NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

on

AN INVESTIGATION OF THE CONSTITUTION OF THE MERCURY-TIN SYSTEM AND PORTIONS OF THE MERCURY-SILVER-TIN SYSTEM

by

Duane F. Taylor

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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AN INVESTIGATION OF THE CONSTITUTION OF THE MERCURY-TIN SYSTEM AND PORTIONS OF THE MERCURY-SILVER-TIN SYSTEM

Abstract

An investigation of the constitution of the mercury-silver-tin system was made by a combination of four techniques: thermal analysis; diffusion and chemical analysis; micro-hardness and metallography; and x-ray diffraction. This system is of interest because it is the basis of dental amalgam, the most important single dental restorative material. Information as to the constitution of these alloys is incomplete for both the ternary system and the mercury-tin binary system. Most of the effort in this study was devoted to the investigation of the mercury-tin system as a prerequisite to a study of the ternary alloys.

The results obtained by the various methods are in substantial but not complete agreement. They indicate that the system is more complex than previously reported. The beta and gamma peritectic temperatures reported by Prytherch were confirmed but the composition limits of the gamma phase were found to differ from earlier values. Composition limits and peritectic temperatures are proposed for two phases: one corresponding to Gayler's delta phase; the other previously unreported. The thermal analysis results indicate the possible existence of three additional phases unconfirmed by other methods.

X-ray diffraction patterns are reported for the gamma and delta mercury-tin phases and micro-hardness values are reported for the alpha and gamma mercury-tin phases as well as all silver-tin and mercury-silver binary phases.

1. INTRODUCTION

1.1 Statement of the Problem

The mercury-silver-tin ternary system has been studied by several workers since Joyner [1] published the results of the first investigation of the system in 1911. Both before and after that date numerous studies have been made of the three associated binary systems. In spite of these efforts, however, the present knowledge of the metallurgy of the system is incomplete. The principal practical application of these alloys is as a dental restorative material, and interest in them has been mainly due to this use. The development of dental amalgams has been largely empirical and in almost all aspects has paralleled or preceded the fundamental studies.

While present dental amalgams have been developed to a stage where they are in many ways the best restorative material available to the dentist and are used for more than three-fourths of all dental fillings, they still have many undesirable features. Any hope for substantial improvement in these materials appears to be dependent upon the development of a better understanding of the underlying metallurgy.

From a purely metallurgical point of view, these alloys are of interest because of the unusual method by which they are fabricated. Dental amalgams are made by mechanically mixing a finely divided, solid silver-tin alloy with the liquid mercury. The hardening process then proceeds by isothermal diffusion and reaction of the components. At normal room or body temperatures such a reaction between a liquid and a solid phase is, ofcourse, restricted to alloys containing a low fusing metal such as mercury or gallium, but even at elevated temperatures is very rare. Perhaps the closest approach is the case of the cemented carbides, but here the reaction between phases is very limited. A better understanding of the mercury-silver-tin system, and of the reactions that occur in the hardening of dental amalgam, is of immediate importance to dentistry and might lead to applications in other alloy systems as well.

1.2 Previous Work

The Silver-Tin System

The presently accepted constitution diagram for the silver-tin system is shown in Figure 1. The liquidus is as reported in the closely agreeing results of Heycock and Neville [2], Petrenko [3], and Murphy [4]. The boundaries of the alpha region are based primarily upon Murphy's [4] metallographic findings, as is the solidus of the beta phase, which was first reported by Puschin [5] on the basis of potential measurements. The gamma phase was discovered by Petrenko [3], whose findings were confirmed by a variety of authors, including Murphy [4], Preston [6], and Nial, Almin and Westgren [7]. An extensive investigation of the boundaries of the one-phase regions below the solidus was conducted by Umanskiy [8] and Owen and Roberts [9], supplementing and confirming earlier findings.

The most comprehensive single paper is that of Murphy [4], and the diagram is essentially as presented by him. References to additional work on this system will be found in the volumes by Hansen [10, 11] and in the Metals Handbook [12].

The Mercury-Silver System

The diagram for the mercury-silver system shown in Figure 2 is mainly based upon the work of Murphy [13], who employed thermal and microscopic techniques. Minor modifications of his diagram were based upon the x-ray diffraction studies of the solid regions of the diagram by Preston [14], Stenbeck [15], and Day and Mathewson [16]. The latter investigation was largely responsible for establishing the limit of solubility of mercury in silver at the beta peritectic temperature. The lower portions of the liquidus are difficult to determine by thermal analysis and have been established mainly by isothermal determinations of the solubility of silver in mercury. This work has been done by several authors [1, 17, 18, 19, 20] who studied overlapping ranges with very good agreement in their results. As in the case of the silver-tin system, bibliographies of other publications on the mercury-silver system may be found in the Metals Handbook [12] and the books by Hansen [10, 11] as well as in the sources already cited.

The Mercury-Tin System

Of the three binary systems considered, the mercury-tin system is the least well understood. This appears due in large part to experimental difficulties associated with the low melting point of mercury.

Figure 3 shows the currently accepted diagram for this system. The liquidus is well established, having been investigated by several authors [5, 21, 22, 23]. Of these the work of van Heteren [22] was the most extensive and probably the most precise, but there is good agreement between his results and the others.

The solubility limit of mercury was determined from the electrode potential measurements of van Heteren [22] and the x-ray diffraction studies of Stenbeck [15]. The gamma phase was first identified by von Simson [24], who established the composition limits essentially as given. Stenbeck [15] confirmed her findings and reported evidence of an additional structure, presumably of higher mercury content.

The beta phase was discovered by Prytherch [25], whose work unfortunately has never been reported except to the extent that it was quoted by Gayler [26]. It appears that Prytherch's [25] diagram was based primarily upon thermal analysis data, showing an arrest at the beta peritectic temperature. The existence of the beta phase was confirmed by the high temperature x-ray diffraction studies of Raynor and Lee [27], although this finding is in apparent opposition to that of Schubert, et al. [28], who concluded that the beta and gamma phases were identical.

The possible existence of a delta phase has been a matter of some dispute. Gayler [26] obtained a series of arrests in the course of thermal analysis of high mercury alloys, which she attributed to a proposed delta phase. Her observations on ternary alloys also appear to require the existence of such a phase. Troiano [29] also supported the existence of a delta phase, but his x-ray findings have been contested by Wainwright [30]. More recent work by Ryge, Moffett, and Barkow [31] has similarly found no evidence for such a phase. Figure 3 has a blank area approximately where the delta phase would be expected to appear, and the portions of the peritectic line reported by Gayler [26] are indicated.

The evidence for the epsilon phase as represented in the figure is almost equally weak. The peritectic temperature is based upon van Heteren's [22] work, and appears well established, but the composition is dependent upon Prytherch's [25] unpublished findings.

This lack of agreement between the results by different methods, and between different authors using similar methods, has caused any conclusions about the high mercury solid phases to be very speculative, and this uncertainty has impeded understanding of the ternary system.

Additional references will be found in the sources previously cited.

The Mercury-Silver-Tin System

There have been few attempts to determine the constitution of the entire mercury-silver-tin system. The earliest of these was by Joyner [1] in cooperation with Knight [32] and with McBain [33]. The main method employed for these studies was the extraction and analysis of liquid from samples annealed at various temperatures. Isothermal sections were prepared by this method at 63°C, 90°C, 166°C, and 214°C [32].

The most comprehensive study to date has been that of Gayler [26], who used thermal analysis and metallography for the determination of the 70°, 84°, and 100°C isotherms as well as a series of pseudo-binary sections. This study has served to clarify most of those portions lying between the silver-mercury boundary and the gamma (silver-tin)- mercury pseudo binary. Very little information relative to the high tin alloys is presented since only eight compositions containing more than thirty percent tin were investigated. In addition, inability to attain equilibrium in the metallographic specimens has led to the indication of thermodynamically impossible boundaries in the isothermal sections. In spite of these deficiencies, however, this study provides the essential basis for any further investigations of the ternary system.

Troiano [29] performed a limited x-ray investigation of the system, and Stenbeck [34] has more recently presented findings based on both x-ray diffraction and metallography. Stenbeck's results have served mainly to clarify the boundaries of the beta phase, but his protracted annealing times (up to twenty-eight months) are of interest and lend weight to his findings. Various other authors have studied portions of the system. Ryge et al. [31] and Mitchell, Schoonover, Dickson and Vacher [35] have studied the gamma (silver-tin)- mercury interaction by x-ray diffraction techniques. Tamman and Mansuri [36] and Tamman and Dahl [37] measured hardness and other mechanical properties.

In addition, there is a voluminous literature on dental amalgams which contain copper and zinc in addition to mercury, silver, and tin. Little of this is of direct application to the understanding of the metallurgy of amalgams, the preponderance being devoted to techniques of manufacture and application. Bibliographies on this subject are given in dental textbooks [38, 39].

1.3 Choice of Experimental Methods

A review of the previous literature leads to the identification of several areas in which present knowledge is incomplete. Most obvious of these is the mercury-tin binary system, where the diagram is not only incomplete but where considerable disagreement persists about nominally established portions of the diagram. This uncertainty has extended to the adjoining portions of the ternary diagram and has been aggravated by the paucity of experimental observations in the tin-rich half of the diagram. The other major failing, at least insofar as the usefulness of the ternary diagram relative to dental application is concerned, is the lack of information below 60°C. Almost all of the published results are based on experiments conducted completely outside the temperature range of interest which lies between 20°C and 37°C.

It thus appeared that the most useful study would be one which helped resolve the tin-mercury diagram and the high tin and low temperature regions of the ternary diagram. To reduce the complexity of the problem it was decided to emphasize the investigation of the mercury-tin system, but where possible to employ methods that were adaptable to the extension of the study into the ternary system.

Six methods were considered seriously. Of the six, four were selected while the other two were rejected for the reasons discussed below. Many alternative methods are possible. The ones chosen were deemed particularly suitable to the study of this system.

Thermal analysis was one of the four methods selected. It has several specific advantages in addition to being a traditional and basic approach. In the mercury-tin system, thermal analysis was the method used in the detection of both the beta and delta phases. Its employment in this study offered a direct check on those findings. At the same time, it provided a tie-in to the well established liquidus data. The main drawback to this method is its susceptibility to suppression of phases in peritectic systems. This tendency can be partially offset by the use of high sensitivity differential techniques and low heating and cooling rates. Diffusion and chemical analysis was chosen as a second method primarily because the diffusion can be performed isothermally and the prolonged retention of nonequilibrium phases formed at higher temperatures can be avoided. It also parallels the normal procedures in the use of dental amalgams and thus might shed some additional light upon the mechanisms of the amalgam setting reaction. The method is more effective in the determination of composition limits than in the determination of the range of temperature stability.

X-ray diffraction was selected as an adjunctive method to the thermal analysis and diffusion techniques. The ability of x-ray diffraction to identify individual crystal structures and thus demonstrate the presence of an individual phase in a mixture is of particular importance when used with diffusion specimens. As a separate method of analysis it permits the confirmation or refutation of the phase sequence proposed by chemical analysis.

The fourth method chosen for use was microhardness determination. It was attractive for several reasons. Metallography of the mercury-tin alloys was known to be difficult, and microhardness studies appeared to offer a substitute approach. Also the technique should be of considerable value in studies of the ternary system. The postulated equilibria for the tin-rich half of the ternary system at low temperatures contain phases of widely different hardnesses. As an example, in the silver-tin system the relatively hard gamma phase is in equilibrium with tin over three-fourths of the diagram. This equilibrium should extend into the adjoining ternary compositions and the disappearance of either of these widely differing phases should be readily detectable. As an additional technique for the identification of individual phases the technique should be of value elsewhere in the ternary alloys.

The two methods considered and rejected were vapor pressure measurement and electrode potential measurement. Under the proper conditions both methods can be extremely effective and efficient. Both were rejected, however, for the same reason, doubt as to whether the necessary conditions would be obtained.*

2. PRESENT RESEARCH

2.1 Materials Used

The composition of the mercury, silver, and tin used in this study are given in Tables 1 to 4. The mercury used was obtained from the Inorganic Chemistry Section of the National Bureau of Standards, where it was refined. The values of Table 1 are their reported maximum values from repeated analyses of various lots, rather than that for the particular lot used.

The silver used was proof silver obtained from the U. S. Mint in the form of electrolytic crystals. Table 2 presents the results of a spectroanalysis performed on this metal.

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* Portions of the original manuscript have been omitted at this point.

Two lots of tin were used. One lot consisted of Baker and Adamson Reagent Grade Tin Sticks produced by the General Chemical Division of Allied Chemical and Dye Corporation. This metal was used for a limited number of the early tin diffusion specimens. The manufacturers' reported analysis is given in Table 3.

The other lot of tin, which was used for all remaining diffusion specimens as well as all thermal analysis, x-ray diffraction and metallographic specimens, was Tadanac Brand Tin Shot obtained from the Consolidated Mining and Smelting Company of Canada Limited. The spectroanalysis results obtained on this tin are presented in Table 4. The spectroanalyses on this lot of tin and on the silver were performed by the Spectrochemistry Section of the National Bureau of Standards.

2.2 Thermal Analysis

Equipment

The results of previous studies of the mercury-tin system which employed thermal analysis as a technique [21, 22, 25, 26] led to the expectation that the thermal effects of interest were apt to be small. The desirability of using low heating and cooling rates to permit closer approaches to equilibrium was expected to increase the problem of observing small heat effects. In order to obtain sufficient sensitivity, a differential method was employed using mercury as a reference substance. This method produces a real increase in sensitivity and is well suited to the detection of transformations in solid alloys [43].

The furnace used for this work was a vertical tube furnace, eleven inches in diameter and twenty-one inches in length. The alundum core had a lumen one and one-eighth inches in diameter and was surrounded with four and one-half inches of insulation. The winding has a resistance when hot of approximately four ohms and was so distributed as to maintain the central ten inches of the tube at a relatively uniform temperature. In use, the lower end of the furnace was closed and the bottom five inches of the tube were plugged with loosely fitting magnesite cylinders.

The power supply to the furnace was provided by three transformers arranged in series. The first was a constant voltage transformer which served to suppress fluctuations in line voltage and prevent their influencing the furnace heating rate. The second and third transformers were common variable transformers and were used in combination to produce sensitivity in controlling furnace temperature. The second transformer was set to the maximum voltage required for a series of tests and thus the full scale of the third transformer was available for regulation.

The specimens were assembled for insertion in the furnace as shown in Figure 4. The temperature and differential thermocouples were inserted in the specimens, and both the experimental and reference specimens were placed in a pyrex sheath. The sheath was nine and one-half inches long, twenty-one millimeters outside, eighteen millimeters inside, and was sealed at one end. A teflon spacer separated the two specimens and was drilled and grooved to permit passage of the thermocouples. A similar spacer above the reference specimen served to hold the end of the four-hole porcelain thermocouple tube. This tube also passed through a hole in the flanged teflon plug which closed the upper end of the sheath.

This assembly in turn fitted inside a heavy-wall copper tube which served to minimize the temperature gradient along the furnace. The flange on the teflon plug substantially filled the inside diameter of the copper tube. When the copper tube and its contents were placed in the furnace, a plug rolled from sheet asbestos was placed around the thermocouple tube and slid down until it filled the furnace lumen just above the top edge of the copper. A flanged magnesite plug was then added to close the upper end of the furnace and to serve simultaneously as a support for the thermocouple tube. Under normal circumstances the copper tube was not removed from the furnace when the specimen was changed but was allowed to remain in the furnace as a liner.

Figure 4 also shows a schematic drawing of the thermocouple arrangement. A twenty-eight gage iron-constantan couple was used to measure the temperature of the specimen. The hot junction of this couple was located in the thermocouple well of the test specimen. The couple then passed out of the furnace through the thermocouple tube to cold junction mercury contacts in an ice bath. From there copper extension wires ran to the potentiometer terminals. The thermocouple was made of enameled wire; however, the hot junction, and the adjacent portions which were in the thermocouple well, were given an additional insulating coating of "Glyptal" varnish. All other portions, except for the part within the thermocouple tube, were additionally protected by braided fiber glass covers.

The thermocouple was calibrated against a platinum-platinum 10% rhodium couple of known calibration at the ice point, 0°C, the steam point, 100°C, and the boiling point of benzyl alcohol 205.2°C. An additional calibration point at 231.9°C was provided by the tests on the 100% tin specimen. This latter point has the advantage of having been determined under the same conditions as the tests on the experimental alloys.

The potentiometer used for temperature measurements was a Leeds and Northrup No. 8662 potentiometer with an integral galvanometer and standard cell. In the range used this instrument read directly to five microvolts, and the observations were estimated to one microvolt. One microvolt is equivalent to 0.02°C for an iron-constantan couple.

Other factors than reading errors contribute to the total uncertainty in the temperature measurement. Among these factors are: residual calibration error in the couple and potentiometer, galvanometer lag during intervals of extremely rapid temperature change, and variation in cold junction temperature. The maximum error from these combined causes is believed to be less than 0.05°C.

The differential temperature was measured by means of a two-junction iron-constantan thermopile arranged as shown in Figure 4. The junctions and lead wires of the thermopile were insulated in the same way as the temperature thermocouple. The thermopile was connected directly to a Leeds and Northrup No. 7552 potentiometer. This instrument was used with an external standard cell and galvanometer. This potentiometer reads directly to one-half microvolt with estimation to one-tenth. The galvanometer used was a Leeds and Northrup No. 2430 with a 2.5 second period and a scale sensitivity of 0.5 microvolts per millimeter. The maximum reading error is believed to be two-tenths microvolt or less. Unless an attempt is made to determine specific heats the absolute value of the differential voltage is less important than the sensitivity of the system. Some of the factors which influence accuracy, such as thermocouple calibration errors, do not influence sensitivity. Other factors, such as terminal temperature, are proportionately more important. The limit of sensitivity was below four-tenths microvolt or approximately 0.004°C difference between the test specimen and the reference specimen. The heat required to produce such a temperature difference in the pure tin sample used in this study was 0.0055 calories.

If it is desired to measure the absolute temperature difference between the test and reference specimens, allowance must be made for the non-linearity of the temperature- potential function for the thermocouple. This causes a constant temperature difference to produce varying potentials as the specimen temperature is changed. The maximum error in absolute temperature difference in this study from this cause is believed to be 1.0 uv or approximately 0.01°C.

In addition to the tube furnace and its accessories, a set of air baths were used for annealing the thermal analysis specimens. These air baths were also used for the diffusion studies and will be discussed in somewhat more detail in that section.

The balance used for proportioning the alloys was magnetically damped, and direct reading up to one hundred milligrams. Weights from one-tenth to one gram were applied by means of a beam rider. A set of "Class S" stainless steel weights was used to provide weights in excess of one gram. The total uncertainty due to instrument errors in weighings with this equipment was 0.2 mg. or less. This amount is negligible in specimens the size of those used for thermal analysis. It constitutes a limiting factor, however, in the accuracy attainable in the much smaller samples used to determine the composition-depth curves in the diffusion experiments.

Specimen Preparation

The thermal analysis specimens were prepared in pyrex tubes, similar in design to those employed by Murphy [13]. Weighed amounts of tin and mercury were placed in the tube and a sealed stuffer tube was added to fill most of the space below the intended seal. The tube was then repeatedly evacuated and flushed with dry hydrogen and was finally sealed with a residual hydrogen pressure of 2-5 mm of mercury. The alloys were then homogenized by heating to 250°C and holding at that temperature for at least one hour, with repeated vigorous shaking. The tubes were then quenched in room temperature water and placed in an air bath at the selected annealing temperature.

The nominal composition of the alloys prepared for thermal analysis is given in Table 5. The compositions are given in both weight and atomic per cent; however, for convenience of discussion the specimens will normally be referred to only in terms of their composition in weight percent. A limited number of analyses indicated that the actual composition of specimens prepared by this technique did not differ significantly from the nominal values.

These compositions were selected to cover the majority of the mercury-tin system, but with emphasis upon ranges expected to be of particular interest. Thus the specimens containing 0 to 10% mercury were chosen to cover the postulated beta phase region [25, 27].

The series of compositions from 18 to 30% mercury were chosen as including the most likely composition of the delta phase proposed by Gayler [26]. The remaining specimens complete the composition range to 80% mercury and include the particular compositions at which Gayler [26] detected the arrests she attributed to the delta phase.

The specimen tubes were made of 15 mm diameter, standard-wall thickness pyrex, while the reentrant well was made from 3 mm diameter, standard-wall pyrex tubing fifteen millimeters long. In order to maintain approximately constant areas for heat transfer, the specimens were prepared to constant volume rather than constant weight. The volume used was three milliliters, which produced a specimen about thirty millimeters long. Thus the end of the thermocouple well was approximately centered in the specimen.

Experimental Procedure

The individual specimen was removed from the annealing oven and assembled with a reference specimen of pure mercury, as shown in Figure 4. No attempt was made to maintain the specimen at the annealing temperature during this process, although the operation was completed as rapidly as possible. In the case of specimens annealed at the higher temperatures (such as 85°C) the necessity of manipulating the specimens resulted in their being cooled at least to a temperature where they could be readily handled. After the thermocouples had been inserted and both specimens positioned in the outer glass tube, the couples were checked for breaks or shorts. The assembled test set-up was then inserted into the furnace. The thermocouples were connected to the potentiometers, the differential couple directly and the reference couple through mercury contacts maintained in an ice bath.

The furnace temperature was previously adjusted to an initial temperature at or below the annealing temperature so that the first test run in each instance was a heating run. The potentiometers were calibrated against their standard cells immediately before the start of a run and at intervals thereafter.

Generally each heating or cooling run was made at a constant voltage. This, of course, produced a variation in the heating rate within a given run. After an initial transient period the heating or cooling rate was found to stabilize, and by proper selection of the applied voltage any desired rate could be obtained in the temperature range of interest. This is probably mainly due to the fact that the total temperature range studied was only about 200°C. For greater ranges the problem would be more severe, but in this instance the results were found to be satisfactory.

Readings of the specimen temperature and of the differential temperature were made at regular intervals, normally every two minutes, except that at the higher heating and cooling rates one-minute readings were taken. In addition, an attempt was made to obtain extra readings at the maximum and minimum differential readings. With the heating rates most commonly employed, this procedure led to readings at approximately 0.5°C intervals.

After the initial heating run and all subsequent heating and cooling runs, the specimen was held at a constant temperature for a period of time to permit the temperature distribution in the furnace to stabilize and to promote at least partial equilibrium of the specimen. In some cases, where substantial variation occurred between the results of annealed and nonannealed runs with the same specimen, it was returned to the oven for extended reannealing prior to additional tests.

Results

The experimental technique chosen worked well. The problems that were encountered in its use appeared to be attributable to the peculiarities of the mercury-tin system rather than to the equipment or method. Two related factors were the main causes of the difficulties that occurred.

First, the results of thermal analysis indicated that the system was much more complex than previously reported. Second, the annealing time required to homogenize specimens was longer than had been anticipated. The combination of these two factors greatly complicated the problem of performing replicate tests on a particular specimen. It now appears that several months' annealing between heating curves may be desirable. Such an annealing schedule requires a prohibitive amount of time if several annealing temperatures need to be investigated. As a result, the majority of the tests made in this study were performed on specimens not annealed to equilibrium. With a peritectic system, where nonequilibrium phases are often retained due to incomplete peritectic reactions, the conditions that existed during cooling of the alloy may be equal or greater in importance than the annealing treatment in determining the shape of the heating curve.

For this reason, it was found to be very difficult to obtain good replicate runs on some alloys. It has been necessary in interpreting the results to compare a series of tests on one alloy and make allowance for nonequilibrium conditions.

A total of one hundred eleven heating and cooling curves were run on the fifteen mercury-tin alloys and the pure mercury and pure tin calibration samples. Heating and cooling runs were customarily alternated with various annealing times preceding each heating curve. A minimum of four test runs were made on each specimen. For convenience of presentation, results will be divided into four groups devoted to calibration, liquidus determinations, high tin alloys, and high mercury alloys.

Calibration. Two types of calibration tests were made. The first, performed with a pure tin specimen, provided a check on the temperature measuring system as well as a comparison curve on a sample with known latent and specific heats approximately equal to those of the test specimens. Figure 5 shows the results from one heating curve on specimen 67, a pure tin specimen.

The dots represent individual observations and for reasons of clarity have been made larger than the observational uncertainty associated with the readings. The readings below 102°C and between 225 and 260°C were made at two-minute intervals. The remainder were made at five and ten-minute intervals. The flat at 231.9°C served as a final calibration point for the temperature thermocouple. In addition, the curve provides several other valuable items of information about the performance of the apparatus.

Of particular interest is the sharpness of the corners of the ends of the constant temperature flat. These corners are commonly rounded by such factors as inadequate stirring, too thick thermocouple sheathes or heat conduction along the thermocouple. Their sharpness indicates that in spite of the complete lack of stirring relatively little distortion is occurring due to these factors.

The course of the curve above the melting point is important because it provides an excellent example of the behavior of a one-phase specimen out of equilibrium with the furnace.

Once melting has been completed, and the specimen has been converted entirely to liquid, a rapid heating occurs, restoring the specimen to equilibrium with the furnace. This heating is shown by the rapid reduction of the differential temperature after the liquidus temperature is passed. The rate at which this reduction occurs is nearly proportional to the difference between the observed and the equilibrium differential temperatures. This is shown by the spacing of the observations which become progressively closer, although the time interval between readings was held constant. This characteristic spacing of points is useful in identifying the liquidus temperature when it is near other energy-absorbing transformations.

The absence of any discontinuities or inflections below the liquidus temperature is an indication that there are no thermal effects due to the furnace that are apt to appear as artifacts in the test results. The broad swing in the differential observations that occurs at low temperatures could be due to differences between the specific heats of the test and reference specimens or to variations in the specific heat of either. As will be seen below, in this instance it is due to a variation in the temperature distribution along the furnace tube.

The second type of calibration test was made to identify just such furnace effects. For this purpose both the test and reference specimens were of mercury and differed negligibly in weight. (See specimens 17 and 66 in Table 5.) The results of one such run are presented in Figure 6.

Since the specimens are substantially identical, they should differ from the local furnace temperatures by about the same amount. Thus, since no transformations occur in mercury in this temperature range, any effects observed under these conditions represent furnace characteristics only. As can be seen by a comparison of the two figures, the swing in differential temperature observed at low specimen temperatures in Figure 5 is similar in shape to that found in Figure 6. The cause of this swing is thus identified as due to a temperature gradient in the furnace rather than to some other cause.

Repeated tests at varying heating and cooling rates with a mercury test specimen, have allowed the identification and measurement of the factors that determine this temperature gradient. It was found that after an initial transient period the temperature difference from this cause could be accurately expressed by an equation of the form $\Delta T = AT_R + B\frac{dT_R}{dt} + C$ where T_R is the temperature of the reference specimen and A, B, and C are constants. A and C are dependent only on the positions of the two specimens in the furnace, while B is determined by the voltage applied to the furnace. Application of this expression as a correction to the values of Figure 5 results in a straight vertical line from the initial reading to the melting point.

Liquidus Determination. The liquidus temperature was determined for each composition studied by both heating and cooling curves. In the case of the cooling curves an excessive supercooling, by as much as 20°C, occurred at times when high cooling rates were used. The maximum temperature reached after such supercooling was inevitably lower than the true liquidus temperature, and such results must be disregarded in determining the proper value. High heating rates similarly produced liquidus values that were too high. As the heating and cooling rates were reduced the resultant liquidus values approached each other. Table 6 presents the observed liquidus temperatures for the alloys studied. The estimated uncertainty of these values ranges from 0.1 to 0.8°C, with an average of about 0.5°C.

It is believed that the main causes of this uncertainty were the small sample size, lack of stirring, and the increased tendency of high purity materials to supercool. Since the liquidus was already reasonably well established, a change in technique to reduce the uncertainty further did not appear justified. The observed values are in good general agreement with earlier values, though averaging slightly lower than those of van Heteren [22].

High tin alloys, 0 to 10% mercury. The results from alloys containing from 0 to 10% mercury are conveniently considered as a group. They cover the alpha, beta, and part of the gamma areas on the diagram (see Figure 3) and were chosen to study the relationship of those phases. This group includes the specimens containing 0, 2, 5, 7, and 10% mercury.

The results on this group of specimens appear to confirm most of Prytherch's [25] diagram for this composition range. Definite arrests were obtained at 223.0 ± 0.5°C and 213.9 ± 0.5°C. These values correspond closely to his peritectic temperatures for the beta and gamma phases. Supercooling was a consistent problem in the cooling curves, as was the attainment of equilibrium in heating curves on annealed specimens. Indeed some of the heating curves were more readily rationalized by an assumption of complete nonequilibrium conditions, that is no interaction between phases. These observations are probably best substantiated by reference to a few examples.

Figure 7 presents the results of a heating run on specimen 27 (5% Hg, 95% Sn). The specimen had been annealed at 85°C for seventy-one days prior to this test. This specimen, as well as the 0, 2, and 7% mercury specimens, showed no thermal effects below 150°C on any heating or cooling run.

The curve shows a heat absorption (shown by a swing to the left) beginning near 173°C and coming to a broad peak at 204°C. As the curve then begins to swing to the right, a sharp change in direction is seen to occur at 208°C showing the onset of an additional energy-absorbing reaction. This reaction continues to 222°C where a very sharp energy absorption occurs which is completed by 223°C with the curve turning abruptly to the right. At 225°C the curve again swings to the left with the maximum differential temperature occurring at 232.0°C. From this point the test specimen heats rapidly toward the reference specimen temperature with the spacing of points indicating that the specimen is completely liquid. The upper portions of the curve are easily identified, although not what would be expected if equilibrium were maintained. The main peak at 232.0°C obviously coincides with the melting point of pure tin and the portion of the curve between there and 225°C with the equilibrium between alpha and liquid. Similarly the very sharp peak at 222-223°C represents the peritectic decomposition of the beta phase. The identification of the remainder of the curve becomes increasingly difficult as lower and lower temperatures are considered. It does not appear possible to reconcile these portions of the curve with Figure 3.

The cooling curve taken after the run of Figure 7 exhibited extreme supercooling with the specimen cooling to 191°C before freezing started. The maximum temperature recorded thereafter was 217.8°C and is certainly well below the true liquidus. A weak peak was observed at 214.4°C but no additional arrests were found down to 155°C. A second heating curve run immediately from that temperature showed only a single energy absorption starting gradually at 199°C and coming to a peak at 222.7°C, above which temperature the specimen appeared to be completely melted.

The strong tin arrest and the lower temperature arrests observed in Figure 7 seem therefore to be the result of the prolonged annealing performed prior to that test. The formation of a coarse-grained two-phase structure containing an alpha phase of low mercury content could account for the 232.0°C peak, but some modification of the gamma region is required to account for the other arrests. This modification will be discussed in more detail later in connection with other related evidence. The curve of Figure 7 is presented at this point primarily because of its strong indication of a peritectic reaction at 223°C.

Figure 8 presents the results of a heating test on specimen 65. This specimen contained 10% mercury and had been cooled from the liquid and then held at 190°C for sixteen hours immediately before the start of the test. This curve showed a strong energy absorption ending abruptly at 213.6°C, which is interpreted as the gamma peritectic temperature. A second inflection occurring at 216.4°C is interpreted as the liquidus and confirmation is offered by the spacing of the observations above and below this temperature. The superimposed absorption which occurs between 195°C and 200°C is interpreted as an alpha plus gamma reaction producing a limited amount of beta.

The heating curves for specimen 28, the 2% mercury alloy, showed arrests at 223°C and 232°C in the annealed condition, and a 223°C arrest and a 230.1°C liquidus in non-annealed samples. The 7% mercury sample showed repeated indications of the 214°C arrest on both heating and cooling.

As mentioned above, all of these alloys showed a marked tendency to supercool. In the instances when the supercooling carried the specimen past a peritectic temperature, there was some tendency for the lower temperature phase to nucleate preferentially with the temperature rise then extending only to the peritectic temperature. This phenomenon was most commonly observed in the 2 and 10% mercury alloys.

When such specimens were cooled to 150°C and then reheated without annealing, the heating curves showed only the gamma peak in the 10% alloy and the beta peak in the 2% alloy. As far as could be determined, the liquidus coincided with these peaks.

If the composition limits of the beta phase as given in Figure 3 are correct, the solid formed under these circumstances in the 2% mercury alloy should have been quite unstable. Nevertheless, in one instance this specimen was below 198°C for two and one-half hours without any apparent decomposition of the beta structure to alpha and gamma.

While the thermal analysis results on this group of specimens has quite effectively confirmed the beta and gamma peritectic temperatures, it has done little to verify the composition limits of these phases. The curves for some runs with long annealing times indicate a possible need for a revision of the tin-saturated boundary of the gamma region of Figure 3.

High mercury alloys, 18 to 80% mercury. As a group, these alloys produced a surprising number and variety of thermal effects. Some of these were strong, routinely detected arrests, while others were much weaker and appeared much less consistently. Of these arrests, some are definitely associated with phase changes, but others may be artifacts or due to second order effects such as super-lattice formation or even specific heat anomalies in a single phase. The stronger the arrest and the more often it was obtained, the more precisely can its temperature be determined. Table 7 lists the temperature of each arrest found and the estimated uncertainty of the determination. It also indicates the composition range of the specimens for which the arrest was detected and, where possible, identifies the associated phase with the type of reaction causing the arrest. A series of figures is presented to indicate the type of results upon which the values of Table 7 are based.

Figure 9 shows a heating curve obtained on the specimen containing 18% mercury, specimen 24. This specimen had been annealed for ninety-eight days at 37°C prior to this test. It shows an energy absorption starting at approximately 51°C and ending abruptly at 91.6°C. The single point at 95°C is in accord with a rapid approach to equilibrium with the furnace following a phase change, but the sharp reversal at that temperature is a unique observation found only in this instance. There is some evidence of weak thermal effects of some sort near 105°C and 119°C, but the overall effect is an energy absorption increasing to a peak at 203.0°C. Immediately above this temperature the specimen is still not melted, nor can the liquidus be determined from this curve.

Figure 10 shows a heating curve on specimen 20, which contains 29.9% mercury. The specimen was held for 15 hours at 25°C before this test. The initial swing to the left as heating starts is merely and adjustment of the specimen to the heating rate. The inflection in the curve near 54°C indicates the start of a heat absorption that continues until about 107°C, where the curve again stabilizes. A second inflection occurs near 120°C and the differential temperature then increases to a peak at 189°C. The indicated liquidus temperature is 195°C. The heating rate on this specimen was approximately 1.5°C per minute, and this causes uncertainty in the determinations by increasing the spacing between points and rounding the changes of direction.

Figure 11 is a heating curve on the same specimen after annealing for ninety-three days at 60°C. This test was performed at a much slower heating rate than the previous one, 0.5°C per minute. Both the increased annealing and the slower rate should serve to sharpen the arrests. The lower inflection in this instance appears at 65.9°C and a sharp peak occurs at 90.8°C. From this point the observations continue a trend toward zero temperature difference until the test was interrupted at 103°C. One subsequent reading taken some sixty minutes later indicates that some additional energy absorbing reaction must occur between 103°C and 121°C.

Figure 12 is a heating curve from a test of specimen 73 after thirteen days annealing at 37°C. This specimen contains 40% mercury. This curve indicates the start of two arrests at 56.0°C and 107.7°C and the end of another at 160.8°C. The liquidus is not readily apparent.

Figure 13 is a cooling curve from a test on specimen 74 containing 60% mercury. This test was performed immediately after the completion of a heating run and the liquid was apparently incompletely homogenized, because the indicated liquidus is too high. Once solidification has started, however, it continues producing a differential temperature maximum at 118.8°C. A discontinuity occurs with a sudden heat evolution at 107°C. The specimen then cools smoothly to 97°C where a heat evolution starts which continues to 88°C. No further arrests were noted from there to the end of the test at 67°C.

In contrast to the preceding figure which shows no supercooling, Figure 14 presents the data from a test where the supercooling amounted to about 15°C. This test specimen was number 18, with 70% mercury. The curve shows two separate arrests below the liquidus occurring over ranges of 99°C to 90°C and 68°C to 62°C.

A second cooling curve on specimen 18, from a test run in which supercooling did not occur, is presented in Figure 15. This curve shows a liquidus value of 118.5°C and exothermic peaks at 117.6°C and 102.4°C. An additional arrest, not well separated from the latter, occurs between 92.8°C and 88.6°C. No additional arrest was found above 72°C.

Discussion

The results obtained on thermal analysis of the samples containing from 18 to 80% mercury indicate the occurrence of an unusually large number of arrests. To explain all of the observed arrests as phase changes would require an extremely complicated diagram, particularly when it is recognized that all of the required phases must almost certainly contain less than 30% mercury.

Of the arrests observed, four seem most likely to be identified with phase transformations, those at 118.0°C, 106.1°C, 91.4°C, and 67.1°C. Each of these arrests are relatively strong, appear in both heating and cooling curves and in specimens over a considerable concentration range. In at least one instance each, these arrests have appeared as sharp discontinuities of the type normally associated with peritectic decompositions. The remaining arrests are deficient in one or more of these qualifications.

The arrest at 55.5°C was not definitely detected on cooling, although it appears strongly and repeatedly on heating, as seen in Figure 12. There are several reasons for this lack related to the nature of the system and the experimental technique. Since no auxilliary cooling was used in conjunction with the furnace, the low temperature limit of the system was about 25°C. As this limit was approached the cooling rate became less and less and the technique more tedious. As a result, cooling curves were rarely pursued below 50°C and often not below 60°C. As a result, the total number of tests on which this arrest could have been observed was reduced. The slow cooling rate increases the minimum heat that can be detected, because a given quantity of heat released over a longer time interval will produce a smaller change in differential temperature.

Cooling curve arrests are most pronounced when the phase of interest is the first or second formed from the liquid on cooling. Because of the shape of the mercury-tin liquidus this condition is met for this phase only in alloys of very high mercury content where the total amount of solid formed is small and the latent heat is thus reduced. Annealing to equilibrium just above the anticipated temperature of the arrest is the preferred method of procedure, but the annealing time required for the last of a series of peritectic phases can be very long.

Altogether, the thermal analysis evidence for this arrest representing a pnase transformation can be rated no more than a strong possibility.

The evidence for the arrest 203.5°C is based on heating curve evidence of the sort seen in Figure 9. It has failed to appear in any of the cooling curves where it would be expected if it represents a peritectic temperature.

As noted in the comments made relative to Figure 7, it appears in many instances that when annealing conditions have been such as to produce a coarse structure, the phases formed during low temperature annealing tend to persist to their melting points, with little evidence of interaction below that point. The arrest at 203.5°C is believed to be an artifact of this type.

If, for example, at the annealing temperature a coarse-grained phase were formed differing only slightly from the gamma phase in mercury content, on heating to its peritectic temperature it should decompose to gamma and liquid. Because of the small composition difference, the liquid formed would be small in amount and might well appear as a fine dispersion within the gamma structure produced by the decomposition.

Due to the lack of stirring, it is possible that this internal liquid could remain isolated from that outside of the original grain. Under these circumstances the material within the original grain might produce a liquidus arrest typical of its own composition rather than that of the specimen as a whole. The composition of the original structure predicted by this mechanism, as determined by the observed liquidus, is approximately 20% mercury.

Similar logic could be applied to the other arrests, but some of the calculated mercury contents appear too high. The mercury content of an alloy with a 198°C liquidus is approximately 27%. However, this arrest has appeared on cooling curves where the proposed mechanism is impossible. There are several other possible causes for these arrests, such as anomalies in either the specific heat or heat of solution of an existing phase, or a rapid change in slope of a two-phase boundary. In the absence of sufficient data to identify the true cause, they are merely recorded in Table 7 as unidentified.

The arrests observed in low mercury alloys appear to confirm the diagram for the high temperature regions as proposed by Prytherch [25], although the temperatures themselves are in better agreement with those of Hansen [11]. The results of the beta eutectoid temperature determinations may serve as confirmation of the reported value, but are probably inadequate as an independent determination. The liquidus values are in general agreement with earlier results, and do not appear to require discussion beyond that which they have already received.

In calibrating the equipment, an attempt was made to identify and evaluate the various factors which affected the observed differential temperatures. Of particular interest was the size of the temperature differences between the test specimen and the furnace, between the reference specimen and the furnace, and along the furnace tube. It was necessary to investigate the effect of technique variables, such as the relative positions of the specimens and the heating rate, upon these temperature differences, in order to eliminate the possibility of misinterpreting furnace effects as phase changes.*

2.3 Diffusion and Chemical Analysis

General Considerations

The use of diffusion and chemical analysis as an experimental method for the study of silver-tin amalgams appears to offer several advantages. One of the most important of these, relative to their dental application, is the simulation of the normal conditions of use of dental amalgams, where hardening occurs by diffusion at body temperature. Diffusion studies should thus be expected to provide information relative to the setting mechanism for these alloys as well as contributing to the understanding of the constitution of the mercury-silver-tin ternary system. This experimental technique also avoids the metastable persistence of high temperature phases that is a common problem in peritectic systems. Murphy [13], in his study of the silver-mercury system, for example, found that the gamma phase was readily formed by the diffusion of mercury into finely divided silver, but that it was completely suppressed by cooling from the liquid state. In particular, because of the high rates of diffusion of mercury into tin reported by Prügel [46] among others, this method appeared particularly suited to the study of the mercury-tin system.

With these advantages in mind, a series of experiments was performed in which ingots of tin and silver were exposed to liquid mercury for varying periods, annealed and then serially sectioned and analyzed. The exposure temperature and time and the annealing time were varied systematically.

Specimen Preparation

The individual specimens used for the diffusion studies were small cylinders approximately 0.65 inch in diameter and 0.40 inch in length. They were machined from induction-melted,

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* Portions of the original manuscript have been omitted at this point.

cast ingots slightly larger in diameter and three to four inches in length. The tin ingots were prepared by vacuum melting in pyrex, while the silver bars were melted in air and chill cast in an aluminum mold. All of the ingots were prepared from the high-purity silver and tin with the exception of a limited number of the initial tin ingots. These were made from Baker and Adamson Reagent Grade Tin Sticks, of the composition given in Table 3.

Under the conditions of the test no differences in behavior could be detected between specimens made from this metal and from the higher purity tin.

The cast ingots were turned in a lathe to remove any surface imperfections and were then cut into cylinders approximately 0.40 inch in length. Any cylinders showing signs of piping or porosity were rejected, and the remainder were weighed and measured as a means of detecting gross internal porosity. If the specimens were stored before exposure to mercury, their surfaces were cleaned immediately before use by a light polishing on 600-grit silicon carbide metallographic paper.

Experimental Procedure

The specimens were exposed to mercury by immersion in saturated mercury solutions at constant temperature. Four nominal temperatures were employed for the tin specimens, 37°C, 60°C, 85°C, and 110°C, while silver specimens were tested at 37°C, 85°C, and 190°C.

In order to avoid excessive initial dissolution of the specimens, saturated solutions of tin in mercury and silver in mercury were prepared at each diffusion temperature. A sufficient quantity of the appropriate solution was placed in a 10 ml. pyrex beaker, the specimen was added, and a perforated cork was pressed down until liquid was exuded through the holes. The beaker was then placed in an air bath at the selected exposure temperature.

A set of four laboratory ovens, differing somewhat in design and temperature control, was used for this purpose. The best oven maintained the nominal temperature with an indicated variation of ± 0.1°C, while the worst varied as much as ± 0.6°C over a single heating cycle. However, it was found possible to reduce the variation in temperature of the specimen itself to less than ± 0.1°C in all cases, by placing the beakers within vacuum dessicators, which were in turn placed within the oven.

Of somewhat more importance was the observed tendency for the mean temperature of the ovens to drift gradually away from the intended temperature over a period of weeks. No way was found to suppress this drift except repeated resetting of the regulators. The maximum error from this cause is believed to have been held to 0.4°C.

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 of 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 before sectioning.

All sectioning was done on a lathe. The specimen was held in a collet and the lateral surface turned down until unreacted tin or silver was exposed. A series of samples was then taken from the mercury containing layer remaining on the end of the specimen. The depth of cut used in taking the samples varied from specimen to specimen, being adjusted so as to provide a minimum sample of eighty milligrams. These samples were then stored at room temperature until analyzed for their mercury content.

Mercury analysis was performed by a modification of the technique of Crawford and Larson [47]. Initial attempts to follow their method produced inconsistent results for tin-mercury samples, apparently due to oxidation of the metal remaining after the mercury was driven off. In all probability this reflected in part a lower tolerance for oxygen due to the small sample size employed as well as decreased resistance to oxidation of tin relative to the high silver dental alloys.

It was found possible to avoid most of the difficulty by elimination of the carrier gas stream. Samples to be analyzed were weighed into porcelain combustion boats previously dried to constant weight. The boats were then transferred to a pyrex tube which could be inserted into a horizontal, electric, tube furnace. One end of the pyrex tube had been sealed previously, and, after the combustion boats were placed within it, the other end was closed with a stopper bearing a three-way stopcock. This permitted connection of the system to a vacuum line and a tank of super dry nitrogen so that the air could be flushed out of the tube. The tube was evacuated to a total pressure of five to ten millimeters of mercury and then refilled with nitrogen. This process was repeated at least five times before the valve was finally closed with the tube in the evacuated condition.

The base of the tube furnace was partially plugged so that, when the sealed end of the pyrex tube was inserted into the furnace until it contacted the plug, the boats were centered in the hot zone of the furnace. The furnace was maintained at a temperature of 500°C at the location of the combustion boats, and the samples were left in the furnace for one and one-half hours. At the end of this period the pyrex tube was slid from the furnace and allowed to cool to room temperature before the vacuum was relieved.

The mercury distilled from the specimens condensed on the cool portion of the tube remaining outside of the furnace, and was removed mechanically before the combustion boats were withdrawn for reweighing. This procedure retained the advantage of the Crawford and Larson [47] technique in that the mercury content was determined as weight loss in the specimen rather than requiring the collection and determination of the mercury driven off. At the same time it minimized oxidation problems due to either leakage or trace contamination of the carrier gas.

All weighings were performed on the balance described in the section on thermal analysis. Calibration runs were made on pure tin and pure mercury samples as well as control samples of known composition. The results indicated that the preponderant source of variation was due to the combination of the small sample size with the limit of weighing precision. The observed standard deviation for individual mercury determinations is approximately 0.15% mercury.

Table 8 shows the conditions of test for all the specimens studied with the exception of calibration runs, specimens tested during the development of the methods, and some few specimens lost due to experimental error. The specimens are grouped by type (tin or silver) and by temperature. The immersion and annealing temperatures were the same for all tin specimens annealed at 37°C and 60°C. In the case of the tin specimens annealed at 85°C and 110°C, however, it was found to be expedient to perform the immersion at 37°C prior to annealing at the higher temperatures.

This procedure was necessitated by the unfortunate results produced when attempts were made to immerse a tin specimen for any extended period at either 85°C or 110°C. Such attempts led to the rapid conversion of the specimen and mercury to a slushy mass of platelike crystals dispersed in the remaining liquid. This process was quite rapid. In some instances a specimen immersed at these temperatures would be completely dispersed in less than twenty-four hours.

One possible explanation for this behavior would be repeated solution and precipitation due to the residual temperature cycling of the air bath. This possibility is supported by the fact that in this temperature range the liquidus curve of the tin-mercury system is quite flat and consequently small temperature variations lead to sizable differences in the solubility of tin in mercury. The observations could be readily explained if the solution occurred preferentially at the surface of the specimen during the heating portion of the cycle and the precipitation occurred predominantly on the growing crystals. On the assumption that some such mechanism was operating, an attempt was made to avoid or reduce this effect by additionally insulating a beaker containing a specimen and mercury with a half-inch thick layer of pyrex wool. This had no clear-cut effect and the phenomenon was not investigated further.

Since considerable information was available about the effect of immersion at 37°C, it was decided to diffuse mercury into the specimens at that temperature and rely on the subsequent annealing at 85°C and 110°C to produce the equilibrium structure. With such a procedure, of course, the necessary absorption occurs primarily at 37°C and the final distribution curve will provide little direct information about the rates of diffusion at the higher temperatures.

Results

When the specimens were removed from the liquid and blown as dry as possible, their surfaces normally exhibited a fine roughness which under a low-power microscope appeared to resemble cobblestones. The individual bumps tended to be rounded and rarely exhibited anything which could be interpreted as a crystal facet. In a few specimens, mostly those with long immersion times at 60°C, a growth of flat crystals occurred randomly oriented relative to the specimen surfaces. These crystals appeared to be regular hexagons as large as two to three millimeters across and about one-tenth as thick. Whether or not such plate-like crystals appeared, the specimen was always enlarged after immersion.

Except for this general increase in the dimensions of the specimen and the change in surface texture, small amounts of mercury penetration produced no observable changes. As the immersion time was increased, it was observed that a circular crack formed at the intersection of the lateral and end surfaces of the specimen. This crack was propagated as mercury penetration continued until, when mercury reached the axis of the specimen, a cone with a 90° apex angle could be readily separated from each end. Cracks in the lateral surface of the specimens also appeared as the mercury penetration approached the specimen axis.

These cracks appear to form only by widening of intergranular spaces between crystals already saturated with mercury. They were not associated with any local increase in the depth of mercury penetration and probably do not influence the overall rate of reaction.

Figure 16 shows a schematic representation of a specimen after immersion in mercury. Views (a) and (b) are transverse and axial sections and indicate mercury penetration as well as characteristic location of expansion cracks. View (c) is an axial section of a specimen as it would appear after the reduction of the lateral surface preparatory to the taking of samples as serial sections from the end.

The results of the analyses for specimen 20 are presented in Figure 17. It exhibits many features common to all of the specimens and in particular of those sectioned immediately after removal from immersion. Each point on the diagram represents the result of an analysis of one entire sample and is plotted at the mean depth of the sample. The diameter of the points approximates the uncertainties of measurement of each value. The range of depth involved in each sample is indicated by the short bars near the lower margin of the figure.

The curve as drawn through the experimental points shows, as expected, a continual decrease of mercury content with depth. It also appears to consist of four distinct sections which are lettered A through D on the figure.

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.

Section C, indicating a layer of rapidly decreasing mercury content, probably represents a mixture of the phase of section B and with that of section D.

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

Considering the curve as a whole, it seems to show the presence of one intermediate tin-mercury phase. The composition limits of this phase may be estimated by extrapolation of the straight line of section B to the mid-depths of the transition zones. Such an extrapolation (as indicated by the dotted lines in Figure 17) leads to an estimated maximum mercury content 20.3% and a minimum of 18.8%. A similar procedure can be followed for the estimation of the maximum solubility of mercury in tin, by extrapolation of the line in section D, in those cases where more than one non-zero point occurs in that section.

Caution must be exercised in reaching such conclusions, since several possibilities for error exist. Since it has been demonstrated radiographically by Gunther and Jehmlich [48] that the initial penetration of mercury into tin is intergranular, the possibility exists that the mercury content of the points in section B is too high because of the inclusion of such intergranular mercury. 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. Although the individual layers may be extremely thin, it is generally held that a separate layer must be formed for each intermediate phase. Rhines [49], for example, states that, "In binary systems, when diffusion occurs at substantially constant temperature and pressure, the layers formed correspond in kind and in order of their occurrence to the single-phase regions, ... no two-phase regions appear."

If such phases exist undetected in section C of Figure 17 then the proper limit for the extrapolation of the line of section B is to the midpoint of the transformation to the first such phase.

Continued diffusion by annealing at the same temperature after removal from the source of mercury was adopted as a means of checking both possibilities. Under such circumstances, continued diffusion of mercury into the specimen should proceed by the elimination first of mercury-rich liquid and then, in order of decreasing mercury content, of intermediate tin-mercury phases. The limit of this process would be either a one-phase solid solution of mercury in tin, or, if the total mercury exceeded that which the tin could dissolve, a mercury-saturated tin phase covered by a layer of a tin-saturated tin-mercury phase.

The curves for all specimens sectioned immediately after removal from mercury at 37°C or 60°C exhibited similar curves, each showing a single flat. In the specimens immersed at 37°C, however, the extrapolated composition limits were approximately 22.3 and 21.0% mercury. Figure 18 shows the results for one such 37°C specimen, specimen 1.

The difference in indicated solubility limits could represent a difference in the quantity of intergranular mercury, although this would be expected to give more erratic variation with depth. It could equally well represent a shift in the composition limits of a single phase with temperature. As a third alternative, these differing limits could represent two entirely different phases. Other evidence indicates that the third choice is the correct one.

One specimen, specimen 16, immersed and annealed for a short time at 60°C produced a diffusion curve showing both flats. The results on this specimen are presented in Figure 19. As can be seen from this figure, the composition limits for the two phases agree well with those found in Figures 17 and 18.

Protracted annealing at either 60°C or 37°C resulted in the production of curves with a third set of indicated limits of mercury content. Figure 20 is typical of such an experiment. The relatively short immersion time and long annealing time used for specimen 19 have resulted in a complete transformation to the third observed phase. Slightly longer immersion and a short anneal produced steps characteristic of both the second and third phases in specimen 8. The results of the mercury analyses for this specimen are shown in Figure 21.

Because the difficulty encountered in producing satisfactory specimens at 85°C and 110°C forced a modification of experimental technique, no tin specimens were available for sectioning immediately after immersion at these temperatures. The technique employed, immersion in saturated mercury at 37°C and annealing at 85°C or 110°C, would be expected to produce additional liquid throughout most of the mercury-containing zone as the specimen was heated to the higher temperature. Thus the specimens treated in this fashion are apt to be "wetter" than specimens which were annealed at immersion temperature. Nevertheless, these specimens exhibited free liquid on their surfaces for an unexpectedly long time. Whereas specimens annealed at 37°C would be "dry" within twenty-four hours, the specimens annealed at 85°C showed liquid on their surfaces after eleven days. The specimens annealed at 110°C showed persistent surface liquid up to fourteen days. Even then the liquid mercury disappeared only after machining had exposed a fresh tin surface with which it could react. Further evidence of a low rate of diffusion at these temperatures is given in Figure 22. When sectioned after five and one-half months of annealing at 85°C, specimen 26 still showed layers of the second and third mercury-containing phases.

All samples from 110°C specimens which contained more than 18.5% mercury showed the presence of liquid. At this temperature there appears to be only one tin-mercury phase intermediate between the liquid and tin. The composition limits of this phase in-dicate that it corresponds to the mercury poorest of the three phases found at 37°C.

Table 9 summarizes the results for all of the individual tin-mercury diffusion specimens. The composition limits for each observed flat were calculated by the extrapolation procedure used in Figure 17 and are tabulated here in accordance with the presumed occurrence of three intermediate tin-mercury phases. Also included is the total depth to the point at which the mercury content is ten percent.

The composition limits reported in this table should be considered as saturated values only when the equalibrium phase was also present in the specimen.

The results on the silver samples were unsatisfactory and inconclusive. With the immersion time 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 in analysis was too large relative to the thickness of the mercury containing layer to permit valid conclusions to be drawn from the results. In addition, these specimens showed considerable local irregularity in depth of penetration and the samples consequently tended to contain mixtures of phases rather than single phases. For these reasons the subject was not pursued beyond the limited number of specimens indicated in Table 8.

Discussion

The method of constant temperature diffusion followed by serial sectioning and alysis appears to be well suited to the study of the tin-mercury system. The rate of penetration is sufficient to produce samples of sufficient size to distinguish between adjoining phases with readily available analytical techniques.

The results indicate the formation of three intermediate tin-mercury phases at 37°C. For convenience in presenting the results, these phases have been referred to above as the "first," "second," and "third," in order of their depth in the specimen or order of formation during annealing.

The "third phase" appears to correspond to the gamma phase of existing diagrams, since even protracted annealing does not cause the appearance of any phase between it and tin. The "second phase" appears to correspond to the delta phase reported by Gayler [26] and decomposes at an appropriate temperature for such identification. The "first phase" is previously unreported but is here tentatively designated epsilon.

Table 10 presents the composition limits for these phases as determined at each experimental temperature.

As shown in the table, these phases all have narrow and closely spaced zones of solid solubility. The most noteworthy finding is the unexpectedly high minimum content found for the gamma phase. This is in sharp contrast to previously reported limits for this phase which indicated minimum mercury contents of the order of eight percent as seen in Figure 3.

This solubility limit appears to be based primarily on the x-ray diffraction work of von Simson [24] and Stenbeck [15], with some indirect evidence being provided by the results of Løvold-Olsen [50], Schubert et al [28] and Raynor and Lee [27].

It is very difficult in most instances to determine what was the previous thermal history of the specimens used for this work. Von Simson's [24] entire description of specimen preparation is as follows:

> Das Mengenverhältnis der Komponenten--es wird in Folgenden immer in Atomprozenten angegeben--wurde durch Auswiegen der Ausgangsmetalle festgestellt, die zweite Komponente--eventuell unter einem inerten Gas--geschmolzen und das Quecksilber hinzugefügt; die Legierung wurde dann mehrere Male unter Ruhren geschmolzen und schliesslich in Drahtform gebracht. Wo es ging, wurde der Draht gezogen, in einigen Fällen in Glaskappillaren gegossen, die dann vorsichtig abgeklopft wurden; die ganz brüchigen Legierungen wurden im Mörser fein gepulvert und auf einen Seidenfaden geklebt.

Almost certainly in the case of the work of both von Simson [24] and Stenbeck [15] and apparently most other work, the annealing times were inadequate to cause the precipitation of tin from the gamma phase formed on cooling from the liquid. As a result, the composition limits of the gamma phase based on their findings are more indicative of the composition range over which the gamma phase is formed at elevated temperatures than of its equilibrium extent at room temperature. The one possible exception to the charge of insufficient annealing is a specimen of Raynor and Lee's [27] which was annealed for two weeks at 150°C. This specimen contained 7.193 atomic percent of mercury (approximately 11.5 weight per cent), and apparently consisted entirely of gamma. While their paper does not deny the presence of tin lines, neither does it report them as it presumably would had they been observed. Possibly even this annealing time is inadequate or the amount of grain size of the precipitated tin was too small to detect. If not, a rather rapid widening or displacement of the gamma region must occur above 110°C to accomodate this observation.*

Although the method employed here should be applicable to the silver-mercury system, provided that adequate immersion times are used, it seems unlikely that it can be satisfactorily extended to the ternary system. The recent work of Clark and Rhines [53] on ternary diffusion in the aluminum-magnesium-zinc system shows that, where one component is allowed to diffuse into alloys of the other two, substantial deviations in the ratio of the two sedentary components occur. As a result, analysis for the diffusing component alone is inadequate. They found it necessary to identify the phases formed in the various diffusion layers by metallography and x-ray diffraction. Some such techniques would seem to be needed for the silver-tin-mercury system. If adequate phase identification methods were available, a study similar to theirs would seem to offer a very suitable method for investigating the setting mechanism of dental amalgam.

2.4 Microhardness and Metallography

General Considerations

As was indicated in that portion of the introduction devoted to choice of methods, the use of microhardness determinations as a means of identifying particular phases in metallographic specimens seemed to be well suited to the mercury-silver-tin system. An extensive program was initially planned for the use of this method for the investigation of the ternary system as well as each of the binary systems. The plan included samples from each of the one and two-phase regions of the silver-tin and mercury-silver diagrams and a set of fourteen mercury-tin specimens covering the composition range from 2.0 to 21.6% mercury. In addition, twenty ternary alloys were included, with particular emphasis upon the tin-rich portion of the system.

Proper application of microhardness testing for the purposes of this study requires metallographic techniques at least adequate

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* Portions of the original manuscript have been omitted at this point.

to locate grain boundaries. In the case of the mercury-tin alloys and the tin-rich ternary alloys, this need was made more pressing because of the apparent complexity of the mercury-tin system indicated by the thermal analysis results. The experiments in this area (discussed below) were in general unsuccessful and indicated that the mercury-tin phases were inadequately distinguished.

At the same time, the results from the diffusion tests demonstrated the very long time required to attain equilibrium in the tin-mercury system even at elevated temperatures. This led to the conclusion that the annealing treatment of many of the previously prepared microhardness specimens was inadequate.

For these reasons, the original program was drastically reduced to include only those binary specimens where the available metallographic techniques would suffice to determine the adequacy of the annealing, and a very few ternary specimens.

Specimen Preparation

The nominal composition, fusion temperature, and annealing temperature and time for each microhardness specimen is given in Table 11. The specimens were prepared with essentially the same equipment and techniques used for the preparation of the thermal analysis specimens. The only change in technique was the use of simple round-bottom tubes without the thermocouple well and the reduction of the sample size to ten grams total weight.

Each sample was fused by heating to the temperature shown in Table 11 and holding at that temperature for at least two hours. All specimens fused at 500°C and above, and certain of the others which were expected to develop high vapor pressures, were fused in a bomb which maintained external pressure on the tube. The bomb employed was of the type described by Gordon, et al. [54]. As recommended by that paper, external pressure was produced by CO_2 added in the form of dry ice. The equation given for the calculation of the amount of CO_2 needed, however, is not applicable to the temperature range used in this study. Instead, the amounts required were calculated from Van der Waal's equation.

These specimens were cooled by removing the bomb to room temperature conditions and allowing the cooling to proceed by convection to the air. Quenching of the bomb resulted in a more rapid reduction of the CO_2 pressure than of the specimen vapor pressure and normally resulted in loss of the specimen.

The specimens not requiring bomb fusion were heated in a furnace which permitted access to the specimen during the heating process. These specimens were shaken at intervals during the fusion period to foster homogenization.

On removal from the annealing furnace these specimens were quenched in room-temperature water. In some instances this treatment resulted in the fracture of the pyrex tube, but never before the specimen had cooled sufficiently so that it could be recovered intact. All such specimens were resealed in another tube prior to annealing.

After annealing, the specimens were sectioned axially, mounted in acrylic resin, and polished. The polishing technique employed Buehler 240, 320, 400, 600 and 600 soft silicon carbide metallographic papers used with a mineral oil and petroleum jelly lubricant for the grinding operations. The polishing proper was performed with graded alpha and gamma alumina on silk, cotton, and bonded rayon cloths. Because of the need for extended polishing in the final stages, low nap clothes were used to minimize surface inequalities.

This technique produced surfaces free from scratches and apparent distortion for the silver-tin and mercury-silver alloys and for the silver-rich ternary alloys. In the case of the tin-mercury alloys difficulty was experienced in obtaining an undistorted scratch-free surface. Adoption of the diamond lap technique of Eyre and Keysselitz [55] may be necessary to completely eliminate the problem. In most instances the quality of the surface produced, though not perfect, was adequate for phase identification and microhardness tests even in the case of the mercury-tin specimens.

A variety of etchants were used. Among them the most useful for silver-tin alloys were found to be: a) 0.2% each H_2CrO_4 and H_2SO_4, b) equal parts of 10% solutions of KCN and $(NH_4)_2 S_2O_8$, and c) 5% aqueous $FeCl_3$. For mercury-silver alloys, the best were found to be: a) the cyanide-persulfate etchant already listed and b) 10% HCl. The success achieved in etching these alloys appears to be closely related to the technique used. It is most important that the etching be performed shortly after the polishing if the best results are to be obtained. Delay appears to increase the tendency for pitting rather than general attack. The ternary alloys in the silver-rich half of the diagram were etched successfully by the series of etchants proposed by Schmitt [56].

The etching problems with the mercury-tin alloys was one of the main reasons for the de-emphasis of this study. No truly satisfactory etchants for this system were discovered, although a considerable number were tried.

Because of the susceptibility of these alloys to deformation during preparation, it would be desirable to either electropolish them or to remove the distorted surface by alternate polishing and etching. Both of these methods suffer from the same difficulty encountered in obtaining a simple etched surface for examination.

The primary cause of the difficulty lies in the fact that tin is more electropositive than mercury and thus more readily removed by etchants. Tin will also replace mercury in solutions in contact with a tin alloy. The net result is an increase in the mercury content of the remaining alloy if the tin is removed or a surface layer of redeposited but unreacted mercury if the replacement reaction occurs.

All of the etchants recommended by Eyre and Keysselitz [55] and the additional non-electrolytic etchants listed by Kehl [57] were tried unsuccessfully. Additional attempts to suppress the solution of the tin by the use of 10% HCl saturated with stannous chloride and to prevent the redeposition of dissolved mercury by complexing it with ethelene-diamine tetra acetic acid were also unsuccessful.

The best results were obtained by selective staining of the alpha phase with a freshly mixed solution of equal parts of 10% HCl and 10% $Na_2S\cdot 9H_2O$. This darkens the tin-rich crystals in coarse-grained structures. However, it will not stain immediately adjacent to any adjoining mercury containing phase and is thus useless in fine-grained structures.

The etching treatment for all specimens was kept intentionally mild so as not to interfere with the reading of the hardness indentations. An attempt was made to obtain the minimum etching that would permit the placement of the indentations entirely within grains.

Experimental Procedure

The microhardness tests were performed by means of a Kentron Microhardness Tester employing a Knoop indenter and a twenty-five gram test load. The calibration of the system was checked by tes on two hardened steel test blocks. One of the blocks had known hardness values at 25, 100, and 500 gram loads, the other at 500 grams. Comparison tests were made at 25, 50, 100, 200, and 500 gram loads and the variation of apparent hardness with load was found to conform to the results of other similar investigations.

In order to achieve consistent results in agreement with the test blocks at low loads, it was necessary to take special precautions to suppress vibration. By placing one-inch thick wood fiber pads and heavy wooden blocks beneath the instrument feet, it was possible to obtain indentation lengths within 2% of the calibration value at the 25-gram load. This indicates a probable absolute error of 4% in the observed hardness values with the observed values being too low. This source of error should not, however, introduce any relative error between the observed hardness of the various phases.

Results

Some results obtained from the microhardness tests are summarized in Table 12. The values reported for tin and silver and for silver-tin and mercury-silver phases were all obtained on one-phase specimens. The values for the mercury-tin phases were obtained on multiphase specimens. Also included in the table are the findings for one ternary specimen which are included as a limited demonstration of the applicability of the method.

Table 12 lists the mean hardness and percent coefficient of variation for each phase. The percent coefficient of variation is given instead of the standard deviation because it permits a direct comparison of the relative precision of the results for the various phases. For the specimens where the grain structure was readily resolved, the coefficient of variation is presented relative both to the mean value for the phase and to the mean values of the individual grains. This permits some evaluation of the cause of the observed uncertainty of the determinations.

By reference to Table 11, the specimen number for each determination may be used to obtain the analysis and heat treatment of the specimen tested. In evaluating heat treatment, allowance should be made for the fact that these specimens stood at room temperature (18 to 28°C) for periods of several days to several weeks after the end of the formal heat treatment before the hardness determinations were made.

The results on several of the silver-tin and mercury-silver phases deserve particular comment. The coefficients of variation for specimens five and six are considerably higher than those for other specimens. Comparing the two coefficients for each of these alloys, it is apparent that although considerable variation occurs among the determinations on a single grain, the majority of the total uncertainty arises as the result of differences between grains. This latter difference is most probably due to varying orientations of a non-isotropic structure relative to the specimen surface and the indentation axes. In the case of the γ Ag-Sn phase, two sets of five indentations made perpendicular to each other on a single grain gave mean hardnesses of 53.4 and 152.9 KHN_{25}.

The values obtained for individual grains of these two phases overlap considerably but the hardness difference between them appears to be real and in the direction indicated. Where extreme anisotropy occurs, a very large number of individual grains must be sampled to obtain precise means. The number sampled here is almost certainly too small for great accuracy. Inspection of the means for individual grains indicates that most of the values for the $\beta_{\text{Ag-Sn}}$ phase lie near the top of the total range observed, and the reported value may therefore be somewhat high.

In several instances ($\alpha_{\text{Ag-Sn}}$, $\beta_{\text{Hg-Ag}}$, $\gamma_{\text{Hg-Ag}}$) there appears to be no significant difference between the coefficients of variation. In these cases the total uncertainty arises due to differences between readings on single grains. In the case of the $\alpha_{\text{Ag-Sn}}$ phase this should probably be interpreted as evidence for isotropy. However, the high percent coefficients of variation found in individual grains of the other two phases may indicate that some other factor is involved. Stenbeck's [15] finding of considerable variation in lattice parameter across the narrow composition range of the $\gamma_{\text{Hg-Ag}}$ phase might imply a parallel variation of hardness with composition in an apparently homogenous structure.

Metallographic examination of the 2% mercury, 98% tin specimens (specimens 32 and 33) showed grains staining as did pure tin separated by a network of non-staining areas. The binary specimens containing more than this amount of mercury were not successfully stained or etched. The dark areas were presumed to represent tin saturated with mercury ($\alpha_{\text{Hg-Sn}}$) and the nonstaining areas to represent the tin-saturated equilibrium phase, which at the testing temperature is γ Hg-Sn.

Although no microstructure could be revealed in specimen 40, two distinct types of indentations were observed which were readily distinguished by their appearance. One showing smooth concave margins gave hardness values coinciding with the α Hg-Sn values from specimens 32 and 33. The other type had irregular margins and hardness approximating that of $\gamma_{\text{Hg-Sn}}$.

Since the available metallographic techniques did not permit the demonstration of grain boundaries in the $\gamma_{\text{Hg-Sn}}$ phase, the coefficient of variation relative to the means of individual grains could not be determined, nor could it be conclusively demonstrated that the measurements were made on one-phase areas, although other considerations made it highly probable. The results on the other mercury-tin specimens are not presented here, for the reasons discussed above, but it is important to note that in none of the limited tests performed on these alloys were measurements obtained indicating a structure significantly harder than that of the gamma phase reported here.

The results of the tests on specimen 55 are included as an example of the possible application of the method to ternary compositions. This specimen showed on microscopic examination a structure consisting mainly of needlelike dendrites in a uniform matrix.

However, in a few places small areas of a third phase appeared as isolated "islands." These "islands" constituted one to two percent of the section and were invariably surrounded with a ring of the same phase that made up the dendrites.

From the lack of attack on the matrix by the etchants, it appeared likely that the matrix was a tin-mercury phase. Similarly, the dendritic structure implied a higher fusion temperature than the matrix. By reference to Gayler's [26] and Stenbeck's [34] diagrams, these phases could be tentatively identified as γ Hg-Sn and β Hg-Ag-Sn respectively. This left the identification of the "islands" to be completed. The hardness tests for this specimen accomplish this readily. The matrix hardness corresponds closely to that of γ Hg-Sn, the hardness of the dendrites fits reasonably between the binary beta values, and the hardness of the islands matches that of silver. It is thus concluded that the fusion temperature was too low or the time too short to completely dissolve the silver.

Since the specimen composition is nonuniform, it is of reduced value for determining phase boundaries. Perhaps, however, the fact that the matrix hardness is identical to that found for binary γ Hg-Sn may be construed as indicating negligible solubility of silver in the gamma phase.

Discussion

The findings of the microhardness studies, even limited as they are, seem adequate to confirm the usefulness of the method in at least certain regions of the ternary system. It may be impractical to attempt to distinguish γ Ag-Sn from β by this technique, but the method should be of great value in the β + γ Hg-Sn and β + γ Hg-Sn + γ Ag-Hg areas and for many binary regions.

These results make it appear likely that the hard phase which Gayler [26] identified on her micrographs as γ_2 was in reality γ_1 (γ Ag-Hg). Interpreting it as such makes it easier to reconcile her boundary for the beta phase with that of Stenbeck [34].

Similarly, the hardness values of Table 12 for the mercury-tin specimens seem to indicate the need for revisions in the low mercury areas of the mercury-tin diagram. Among the portions in apparent need of revision is the tin-saturated boundary of the γ Hg-Sn region.

The occurrence of α Hg-Sn in specimen 40 is an obvious indication that this boundary must lie at mercury contents greater than 12.00% mercury at 85°C. Just how much greater is difficult to estimate in the absence of an adequate technique for metallographic estimation of the relative amounts of the two phases. Conceivably the proportion of the phases could be estimated from the hardness measurements if a sufficient number of randomly placed indentations were measured. From the relative ease in finding α Hg-Sn areas in this specimen it would appear that the boundary must lie at fifteen percent mercury or above.

Another portion of the mercury-tin diagram that may require revision on the basis of these results is the beta eutectoid temperature. If Figure 3 were correct as drawn, specimen 33, which was annealed at 190°C should have had a coarse-grained alpha and gamma structure at the annealing temperature and should have retained it on cooling to room temperature. The amount of γ Hg-Sn should be much smaller than that of the α Hg-Sn, and if the low-mercury boundary of the gamma phase curves as indicated by specimen 40, it should precipitate secondary α Hg-Sn on cooling.

Specimen 32 should have consisted of approximately equal parts of alpha and beta at the annealing temperature, and on cooling the beta should decompose to alpha and gamma and the gamma should precipitate further alpha on cooling.

The results on specimen 33 agree with these predictions to the extent that they can be tested, although the precipitated alpha phase was not detected. In contrast, it is difficult to fit the results on specimen 32 into the proposed scheme. The amount of coarse-grained alpha appears too great and the hardness of the unstained areas is too uniform to expect them to be the result of a doubly decomposed beta phase.

It is possible that the alpha formed on cooling is preferentially deposited on preexisting alpha grains or that nearly complete coalescence of the precipitated alpha occurs at room temperature. Neither appears likely. The alternative, that the eutectoid temperature lies above 210°C, is almost equally unacceptable. Perhaps this is excessive emphasis to place on a single specimen, but it must certainly be considered as evidence against the indicated eutectoid temperature.

2.5 X-ray Diffraction

Specimen Preparation

X-ray diffraction patterns were obtained on a total of twenty mercury-tin specimens with mercury contents ranging from 5.0% to 22.1%. The specimens were prepared by two different techniques, with fourteen of them being derived from diffusion specimens while the remaining six were fused and annealed.

The technique employed in the preparation of the specimens by diffusion was identical with that by which the samples were obtained for mercury analysis. The samples which were used for the diffraction studies were selected, on the basis of the analyses of other samples from the same diffusion specimen, to provide evidence about the structures of the phases found in diffusion studies. The mercury content of these specimens was determined by interpolation of the composition-depth results from adjacent analyzed samples.

The remaining six specimens were prepared by sealing weighed portions of the component metals in a pyrex tube in vacuum or an inert gas atmosphere. The alloy was fused at 250°C, and quenched. The ingot was then annealed for a short period in the tube. After removal from the pyrex tube the specimen was reduced to a coarse powder by turning on a lathe.

This procedure was intended to correspond approximately to the specimen preparation techniques used by previous investigators, although, as noted above, the information as to the exact techniques they used is often incomplete. The annealing times used in this study appear to exceed those of Stenbeck [15] and von Simson [24] but are less than those used by Raynor and Lee [27].

The composition and source of the x-ray diffraction specimens produced by diffusion are listed in Table 13. The composition and heat treatment of the x-ray diffraction specimens produced by fusion are given in Table 14.

Experimental Procedure

All of the diffraction patterns were obtained on a Norelco X-ray Spectrograph using copper $K\alpha$ radiation. This instrument is equipped with a goniometer having an auxiliary rotating device which rotates the specimen about an axis perpendicular to its surface throughout the test. This rotation produces more uniform curves when the specimen is small, as were the majority of those used in this study.

The specimens were prepared for the tests by sprinkling the particles onto a thin layer of petroleium jelly spread on the surface of the plastic mount. The diffraction curve was run over the range from 20° to 165° 2θ at a rate of 1° 2θ per minute, with a chart speed of one-half inch per minute. This scanning rate and chart speed were found to produce very satisfactory curves with good resolution.

Even at 2 θ angles as low as 65°, the α_1 and α_2 peaks were normally resolved on the curves from specimens prepared by diffusion. At 2 θ angles above 110° they were often resolved to the background level. The resolution was somewhat poorer on cast specimens with the α_1 and α_2 lines routinely resolved only above 80° 2 θ.

Results

The results of the x-ray diffraction tests on the specimens produced by diffusion correlate closely with the mercury content. Those specimens having mercury contents between 21.0 and 22.2% mercury, that is specimens selected from "first phase" regions of diffusion specimens, uniformly produced curves of the type shown in Figure 24. This curve was obtained from specimen number 3 and is readily indexed as a simple hexagonal structure with the parameters reported by Raynor and Lee [27] for the gamma mercury-tin phase. The individual peaks in Figure 24 are labeled on this basis.

In addition to the mercury-tin lines, there appear in Figure 24 a set of lines labeled M. These lines have been traced to the resin used as a specimen support, and they appear only on those curves where the specimen was too small to cover the support completely. Test curves on the specimen support alone show peaks at each of the indicated angles and also very nearly at the angles where the 001 and 002 peaks occur.

Although the diffraction curves were run from 20° to 165° 2 θ, only the portions between 25° and 80° are reproduced here. Most of the changes of interest occur within this interval, and restricting the range greatly increases the clarity of the illustrations.

All of the specimens taken from "third phase" portions of diffusion specimens (17.8 to 18.6% mercury) gave diffraction patterns similar to Figure 24 except for the almost complete suppression of the 001, 002, and 003 peaks. Minor changes occur in the peak heights of other lines but these are the most characteristic. All of the lines which are present appear at the same angles as in Figure 24.

Specimens having mercury contents between 18.6 and 21.0% gave patterns in which the ratios of the 001, 002, and 003 lines to the 100, 200, and 300 lines respectively increased approximately in proportion to mercury content.

Figure 25 shows a curve derived from specimen 10 which contained 18.72% mercury. Even this small amount of mercury in excess of the 18.6% limit has caused the reappearance of the 001 peak, although the 002 peak cannot be distinguished from the diffuse peak due to the support. More mercury increased the relative height of these peaks but in no instance did the 001 or 002 line of a "second phase" specimen exceed eighty percent of the peak height of the 100 or 200 line. In contrast, in all of the "first phase" specimens the 001 and 002 lines were stronger than the associated 100 and 200 lines.

Table 15 presents a summary of the x-ray diffraction findings on diffusion samples with the specimens rearranged in order of mercury content. Only three specimens appear to merit further comment. Specimen 9 appears out of place. Its composition and source place it as a "second phase" specimen, but its x-ray diffraction pattern showed 001, 002, and 003 lines among the strongest found. The cause of this conflict is not known.

The mercury content of specimen 6 similarly appears to be too low for the observed pattern. In this case, however, the mercury content is probably at fault. This specimen was the only one tested without sectioning, so that the pattern was obtained from the surface of the intact specimen rather than from a powdered layer. The mercury content was estimated from the composition-depth curve for the opposite end of the ingot.

On the basis of its composition and the shape of the diffusion curve, tin lines were expected in the pattern of specimen 11. They were not found. Inspection of the sample showed it to consist of two obviously different types of particles, one fine and granular, and gray in color, the other small, curled chips more nearly white in color. The mercury content of the mechanically separated chips was found to be about four percent. If this mercury were distributed as a thin surface layer of a tin-mercury phase, it might cover the tin and explain the absence of tin lines.

The x-ray diffraction patterns from the cast and annealed specimens showed a somewhat similar dependence upon mercury content as shown in Table 16. In no instance was the pattern of the cast specimens of the type which has been called "complete hexagonal" in the diffusion specimens. It is believed that the short time at a low annealing temperature was inadequate to resolve a mixture of phases produced on cooling. The occurrence of tin lines in specimens 19 and 20 seems to indicate that the annealing of these specimens has been more nearly adequate.

In contrast, tin lines are absent from the patterns for specimens 17 and 18, which were somewhat more thoroughly annealed.

This absence might have several interpretations, which will be discussed in the following section.

Discussion

The results of the x-ray diffraction studies provide no dramatic and conclusive evidence for the establishment of new phases in the mercury-tin system. They do, however, provide considerable corroboration for the results of the diffusion and analysis techniques. Probably most important, they offer some hope of reconciling the somewhat divergent findings of the other investigators who employed x-ray diffraction techniques.

The results of this study indicate the existence of two or more phases between 17.8 and 22.2% mercury which have hexagonal structures at normal room temperatures. Although several specimens were tested with compositions in the immediate vicinity of that for which Stenbeck [15] reported a line doubling which he attributed to an orthorhombic structure, no evidence of such a structure was found. Since the gamma phase is reported to extend to much lower mercury contents at elevated temperatures, it is conceivable that his results were the product of lattice parameter variations caused by variation in mercury content in unannealed specimens. He does not report any annealing treatment for his specimens.

The structure found for diffusion specimens with 21.0 to 22.2% mercury can be easily considered to be a simple hexagonal with one atom per unit cell as reported by von Simson [24]. So also can most of the structures containing 18.7 to 21.0% mercury which were labeled "transition" structures. However, the structure in equilibrium with tin at room temperature, the "incomplete hexagonal" in which the 00X lines are missing, cannot be explained with such a simple structure. No alternate structure is proposed, but it is obvious that in order for such lines to be suppressed, a more complex unit cell is required. A doubling of each of the lattice parameters results in a cell with eight atoms, which offers an attractive possibility of a seven-to-one ratio of atoms. The equivalent weight percentage [19.4] falls in the region of interest.

The problem remains as to why the structure in equilibrium with tin has been reported as simple hexagonal if these lines are absent. One possibility is related to incomplete annealing. As seen in the case of specimen 16, a composition which in a diffusion specimen would result in the complete absence of the 00X lines, does not do so in a cast specimen even after a short anneal. Cast specimens containing 8 to 14% mercury, as von Simson's [24] did, might well produce at least some of the phase responsible for these lines and show a "transition" pattern. It is of interest to note that she reports the 001 line as weak and that she found the 002 line on only one side of the film.

No previous investigator seems to have studied a specimen in the narrow range of 17.8 to 18.6% mercury. Even so, extended annealing would apparently be required to produce a uniform structure in cast specimens. It is a matter of some concern that Raynor and Lee [27], who investigated a specimen annealed for two weeks at 150°C with 7.193 atomic percent mercury (11.5 wt.%) did not report the absence of these lines. This specimen lies between specimens 17 and 19 in composition and was annealed at approximately the same temperature for a longer period. The only possibility seems that they may have relied on the agreement for the other lines and not reported the absence. They make no report of the relative intensity of the observed lines or of the occurrence of tin lines.

The occurrence of tin lines in the pattern of specimen 19 but not those of specimens 17 and 18 needs to be considered. Since the annealing conditions were more thorough for the latter specimens, it is tempting to assume that, where specimen 19 indicates a displacement of the gamma phase to higher mercury contents, specimens 17 and 18 fall within the gamma region.

If the gamma region is as curved as the diffusion results indicate, some allowance must be made for the possibility that the tin in specimen 19 precipitated at room temperature after the anneal but before the test. On this assumption, the absence of tin lines in specimens 17 and 18 may merely indicate that it is too small in amount or too finely divided to show.

The same possibility, of low temperature transformation, implies that the findings on these specimens do not preclude the existence of a different structure at the annealing temperature, as might be inferred from the thermal analysis results.

Obviously high temperature diffraction studies would be needed to check this possibility. The work of Schubert et al. [28] covered this range, but their annealing times were inadequate and led them to miss the existence of the beta phase.

2.6 Proposed Tin-Mercury Diagram

The proposed tin-mercury diagram based upon the findings of this study is shown in Figure 26. An enlargement of the tin-rich end of the diagram is shown in Figure 27.

In drawing the boundaries in the diagram an attempt has been made to reconcile the results from the various test methods and the findings of previous investigators. Where conflicts occur between the different sources an attempt has been made to allow for the relative uncertainty of the individual findings.

The liquidus curve essentially follows that of van Heteren [22] except that it has been lowered slightly in the alpha + liquid and beta + liquid regions where he had no observations. This lowering is based on the thermal analysis results of this study and appears to agree with Prytherch's [25] results in the same region. The alpha phase boundaries are based mainly on those as drawn by Hansen [11]. The maximum solubility of mercury in tin has been indicated to be one percent by van Heteren's [22] electrode potential measurements, and the thermal analysis and metallographic results of this investigation confirms that this limit must be less than 2.0% mercury. There appears to be no other applicable data.

The existence of beta phase at elevated temperature appears to be well established. Our thermal analysis studies confirm Prytherch's [25] finding of a peritectic arrest although the value obtained is slightly lower than that of Figure 3. The only evidence against the occurrence of this phase was the work of Schubert et al.[28] which apparently was in error because of inadequate annealing of the specimens. In a note added in publication, they acknowledged that Raynor and Lee's [27] results were conclusive.

Although the existence of this structure is quite certain, the composition limits are unsupported by experimental data. As drawn in Figures 26 and 27, they merely follow Figure 3 for lack of any better information. The limits appear reasonable and are not contrary to theory.

The beta eutectoid temperature is very poorly established. As discussed in the individual sections, the thermal analysis results appear to confirm, while the metallographic results deny, that the 198°C value of Figure 3 is approximately correct. Indeed, if reliance is placed upon the location of the experimental points in Prytherch's [25] diagram, as noted in the comments on Gayler's [26] paper, this temperature was never established experimentally. For lack of other evidence, it is indicated here at 197°C on the basis of the thermal analysis results.

The gamma peritectic temperature of 213.9°C also is based on thermal analysis results and agrees well with Hansen's [11] value of 214°C. The composition of the gamma peritectic is set at 9% mercury primarily on the basis of x-ray results of von Simson [24] and Stenbeck [15]. Since their results can be explained only on the basis of incomplete annealing at low temperature, it is perhaps risky to assume that their specimens were at equilibrium above 200°C. From the liquidus values it is obvious that this point must be at 14% mercury or less, but there is no evidence for a location other than the one indicated.

The remainder of the gamma region has been considerably altered. The tin-saturated boundary has been moved to agree with the results of the diffusion studies below 110°C, as has the mercury-saturated boundary. Between 110°C and 197°C the tin-saturated boundary has been drawn to allow for the x-ray diffraction results on cast specimens. The mercury-saturated boundary above 110°C has been drawn arbitrarily since no data are available in this region.

The overall picture of the gamma region as a narrow band swinging to higher mercury contents at lower temperatures is somewhat unusual because of the size of the swing relative to the width of the region. This construction serves nicely, however, to explain certain heat absorptions that occur in low mercury content thermal analysis specimens. In many instances the specimen had been annealed at an elevated temperature for a while before the start of the run. Portions of the specimen should thus have consisted of gamma saturated with tin. If the proposed diagram is correct, these portions would soon be heated across the gamma region and liquid would start to form with an absorption of heat. One example of this type of reaction is seen in Figure 7.

Two additional peritectic phases labeled delta and epsilon are shown on the diagram. They are located on the basis of the combined thermal analysis and diffusion results. The delta phase was present in 85° diffusion specimens but not in 110°C specimens. It is thus readily associated with the 91.4°C arrest observed on thermal analysis. This thermal arrest is very strong and coincides with that found by Gayler [26].

The epsilon phase composition limits are similarly set from the observed composition range for the "first phase" in diffusion specimens, and are even more certain than those of the delta region. The peritectic temperature is not so definitely known. The arrest found on thermal analysis at 67.1°C is strong and well defined and seems certainly to represent a peritectic temperature. If this temperature is associated with the epsilon phase, however, "first phase" layers should have routinely appeared in the 60°C diffusion specimens but did not.

The arrest at 55.5°C is less well defined, since it was found on heating curves only. Nevertheless, if the uncertainty range for this arrest is stretched to its maximum, it is easier to accept that one 60°C diffusion specimen was two degrees cold than that all of the others were regularly five degrees too hot. As a result, the peritectic temperature of the epsilon phase is indicated as 58°C.

The peritectic phase at -34.6°C found by van Heteren [22] and placed by Prytherch [25] at $HgSn_3$ has not been investigated and is merely reproduced as previously stated. It is designated here as zeta.

This leaves three strong thermal arrests at 67.1°C, 106.1°C, and 118°C, which on the basis of the thermal data alone would appear to definitely represent peritectic phase formations, to be explained. No other affirmative data for these phases has been found. As mentioned above, the 67.1°C arrest might be associated with the "first phase" structure, but if so an additional higher mercury phase would be required and should have been found in the 37°C diffusion specimens.

It appears more likely that the 67.1°C arrest is associated with an undetected phase lying between 19.0 and 21.0% mercury. Similarly the 106.1°C arrest may indicate an additional phase between the proposed gamma and delta phases. Such a closely spaced series of phases seems quite unlikely, and these arrests may instead represent second order transformations rather than phase changes. For these reasons these arrests are merely indicated by dashed lines in the figures.

The arrest at 118.0°C is similarly strong and well defined. Since, however, it lies outside of the temperature range studied by diffusion, even less can be inferred about the composition properly associated with it or the nature of the transformation. This arrest is also indicated by a dashed line.

The remaining thermal arrests at higher temperature were less definite in nature, and hence are not indicated in the diagram. Some slight possibility exists that they also represent phases. The findings of Günther and Jehmlich [48] seem to imply such a complex series of phases, although they do not identify any of the corresponding compositions.

3. CONCLUSIONS

This investigation was undertaken with the objective of enlarging the knowledge of the metallurgy of dental amalgams and of developing techniques by which these alloys could be studied. It has emphasized the study of the mercury-tin system as being the portion of the mercury-silver-tin system most in need of improved understanding. The results indicate that progress has been made toward these objectives, not only in terms of increased knowledge but also by defining more closely the areas in which additional work is required and the problems which remain to be solved. In many instances a suitable method for attacking the individual problem also has been found.

In the mercury-tin system, the results have demonstrated that the system is more complicated than was previously reported. The existence of the beta phase has been confirmed by determination of the separate peritectic temperatures of the beta and gamma phases as indicated by Prytherch [25]. The limits of the gamma phase have been shifted, Gayler's [26] delta phase has been confirmed, and an additional epsilon phase has been discovered. It has also been shown that each of the methods employed is of definite value when used in combination with the others.

The main question about the mercury-tin system raised by this study is the nature of the transformations associated with the series of arrests observed above 100°C in the thermal analysis experiments. This problem seems susceptible to solution by further thermal analysis, particularly by means of heating curves on specimens containing between 60 and 18% mercury which have been well annealed above the delta peritectic temperature of 91.4°C. Alternative approaches could be elevated temperature x-ray diffraction or the extension of the diffusion studies to this temperature range.

Further thermal analysis studies in the low temperature range (near 37°C) is desirable to determine more precisely the peritectic temperature of the epsilon phase and to identify the source of the 67.1°C arrest. In each case particular care would be needed to insure the adequacy of annealing of the specimens.

The composition limits and eutectoid temperature of the beta phase remain to be confirmed in order to complete the diagram. This appears best approached by a series of elevated temperature x-ray diffraction patterns. A set of three or more specimens annealed in the beta range and tested at successively lower temperatures should provide the needed information.

Of the four methods employed in this study, x-ray diffraction and microhardness determination have been the least useful in the mercury-tin system; x-ray diffraction because of the very similar patterns obtained throughout the range of interest, and microhardness because of the lack of adequate available metallographic techniques.

A somewhat different situation exists when ternary alloys are considered. The increased complexity of ternary alloys and the observed slowness of the system to attain equilibrium indicates that the usefulness of thermal analysis may be restricted to those areas adjacent to the binary alloys. On the other hand the usefulness of microhardness determinations in large areas of the ternary diagram is assured. If a metallographic method for revealing the microstructure of mercury-tin alloys were available, the determination of microhardness might become the best single technique for studying the system.

The development of this metallographic method appears to be the main technique problem in the study of these alloys. Granted such a method, the mercury-silver-tin system could be studied by means of ternary diffusion couples at low temperatures, with the phases formed being identified by x-ray diffraction and microhardness. In this fashion the formation of high temperature phases could be avoided and the setting reactions of dental amalgam could be followed directly.

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TABLE 1

Composition of the Mercury* Used for the Preparation of Specimens

Element	Maximum Content ppm
Combined noble metals............. (Ag, Au, Ir, Os, Pt, Pd)	1.0
Combined base metals.............	0.1
Mercury..........................	Balance

---

[*] Refined mercury, Inorganic Chemistry Section, National Bureau of Standards.

TABLE 2

Composition of the Silver* Used for the Preparation of Specimens as Determined by Spectroanalysis

Element**	Amount Present ppm
Ag	Major Constituent
Al	2
Cu	3
Fe	0.5
Mg	0.5
Mn	0.5
Si	0.5

*Electrolytic crystal proof silver, U. S. Mint.

**The following elements were tested for but not detected:
As, Au, B, Be, Bi, Cd, Ca, Cr, Ga, Ge, Hf, Hg, In, La, Mo, Ni, Pb, Pd, Pt, Rh, Ru, Sb, Sn, Ti, V, Y, Zn, Zr.

TABLE 3

Composition of the Tin* Used for the Preparation of Initial Diffusion Specimens as Reported by the Manufacturer

Element	Maximum Content ppm
As	3
Cu	20
Fe	100
Pb	100
Zn	100
Sn	Balance

*Baker and Adamson Reagent Grade Tin Sticks, lot G303.

TABLE 4

Composition of the Tin* Used for the Preparation of Specimens as Determined by Spectroanalysis

Element	Amount Present ppm
Ag	1
As	40**
Bi	1.5
Cd	1
Co	1.5
Cu	15
Fe	2
Mg	0.5
Ni	3
Pb	15
Sb	10

*Tadanac Brand High Purity Tin Shot, lot HPM 522.

**Approximate value only, an error of 20 to 50% of the indicated value is likely.

TABLE 5

Nominal Composition of the Specimens Used for Thermal Analysis

Specimen		Mercury Content*	
Number	Weight grams	Weight %	Atomic %
17	42.0045	100.00	100.00
18	33.3382	70.00	57.99
19	30.0058	50.00	37.17
20	25.7081	29.90	20.15
21	26.3001	23.96	15.71
22	25.6292	21.97	14.28
23	25.0002	20.00	12.89
24	24.3834	17.97	11.47
26	23.6546	7.00	4.26
27	23.1624	5.02	3.03
28	22.4493	2.00	1.19
65	24.4456	10.00	6.17
66	42.0056	100.00	100.00
67	22.2526	0.00	0.00
72	26.0311	27.00	17.96
73	27.5073	39.99	28.28
74	31.2525	60.00	47.02
75	35.0037	80.00	70.30

*Balance Tin.

TABLE 6

Liquidus Temperatures of Mercury-Tin Alloys as a Function of Composition

Mercury Content		Specimen Number	Liquidus Temperature Degrees Centigrade
Weight %	Atom %		
0.00	0.00	67	231.9
2.00	1.19	28	230.1
5.02	3.03	27	222.9
7.00	4.26	26	219.3
10.00	6.17	65	218.4
17.97	11.47	24	208.3
20.00	12.89	23	204.0
21.97	14.28	22	203.2
23.96	15.71	21	199.5
27.00	17.96	72	197.5
29.90	20.15	20	191.6
39.99	28.28	73	176.1
50.00	37.17	19	157.5
60.00	47.02	74	139.0
70.00	57.99	18	118.9
80.00	70.30	75	99.0
100.00	100.00	66	---

TABLE 7

Arrests Observed on Thermal Analysis
of Mercury-Tin Alloys

Temperature	Estimated Uncertainty	Composition Range	Identification and Comments
°C	°C	Wt. % Hg.	
231.9	0.02	0-5	Tin liquidus
223.0	0.5	2-10	Beta peritectic
213.9	0.5	2-20	Gamma peritectic
203.5	1.0	18-22	Structural Artifact
197.0	1.5	2-10	Beta eutectoid
196.0	1.5	24-27	Unidentified
188.0	2.0	7-27	Unidentified
160.0	4.0	27-40	Unidentified
118.0	0.5	18-70	Phase change
106.1	0.5	18-70	Phase change
91.4	0.5	18-80	Gayler's delta peritectic
67.1	2.0	30-70	Phase change - peritectic
55.5	2.5	18-70	Phase change - heating only

TABLE 8

Immersion and Annealing Conditions for Diffusion Specimens

Specimen Number	Immersion		Annealing	
	Temperature °C	Time Hours	Temperature °C	Time Hours
	Tin Specimens			
1	37	65		
2	37	72		
3	37	73	37	41
4	37	73	37	611
5	37	124	37	242
6	37	124	37	338
7	37	144		
8	37	144	37	130
9	37	165		
10	37	170		
11	37	264		
12	37	264	37	768
13	37	336		
14	37	336	37	168
15	37	366		
16	60	114	60	75
17	60	114	60	510
18	60	125	60	240
19	60	125	60	1536
20	60	293		
21	60	293	60	721
22	60	356		
23	60	356	60	606
24	37	222	85	258
25	37	222	85	335
26	37	222	85	3931
27	37	222	110	332
28	37	222	110	526
29	37	222	110	672
30	37	222	110	794
	Silver Specimens			
31	85	147	37	76
32	85	147	85	92
33	190	147	190	119

TABLE 9

Composition Limits for the Observed Tin-Mercury Phases for Individual Diffusion Specimens

Specimen Number	Mercury Content						Depth at 10% Mercury Inches
	"Third Phase"		"Second Phase"		"First Phase"		
	Minimum Wt. %Hg	Maximum Wt. %Hg	Minimum Wt. %Hg	Maximum Wt. %Hg	Minimum Wt. %Hg	Maximum Wt. %Hg	
1					21.10	22.30	.023
2					21.00	23.00	.029
3			19.00	20.05			.037
4			19.00	20.50			.038
5	18.35	18.50	19.15	19.50			.048
6	17.80	18.80					.049
7			19.20	20.20	21.50	22.05	.042
8	17.95	18.50	18.95	19.35			.050
9					21.30	22.60	.047
10					20.90	21.90	.046
11					20.80	22.20	.089
12	17.90	18.65					.089
13					20.90	22.20	.079
14			19.20	20.20			.077
15					20.80	22.00	.076
16			19.30	20.05	21.20	22.20	.070
17	17.80	18.70	18.95	19.00			.071
18	18.60	18.70	19.00	19.05			.054
19	17.75	18.65					.041
20			18.90	20.15			.077
21	17.80	18.65					.113
22			19.40	26.10			.100
23	17.75	18.55	18.90	20.05			.142
24			Samples Lost				
25			19.00	20.15			.096
26	17.50	18.50	18.90	19.65			.110
27			Samples Lost				
28	17.55	18.60					.092
29			Samples Lost				
30	17.50	18.80					.096

TABLE 10

Composition Limits for the Gamma, Delta, and Epsilon Tin-Mercury Phases as a Function of Diffusion Temperature

Temperature °C	Mercury Content					
	Gamma		Delta		Epsilon	
	Minimum Wt. %Hg	Maximum Wt. %Hg	Minimum Wt. %Hg	Maximum Wt. %Hg	Minimum Wt. %Hg	Maximum Wt. %Hg
37	17.9	18.8	19.0	20.1	20.9	22.3
	(11.40)*	(11.90)	(12.20)	(12.95)	(13.50)	(14.55)
60	17.8	18.6	19.0	20.1	21.2	22.2
	(11.35)	(11.90)	(12.20)	(12.95)	(13.75)	(14.45)
85	17.5	18.5	18.9	20.1		
	(11.15)	(11.85)	(12.15)	(12.95)		
110	17.5	18.6				
	(11.15)	(11.90)				

*Equivalent atomic percentages.

TABLE 11

Composition and Thermal History of Microhardness Specimens

Specimen Number	Composition			Thermal History		
	Mercury Wt. %	Silver Wt. %	Tin Wt. %	Fusion Temp. °C	Annealing Temp. °C	Annealing Time Days
1			100.00	Chill cast	190	10
2		100.0		Chill cast	400	5
4		94.97	5.03	Chill cast	400	5
5		84.79	15.21	Chill cast	400	5
6		73.59	26.41	Chill cast	400	5
7		87.00	13.00	Chill cast	(400 (460	(11 (12
8		76.00	24.00	Chill cast	(400 (460	(11 (12
10	40.02	59.98		800	210	17
11	54.99	45.01		700	210	17
12	59.98	40.02		650	210	17
29	18.40		81.60	250	85	50
30	19.58		80.42	250	85	50
31	21.60		78.40	250	60	50
32	2.00		98.00	250	(190 (210	(42 (14
33	2.00		98.00	250	190	42
34	5.01		94.99	250	(190 (210	(42 (15
35	5.01		94.99	250	190	42
36	7.00		93.00	250	(190 (210	(42 (15
37	7.02		92.98	250	190	42
38	9.96		90.04	250	(190 (210	(42 (15
39	11.01		88.99	250	(190 (210	(42 (15
40	11.97		88.03	250	85	55
41	14.06		85.94	250	85	55
42	16.00		84.00	250	85	55
43	70.00	30.00		600	85	42
44	65.00	35.00		600	85	42
45	67.50	27.50	5.00	550	60	40
46	20.00	75.00	5.00	800	60	18
47	20.02	70.00	9.98	800	60	18
48	20.01	65.00	14.99	700	60	23
50	59.96	30.03	10.01	500	60	42
52	19.98	40.00	40.02	450	60	56
53	30.00	30.00	40.00	250	60	56
54	40.00	20.00	40.00	250	60	56
55	20.00	20.00	60.00	250	60	56
56	10.00	10.00	80.00	250	60	56
57	15.00	10.01	74.99	250	60	49
58	20.01	10.04	69.99	250	60	49
59	25.00	10.00	65.00	250	60	49

(continued)

TABLE 11 - Continued

Specimen Number	Composition			Thermal History		
	Mercury Wt. %	Silver Wt. %	Tin Wt. %	Fusion Temp. °c	Annealing Temp. °C	Annealing Time Days
60	30.00	10.00	60.00	250	60	49
61	10.00	5.00	85.00	250	60	49
62	15.01	5.00	79.99	250	60	49
63	20.00	5.00	75.00	250	60	49
64	25.00	5.00	70.00	250	60	49
70	19.98	60.04	19.98	650	60	18
71	39.99	45.00	15.00	550	60	17

TABLE 12

Observed Microhardness of Individual Mercury-Silver-Tin Phases

Phase	Specimen Number	Hardness KHN_{25}	Percent Coefficient of Variation	
			Specimen*	Grain**
Tin	1	8.8	10.2	4.1
Silver	2	42.4	10.8	3.1
α Ag-Sn	4	64.6	5.4	5.3
β Ag-Sn	5	156.4	32.4	8.2
γ Ag-Sn	6	108.1	51.2	19.8
α Hg-Ag	10	60.1	17.6	10.9
β Hg-Ag	12	91.2	13.5	14.4
γ Hg-Ag	43	142.8	14.9	14.6
α Hg-Sn	32	15.3	5.3	4.0
	33	15.5	16.2	3.9
	40	16.0	12.1	
γ Hg-Sn	32	20.3	9.0	
	33	20.2	13.4	
	40	22.4	4.9	
"Islands" (Silver)	55	47.1	15.3	
Dendrites (β)	55	126.7	10.2	
Matrix (γ Hg-Sn)	55	21.9	14.8	

*Calculated with respect to the mean of all determination of the hardness of the phase made on that specimen.

**Calculated with respect to the mean hardness of the individual grain.

TABLE 13

Composition and Source of the X-Ray Diffraction Specimens Produced by Diffusion

Specimen Number	Mercury Content Wt. %	Diffusion Specimen	Sample Depth Inches
1	22.10+	7	0.0025
2	21.83	7	0.0125
3	21.72	11	0.0250
4	19.20	8	0.0075
5	18.19	8	0.0375
6	(20.00)	15*	Surface
7	21.94	1	0.0075
8	19.88	1	0.0375
9	19.78	22	0.0500
10	18.72	21	0.0500
11	12.58	21	0.1075
12	19.27	26	0.0135
13	18.29	26	0.0555
14	18.07	28	0.0550

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[*] This specimen was annealed for 168 hours at 37°C after removal from the mercury, in addition to the treatment indicated in Table 8.

TABLE 14

Composition and Heat Treatment of the X-Ray Diffraction Specimens Produced by Fusion

Specimen Number	Mercury Content Wt. %	Annealing	
		Temperature °C	Time Hours
15	21.75	70	2
16	17.83	70	2
17	12.51	160	2
18	12.45	160	4
19	10.23	150	2
20	4.95	150	2

TABLE 15

Observed X-Ray Diffraction Patterns as a Function of Mercury Content in Diffusion Specimens

Mercury Content Wt. %	Specimen Number	Observed Pattern
22.10+	1	Complete hexagonal
21.94	7	Complete hexagonal
21.83	2	Complete hexagonal
21.72	3	Complete hexagonal
(20.00)	6	Complete hexagonal
19.88	8	Transition*
19.78	9	Complete hexagonal
19.27	12	Transition
19.20	4	Transition
18.72	10	Transition
18.29	13	Incomplete hexagonal**
18.19	5	Incomplete hexagonal
18.07	14	Incomplete hexagonal
12.58	11	Incomplete hexagonal

*Ratio of 001 to 100 peak height less than 0.8.

**001, 002, and 003 lines absent.

TABLE 16

Observed X-Ray Diffraction Patterns as a Function of Mercury Content in Cast Specimens

Mercury Content Wt. %	Specimen Number	Observed Pattern
21.75	15	Transition*
17.83	16	Transition**
12.51	17	Incomplete hexagonal
12.45	18	Incomplete hexagonal
10.23	19	Incomplete hexagonal-tin trace
4.95	20	Incomplete hexagonal-tin

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*Ratio of 001 to 100 peak height 0.75.

**Ratio of 001 to 100 peak height 0.30.

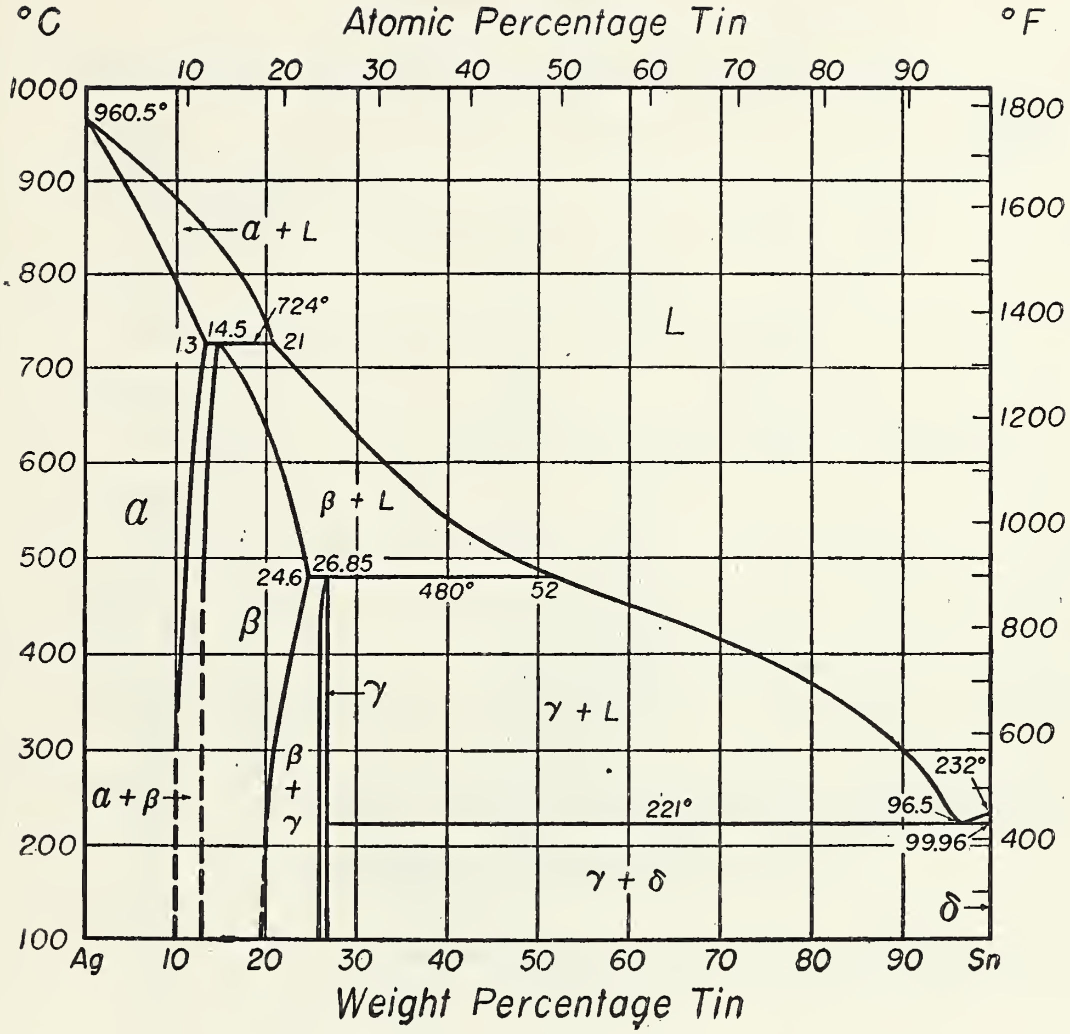

Figure 1. The Silver-Tin Constitution Diagram.[12].

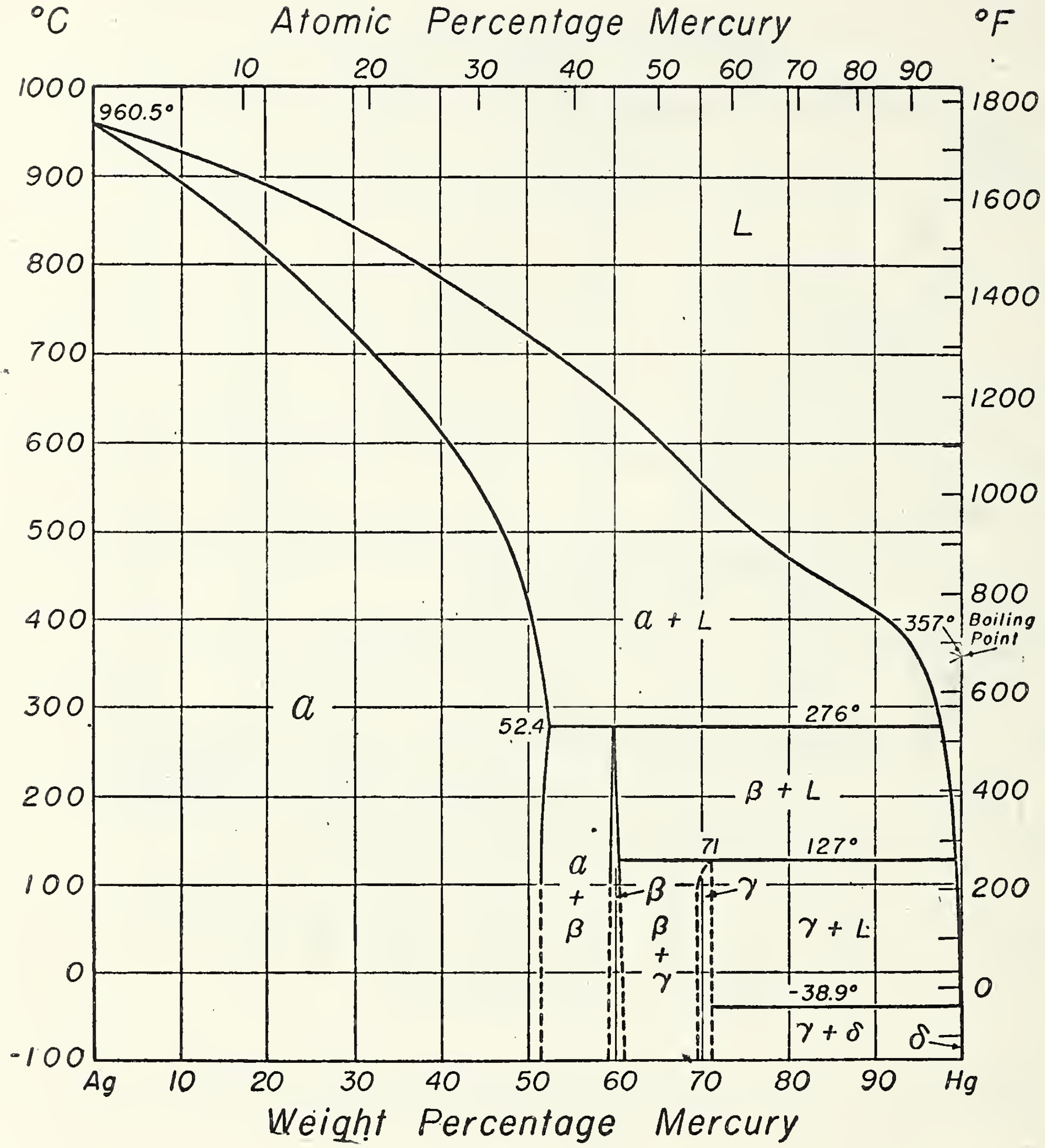

Figure 2. The Mercury-Silver Constitution Diagram [12].

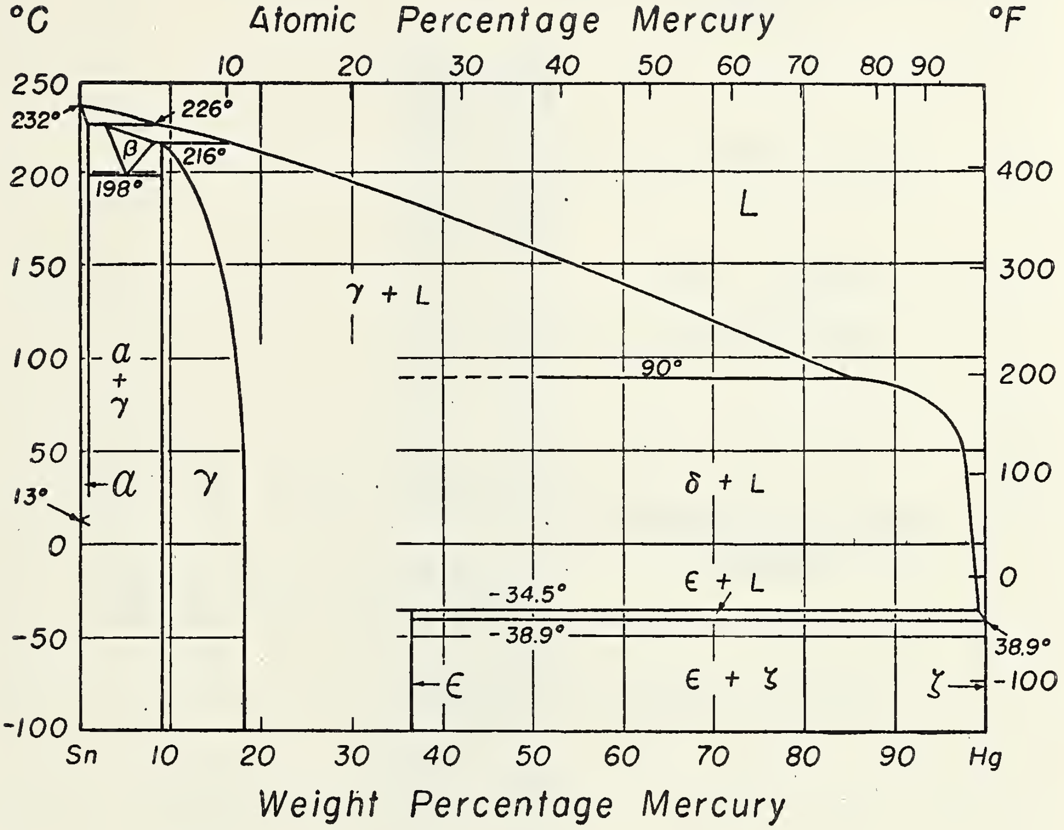

Figure 3. The Mercury-Tin Constitution Diagram [12].

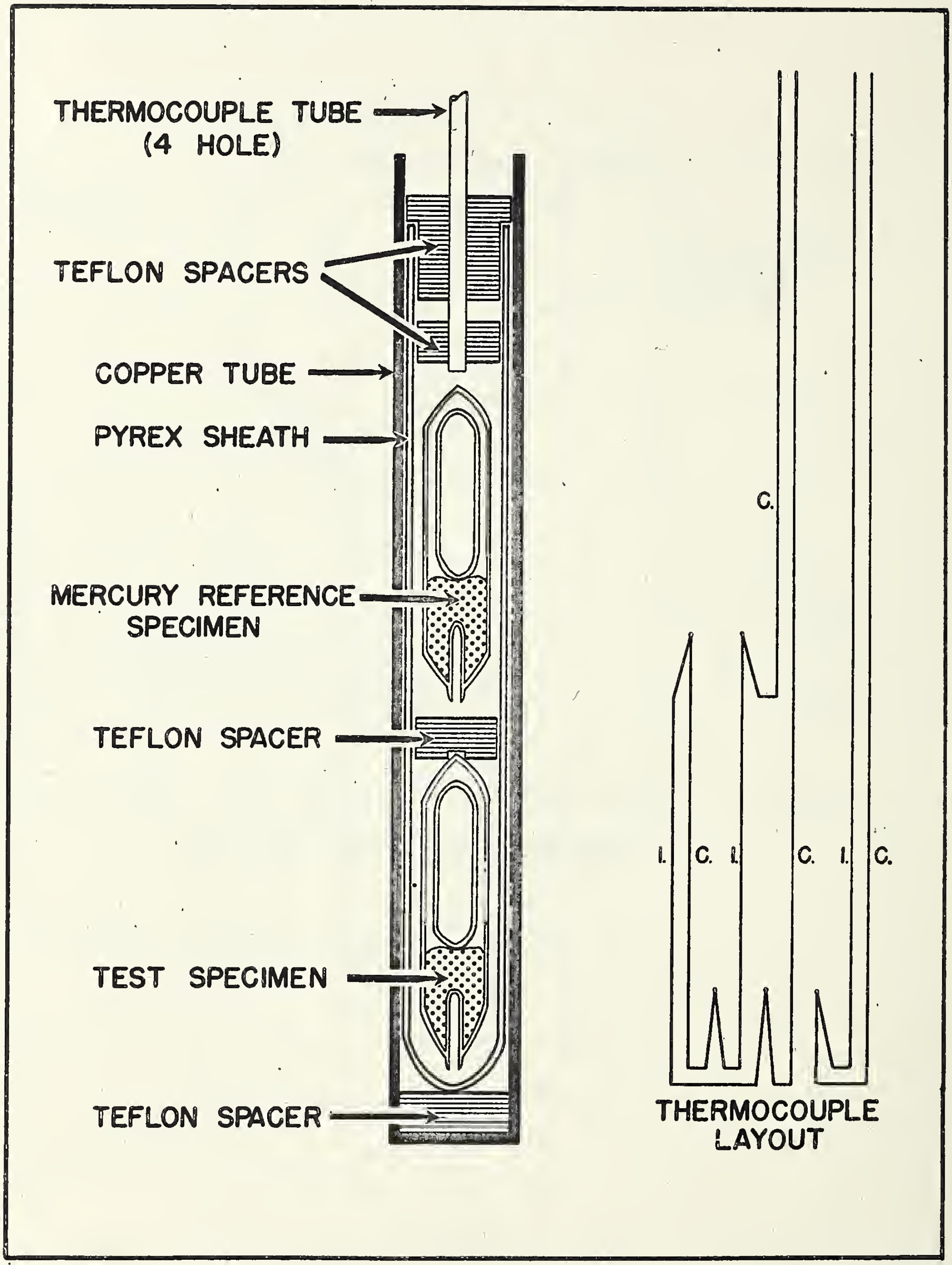

Figure 4. Thermal Analysis Specimen Arrangement.

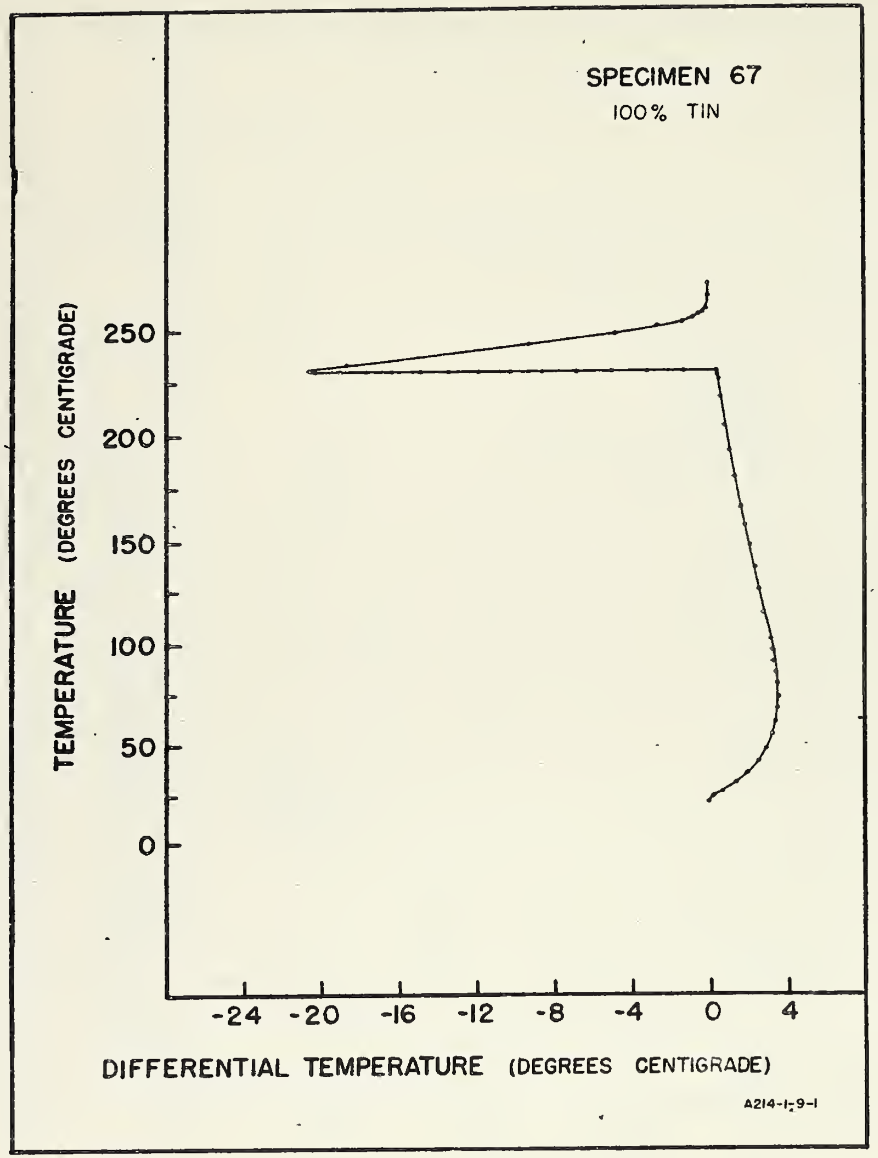

Figure 5. Heating Curve for Pure Tin.

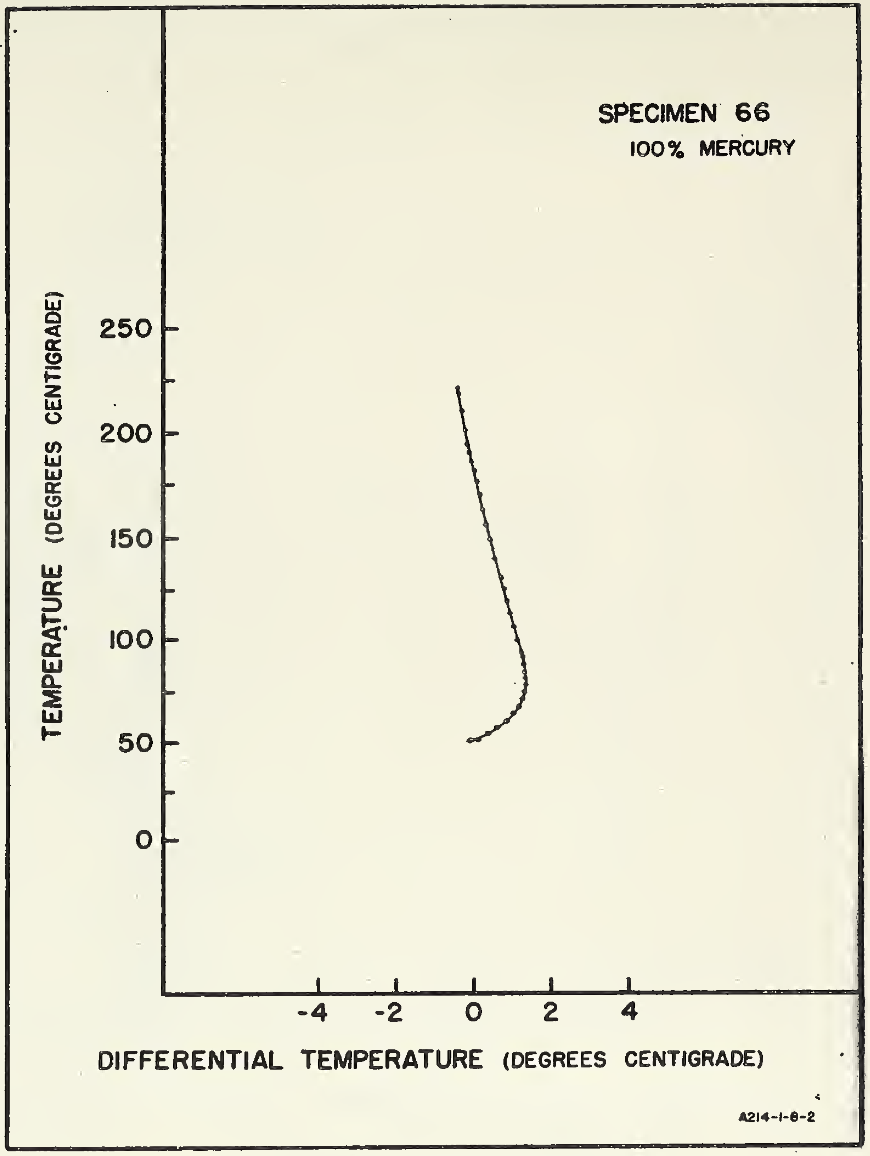

Figure 6. Heating Curve for Pure Mercury.

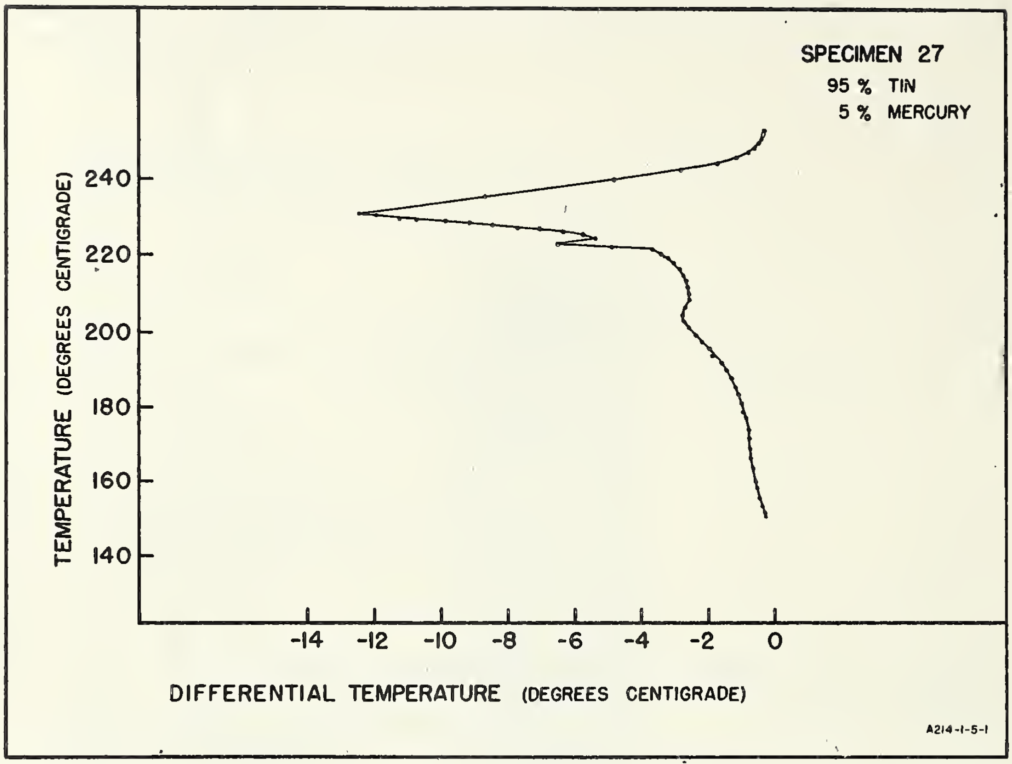

Figure 7. Heating Curve for 5% Hg 95% Sn Alloy.

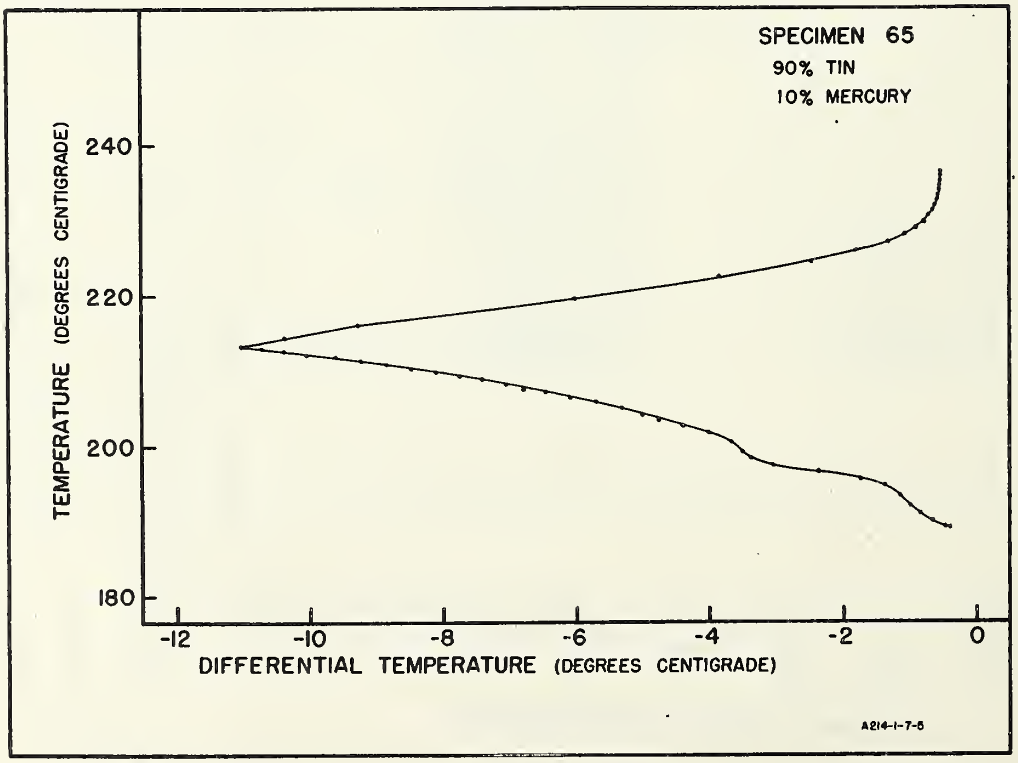

Figure 8. Heating Curve for 10% Hg 90% Sn Alloy.

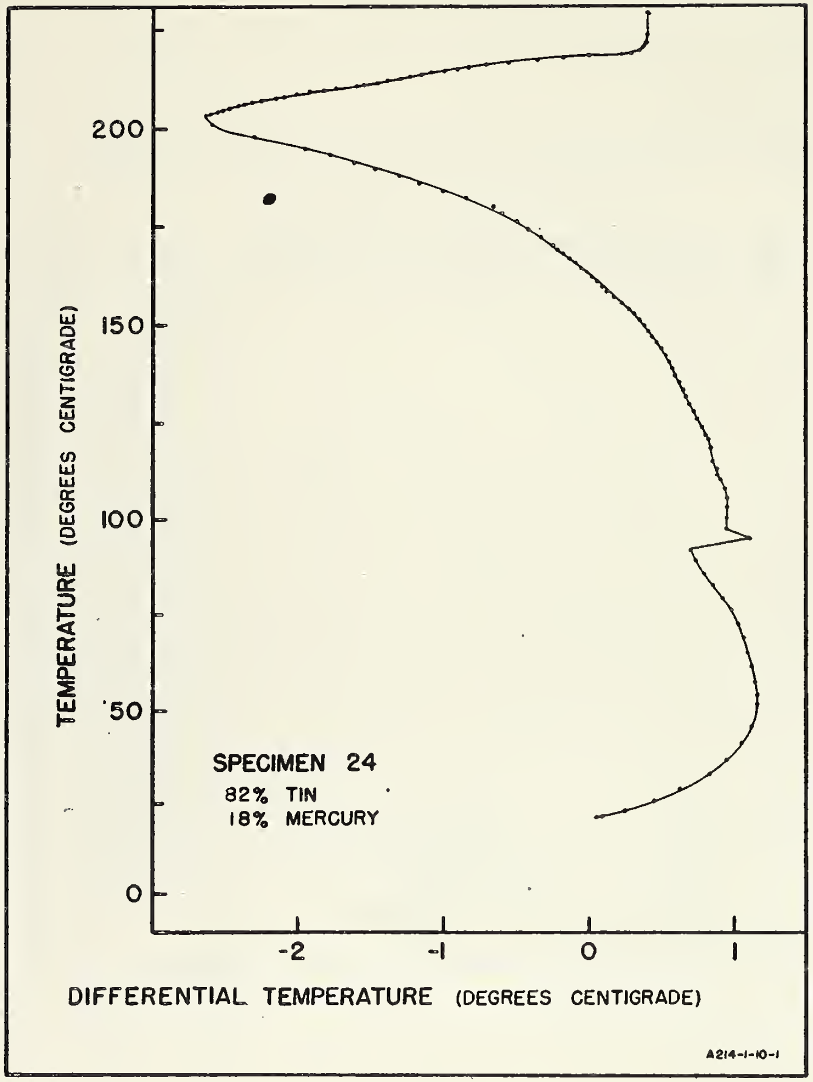

Figure 9. Heating Curve for 18% Hg 82% Sn Alloy.

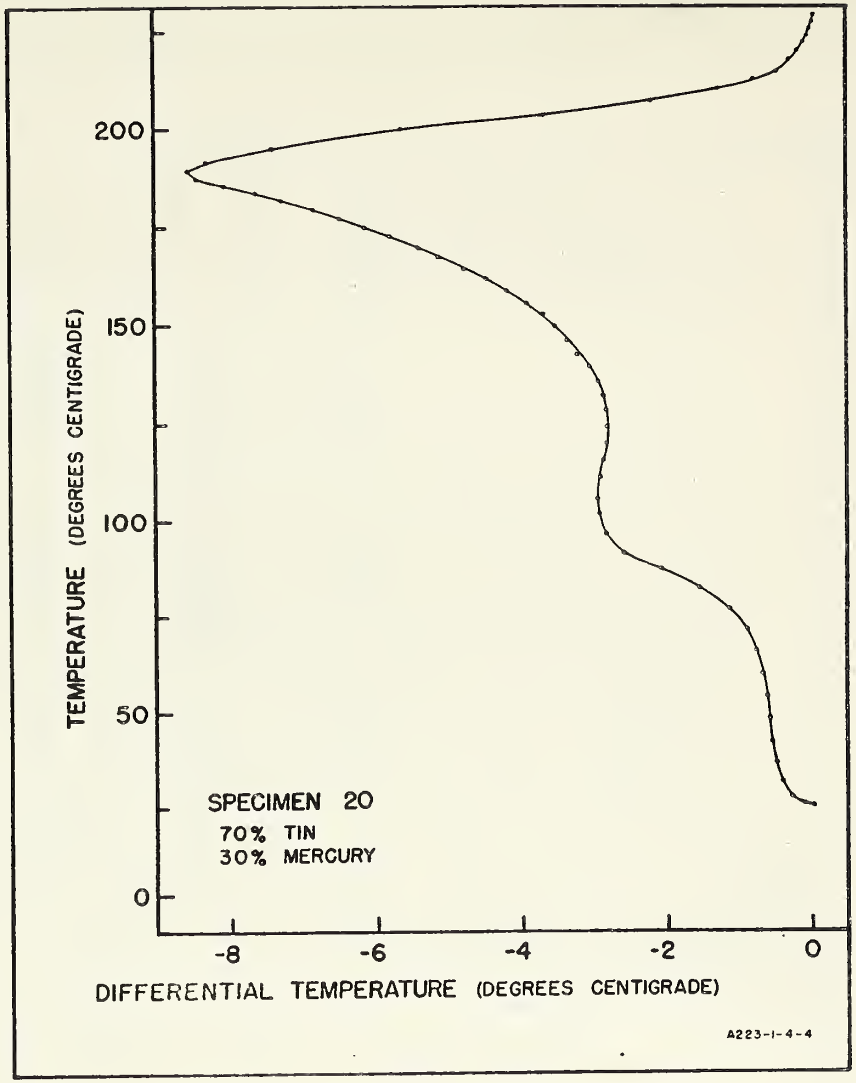

Figure 10. Heating Curve for 30% Hg 70% Sn Alloy.

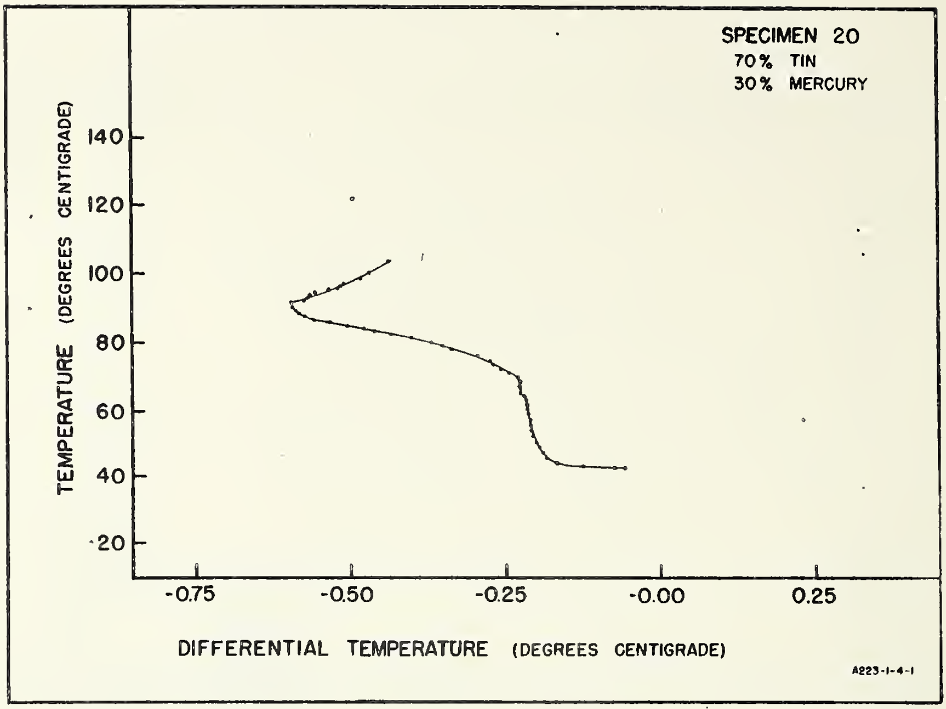

Figure 11. Heating Curve for 30% Hg 70% Sn Alloy After Annealing.

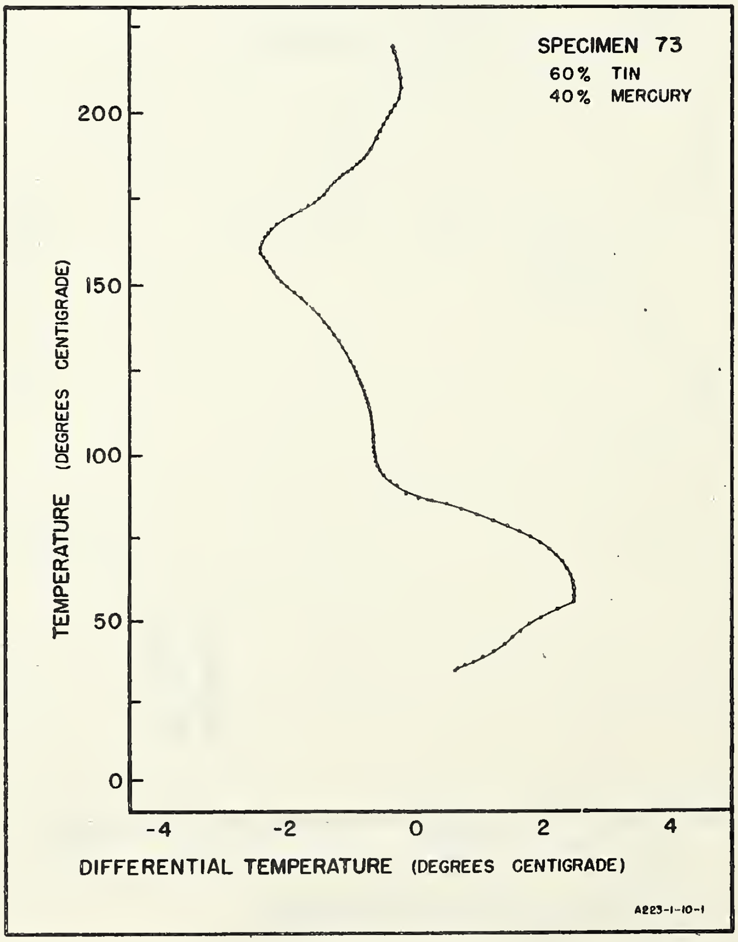

Figure 12. Heating Curve for 40% Hg 60% Sn Alloy.

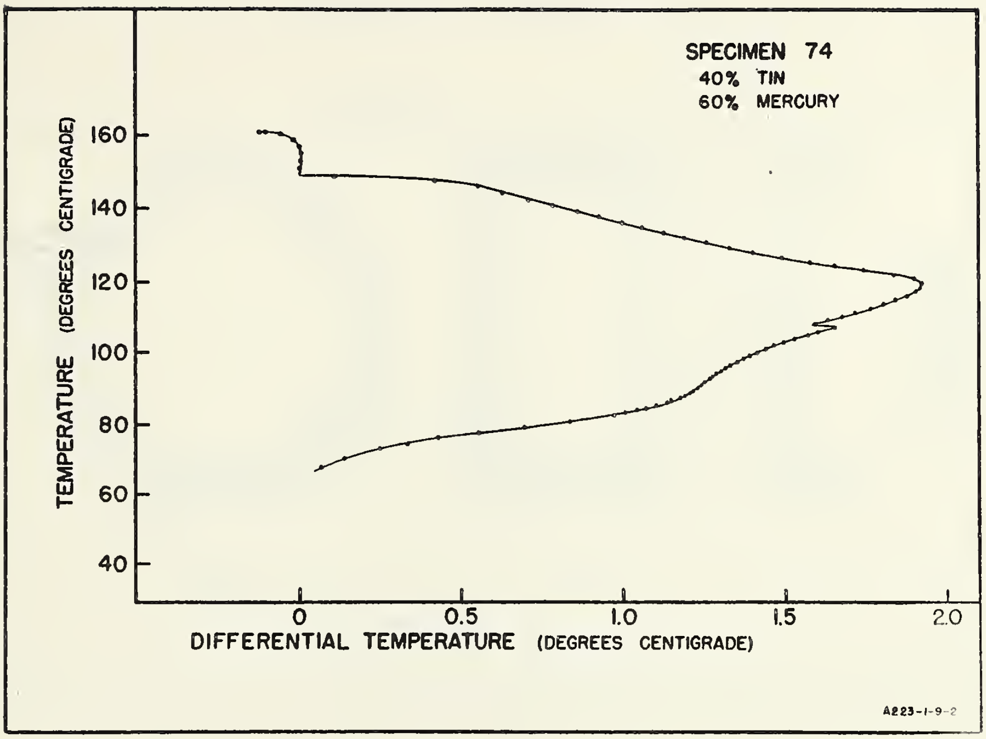

Figure 13. Cooling Curve for 60% Hg 40% Sn.

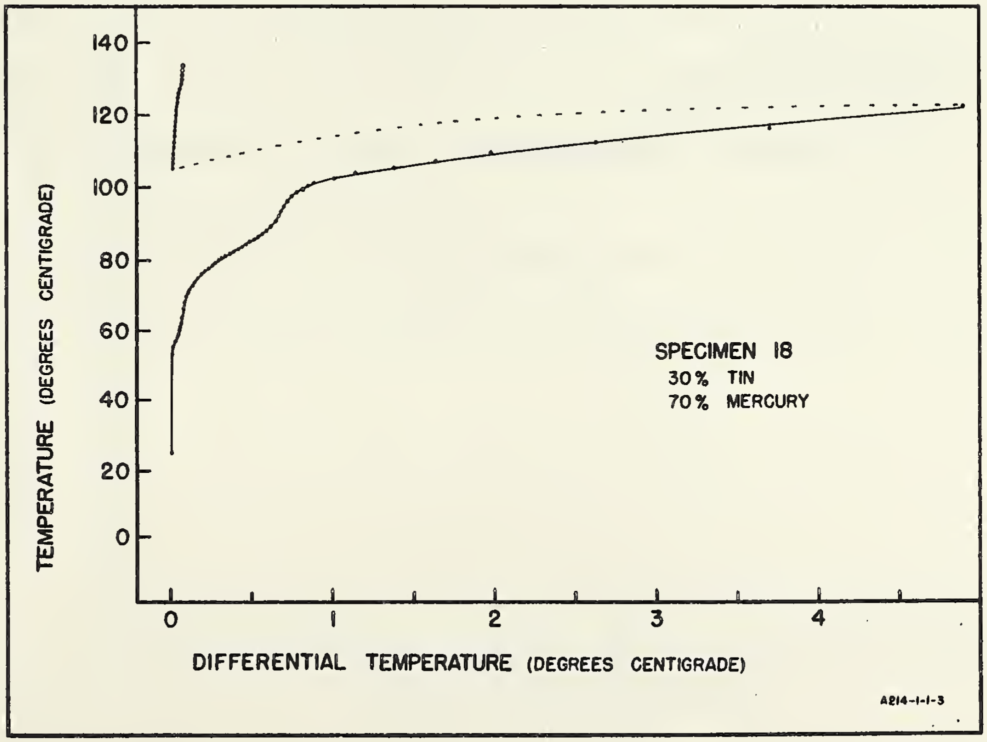

Figure 14. Cooling Curve for 70% Hg 30% Sn Alloy.

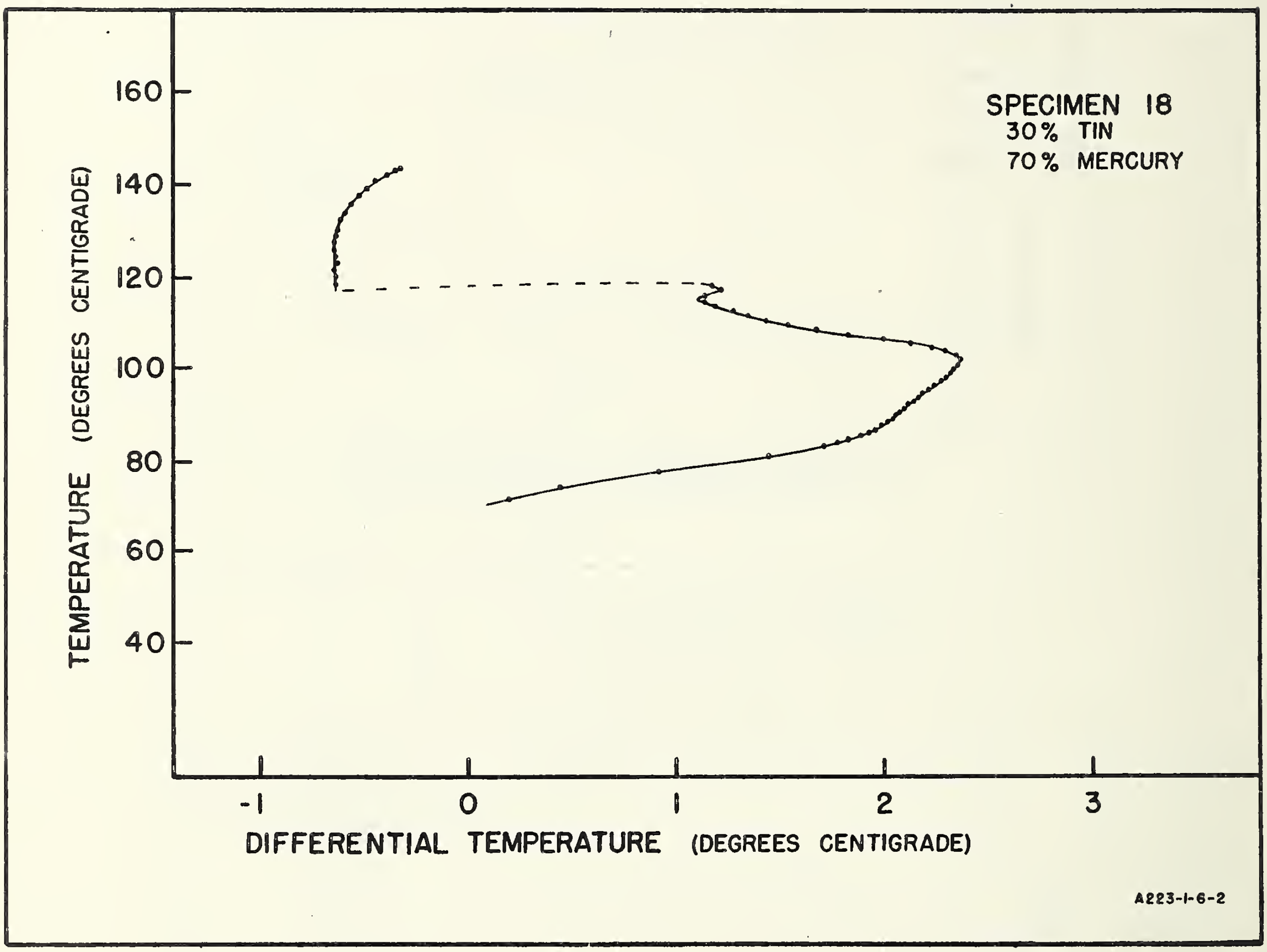

Figure 15. Cooling Curve for 70% Hg 30% Sn Alloy Without Supercooling.

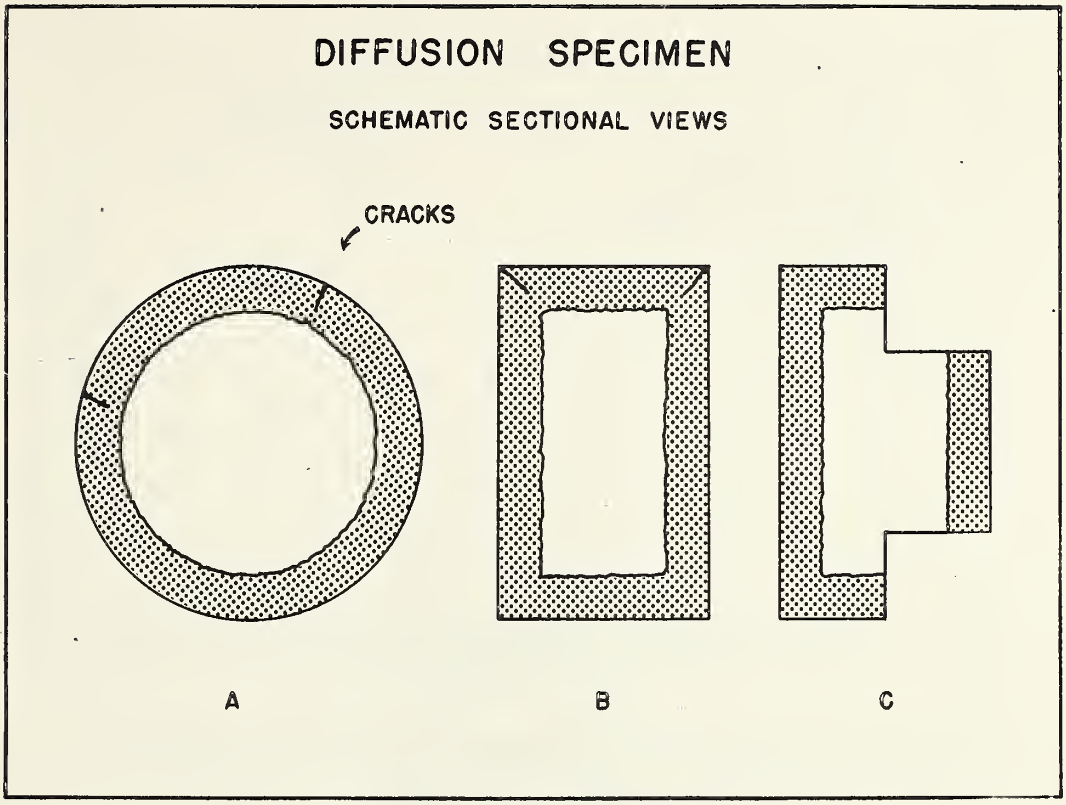

Figure 16. Schematic Sectional Views of Diffusion Specimen.

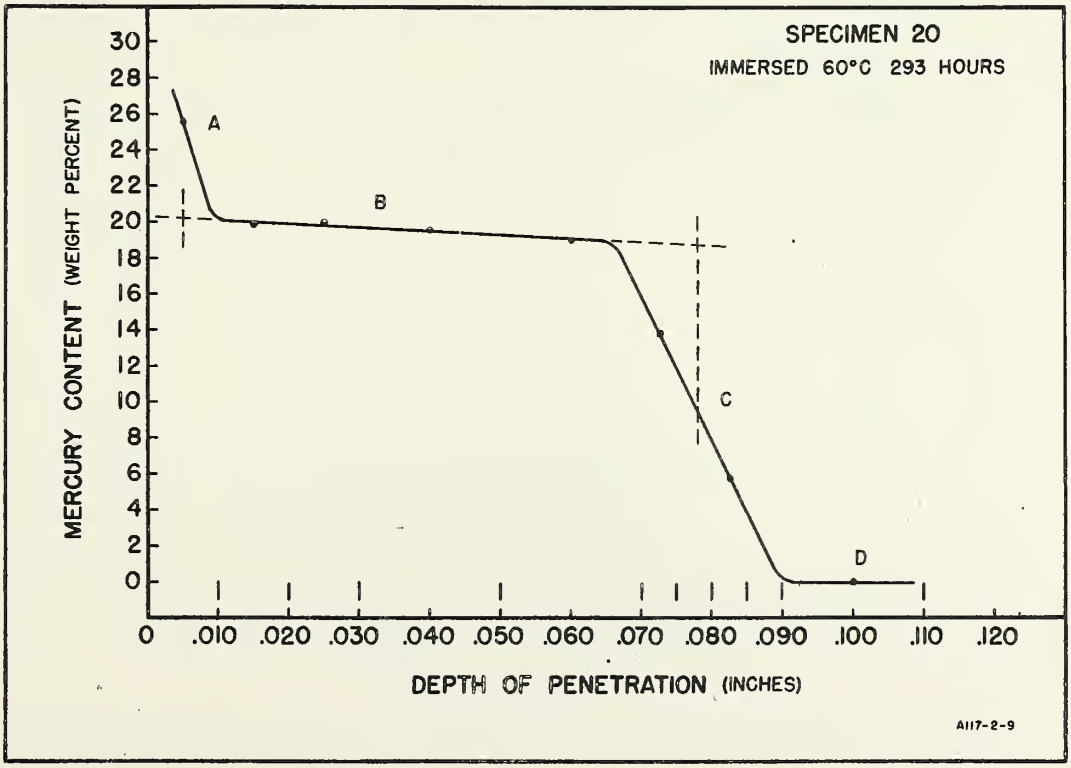

Figure 17. Concentration-Depth for Specimen 20.

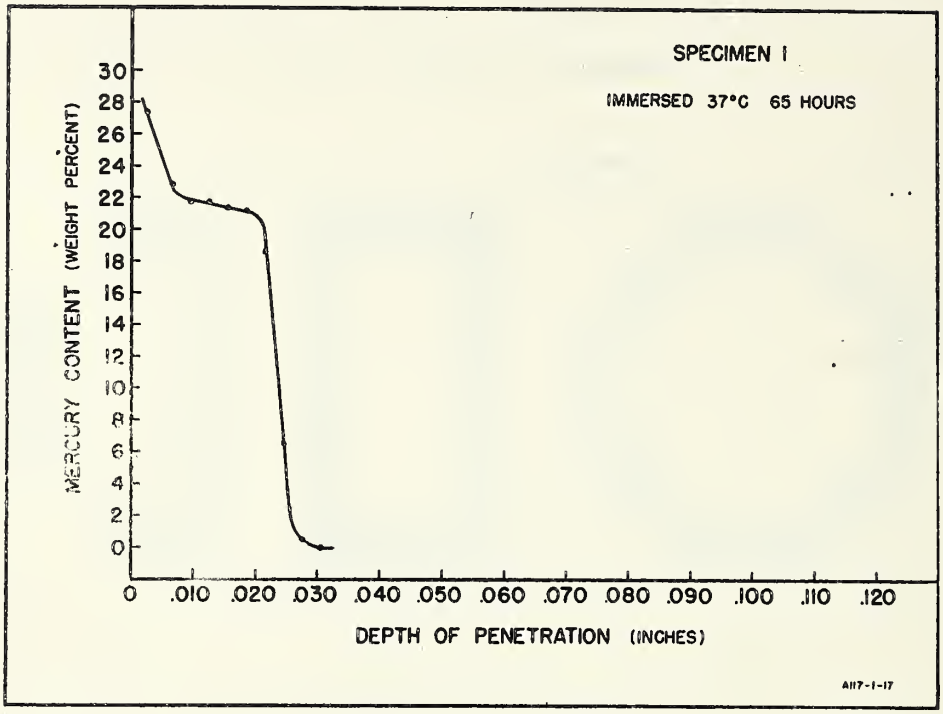

Figure 18. Concentration-Depth Curve for Specimen 1.

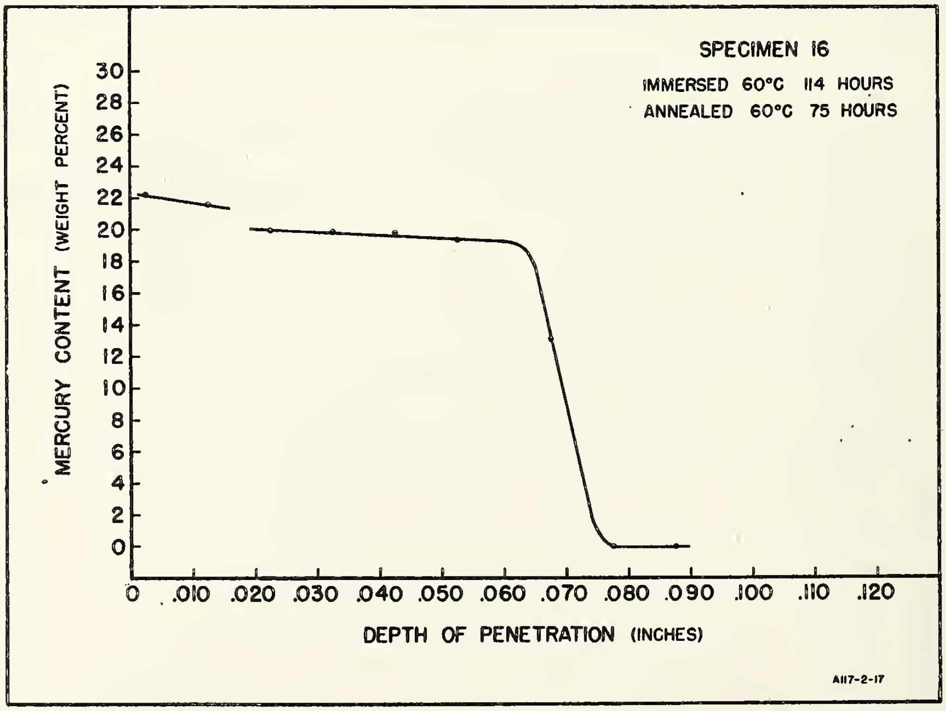

Figure 19. Concentration-Depth Curve for Specimen 16.

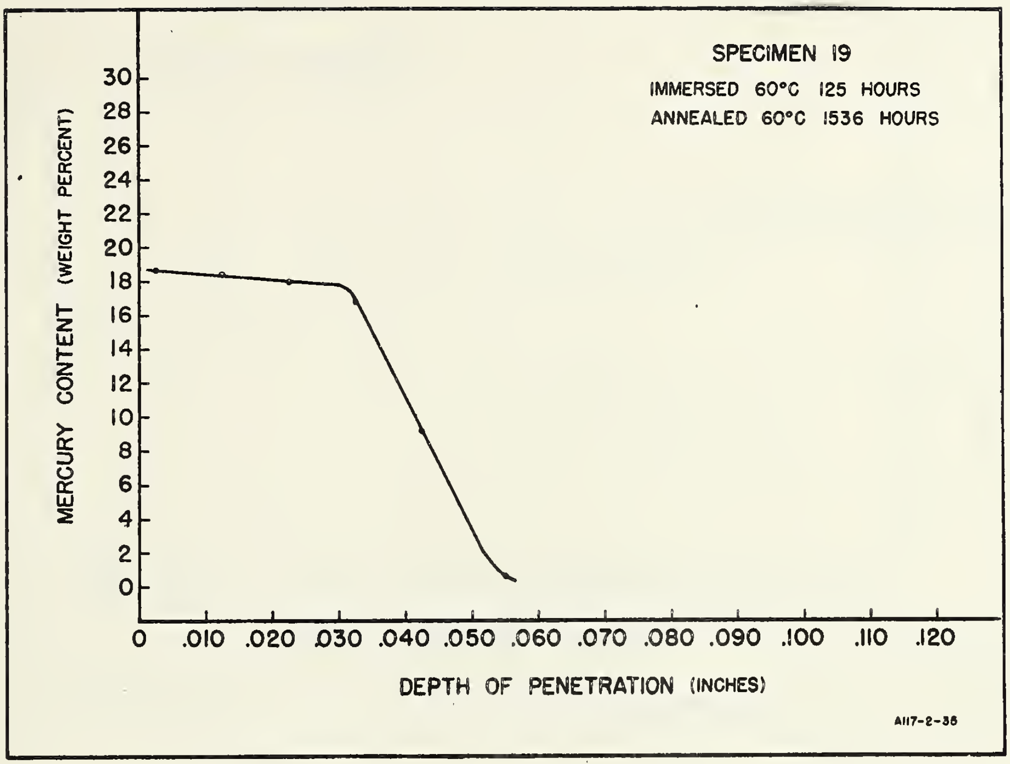

Figure 20. Concentration-Depth Curve for Specimen 19.

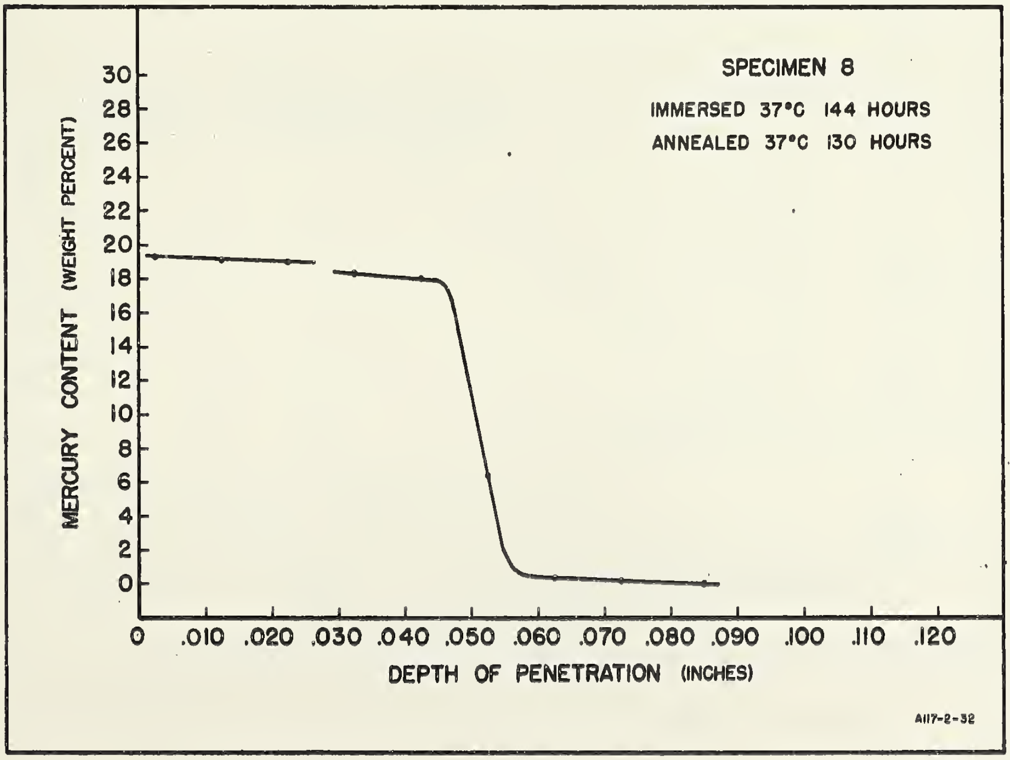

Figure 21. Concentration-Depth Curve for Specimen 8.

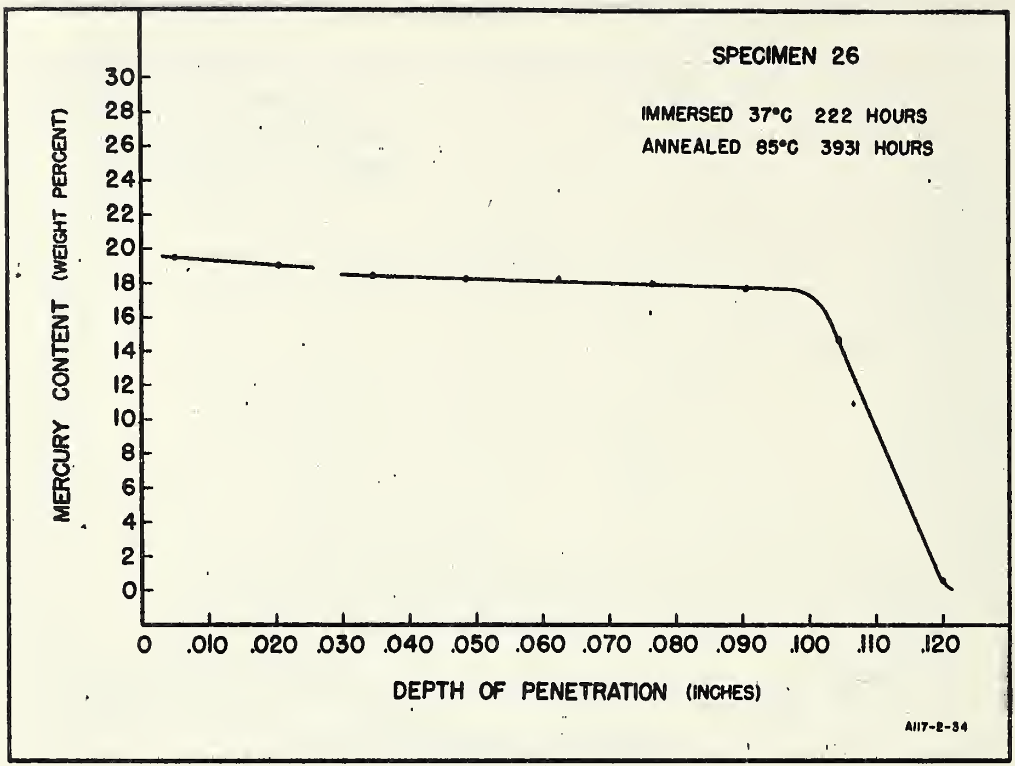

Figure 22. Concentration-Depth Curve for Specimen 26.

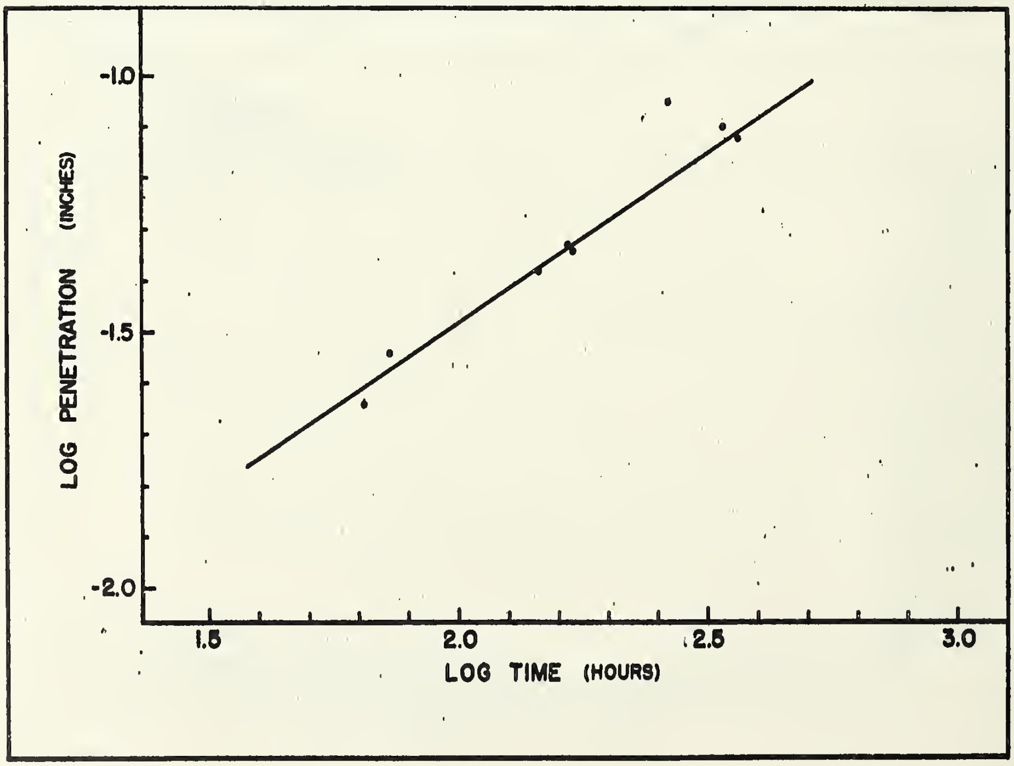

Figure 23. Mercury Penetration as a Function of Time.

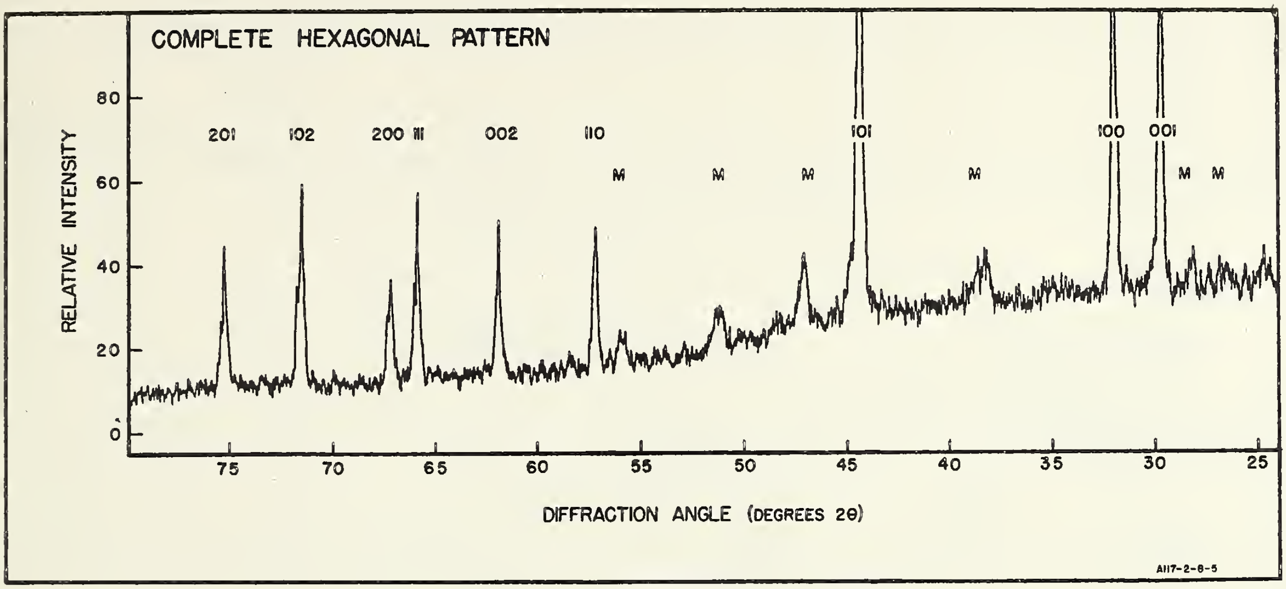

Figure 24. "Complete Hexagonal" X-ray Diffraction Pattern.

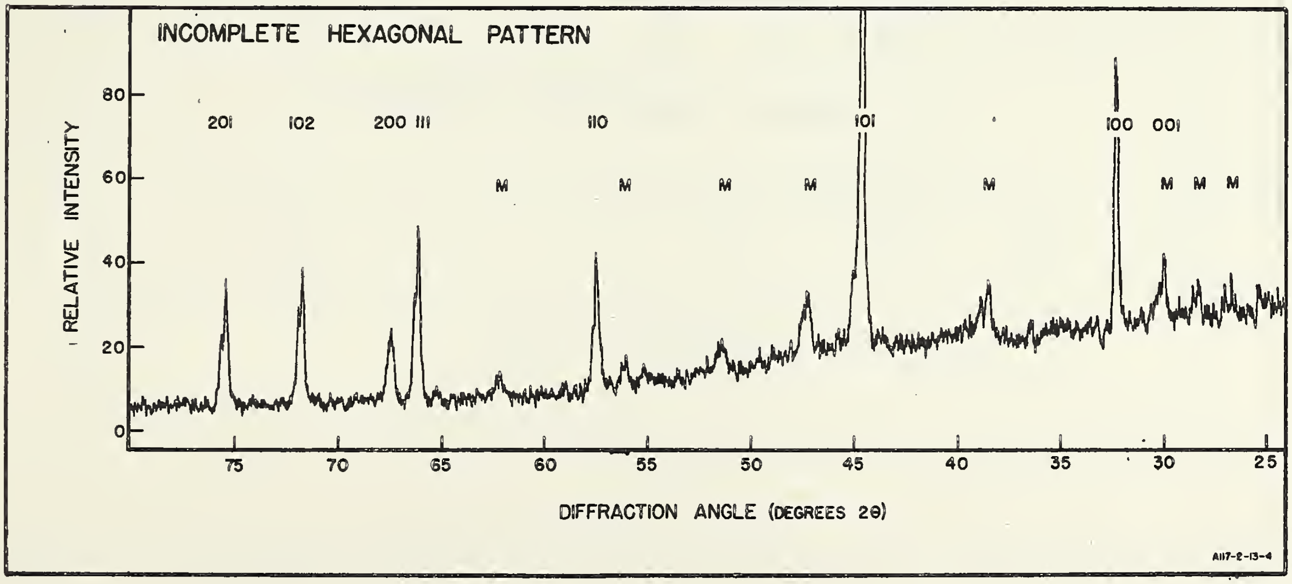

Figure 25. "Incomplete Hexagonal" X-ray Diffraction Pattern.

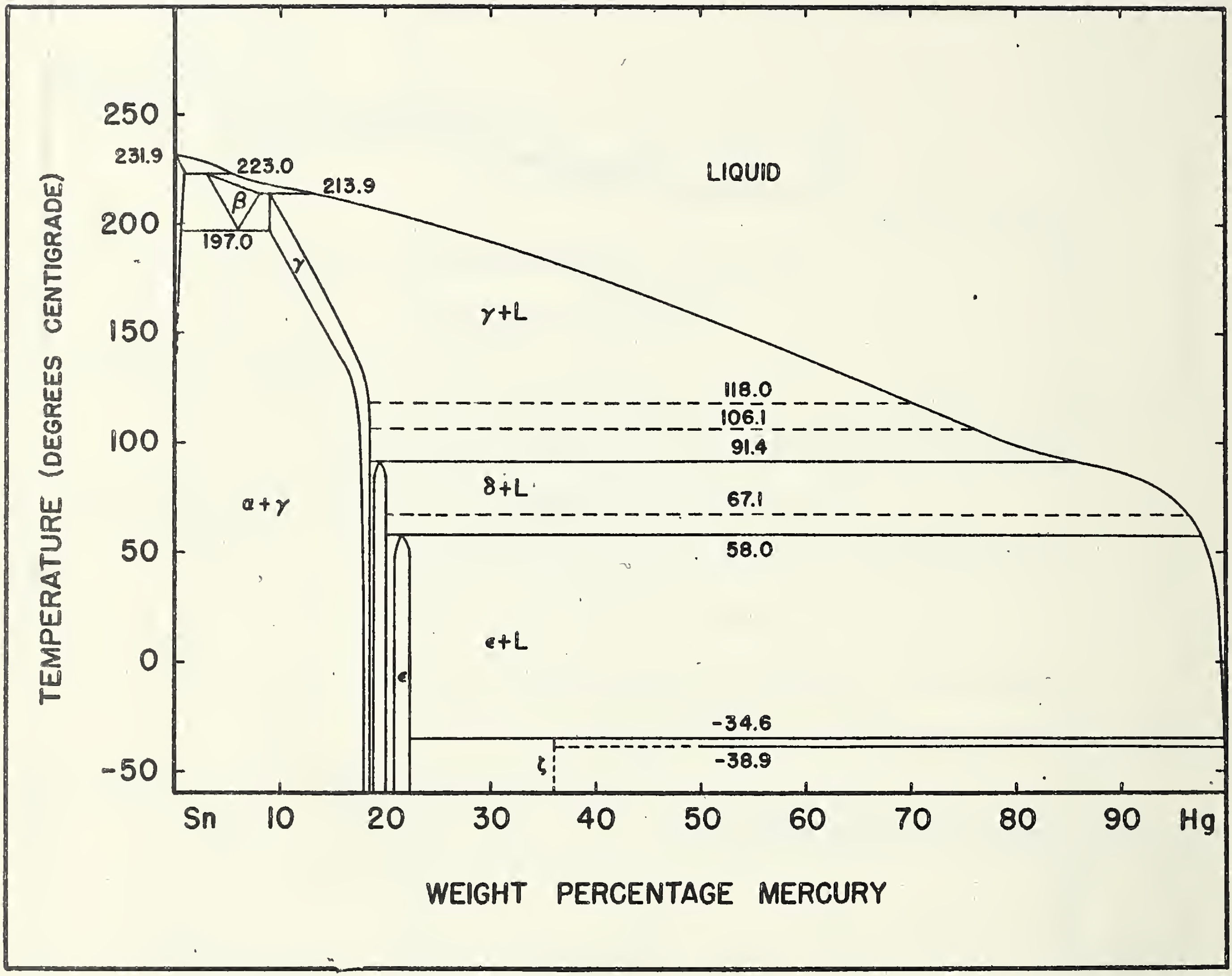

Figure 26. Proposed Tin-Mercury Constitution Diagram.

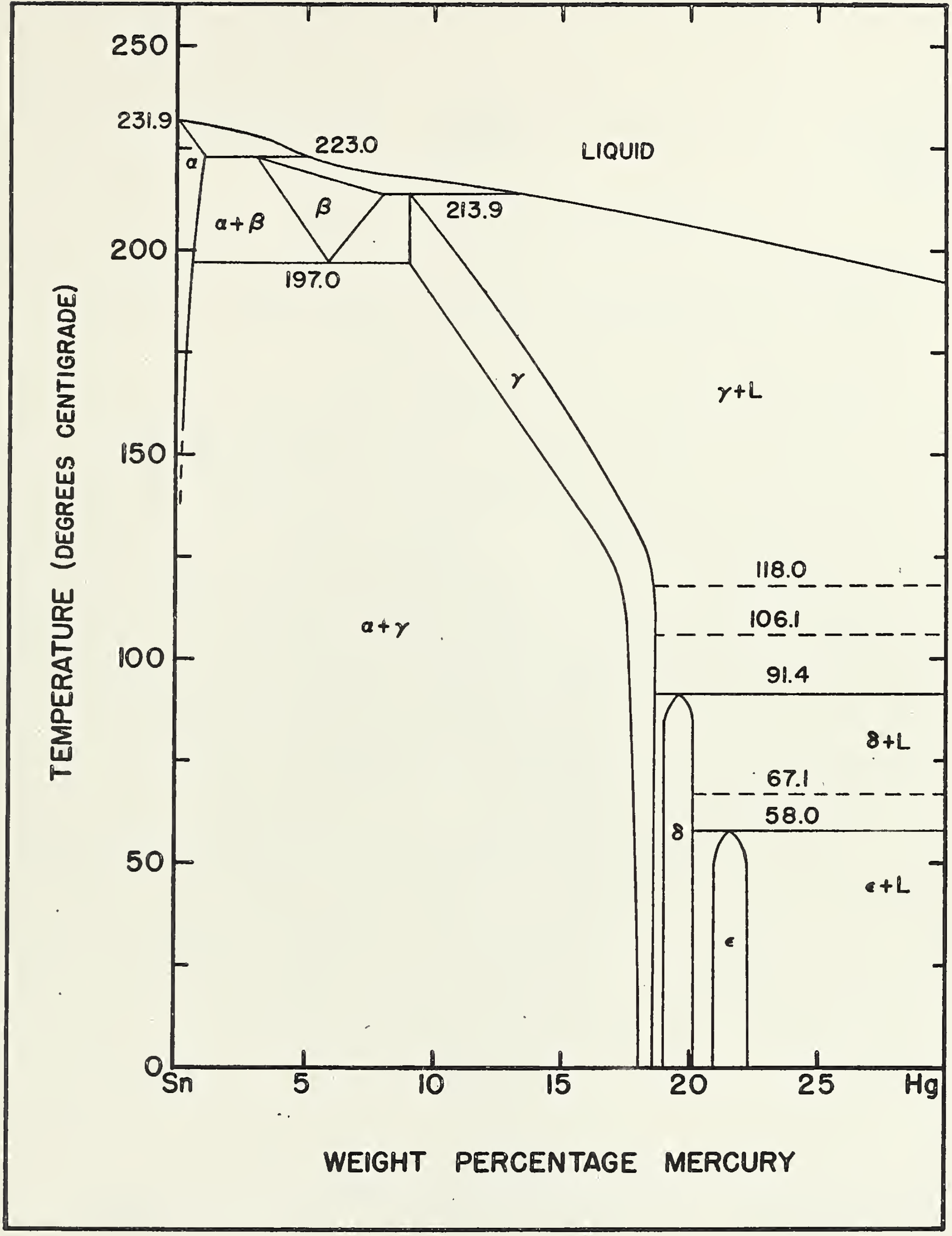

Figure 27. Enlarged Tin-Rich Portion of Proposed Constitution Diagram.

U.S. DEPARTMENT OF COMMERCE
Frederick H. Mueller, *Secretary*

NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

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RADIO SYSTEMS. High Frequency and Very High Frequency Research. Modulation Research. Antenna Research. Navigation Systems. Space Telecommunications.

UPPER ATMOSPHERE AND SPACE PHYSICS. Upper Atmosphere and Plasma Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.

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