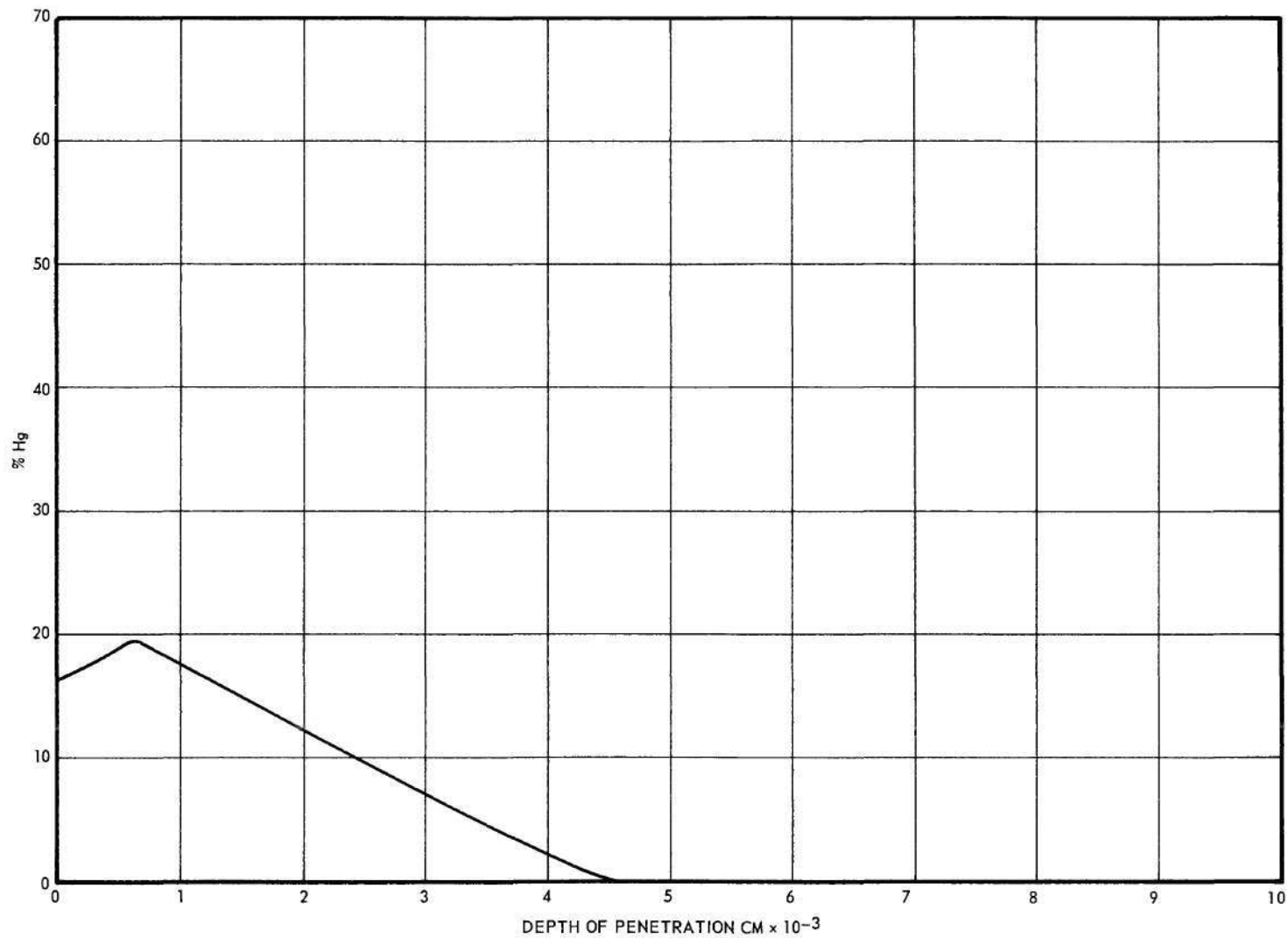


Figure B-18. Typical Diffusion Penetration Curve for Per Cent Mercury as a Function of Depth, Exposed to Ultrasonic Energy for .67 Hours at 80°C.

BIBLIOGRAPHY*

1. J. W. Koger, *A Study of the Kinetics of the Mercury Reaction with the Silver-Tin Dental Alloys*, Master's Thesis, Georgia Institute of Technology (1965).
2. G. Ryge, J. C. Moffett, and A. G. Barkow, "Microstructural Observations and X-ray Diffraction Studies of Silver-Tin Amalgams," *Journal Dental Research*, 32, 152-67, April (1953).
3. E. W. Skinner and R. W. Phillips, *The Science of Dental Materials*, (5th Ed.), W. B. Saunders Co., Philadelphia and London (1960).
4. M. L. V. Gayler, "Dental Amalgams," *Journal Institute Metals*, 60, 407-19 (1937).
5. J. A. Mitchell, I. C. Schoonover, G. Dixon, and H. C. Vachec, "Some Factors Affecting the Dimensional Stability of the Ag-Sn-(Cu-Zn) Amalgams," *Journal Dental Research*, 34, 744, Oct. (1955), (Abstract).
6. J. A. Mitchell, G. Dickson, and I. C. Schoonover: "X-ray Diffraction Studies of Mercury Diffusion and Surface Stability of Dental Amalgams," *Journal Dental Research*, 34, 744, Oct. (1955), (Abstract).
7. R. J. Schnell: *Resistivity of Silver-Tin Amalgams*, Master's Thesis, Indiana University School of Dentistry (1958).
8. F. Günther and G. Jehmlich, "Roentgenographic Investigation of Diffusion in the Tin-Mercury System," *Z. Metallk*, 50, 288-93 (1959).
9. C. V. Simon, "Röntgenuntersuchungen an Amalgamen," *Zeits. Phys. Chem.*, 109, 187 (1924).
10. S. Steenbeck, "Röntgenanalyse der Legierungen von Quecksilber mit Silber, Gold, und Zinn," *Zeits. Anorg. Chem.*, 214, 23 (1933).
11. D. F. Taylor, "An Investigation of the Constitution of the Mercury-Tin System and Portions of the Mercury-Silver-Tin System," *National Bureau of Standards Progress Report 7096*.
12. W. H. Crawford and J. H. Larson, "Residual Mercury Determination Process," *Journal Dental Research*, 34, 313-17 (1955).

* Abbreviations for journals correspond to those given in the "List of Periodicals" published by *Chemical Abstracts* (1961).

13. H. Winterlager and W. Schlosser, "Reactions Between Solid and Liquid Metallic Phases," *Metall.*, 14, 1-6, (1960).
14. A. I. Bykhouskii, "Diffusion of Mercury in Tin," *Fiz. Metal. i Metalloved.*, 15, 95 (1963).
15. A. Sawatzky and F. E. Jaumat, Jr., "Diffusion of the Elements of the IB and IIB Sub-Groups in Ag.," *Transactions AIME*, 209, 10 (1957) and *Journal of Metals*, 9 (1957).
16. F. Baumgartl, "Diffusion and Ultrasonics," *Chem. Zentr.*, II, 1594 (1950).
17. V. C. Hagen, H. H. Rust, and F. Lebowsky, "Investigations on Problem of Effect of Ultrasonics on Diffusion," *Naturwiss.*, 38, 5-6, 1 (1951).
18. N. N. Dolgoplov, V. M. Fridman, and N. M. Karavev, "The Effects of Ultrasonic Vibration on Diffusion Processes," *Doklady Akad. Nauk. S.S.S.R.*, 93, 305-6 (1953).
19. W. Rozanski, "Diffusion in Metals in the Presence of Ultrasonics," *Zeszyty Nauk. Akad. Gorniczo Hutniczej. Met. Odlewnictwo* No. 3, 17 (1959).
20. F. N. Rhines, "Study of Changes Occurring in Metal Structures During Ultrasonic Welding," *Summary Report TP 82-162*, NASA, Huntsville, April (1962).
21. D. E. Gucer, "Design for the Application of Ultrasonic Energy to Metallurgical Processes," *Istanbul Teknik Universitesi Bultoni*, 13, No. 2, 69-82 (1960).
22. P. A. Parkhutik, "Aging of Alloys in a Non-Uniform Field of Ultrasonic Vibration," *Metallovedenie i Termicheskaya Obrabotka Metallov*, No. 1, 44-47 (1964).
23. O. Meyer, W. Erlender, and W. Schmidt, *Archiv Eisenh.* 6, 241-45, (1932-3).
24. G. Mahoux, *Comptes Rendus*, 191, No. 25, 1328-30 (1930).
25. E. W. Skinner and G. T. Mizera, "Condensation of Amalgam with Ultrasonic Energy," *J. Pros. Dent.*, Jan. (1958).
26. R. E. Reed-Hill, *Physical Metallurgy Principles*, D. Van Nostrand Co., Inc., Princeton, New Jersey (1964).
27. G. Grube and A. Jedelev, *Zeit Elektrochem.*, 38, 799 (1932).

28. L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*, McGraw Hill Book Co., Inc., New York, Toronto, London (1953).

Other References

M. Hansen, *Constitution of Binary Alloys*, McGraw Hill Book Co., Inc., New York (1958).

P. G. Shewmon, *Diffusion in Solids*, McGraw Hill Book Co., Inc., New York, San Francisco, Toronto, London (1963).