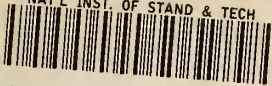


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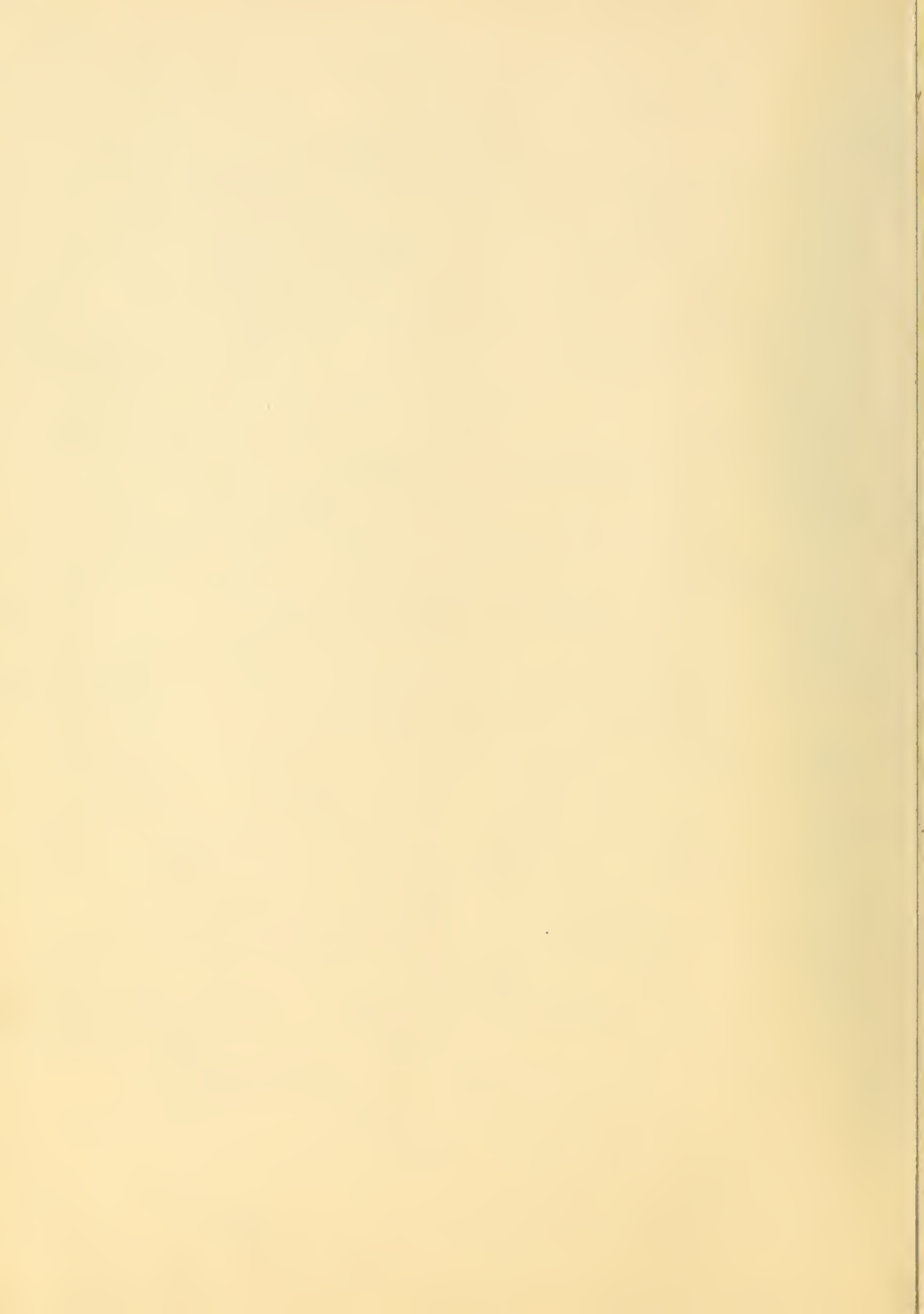


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Technical Note

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DETAILED TECHNIQUES FOR PREPARING AND USING HARD GALLIUM ALLOYS

GEORGE G. HARMAN



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

AUG 5 1965

130,745

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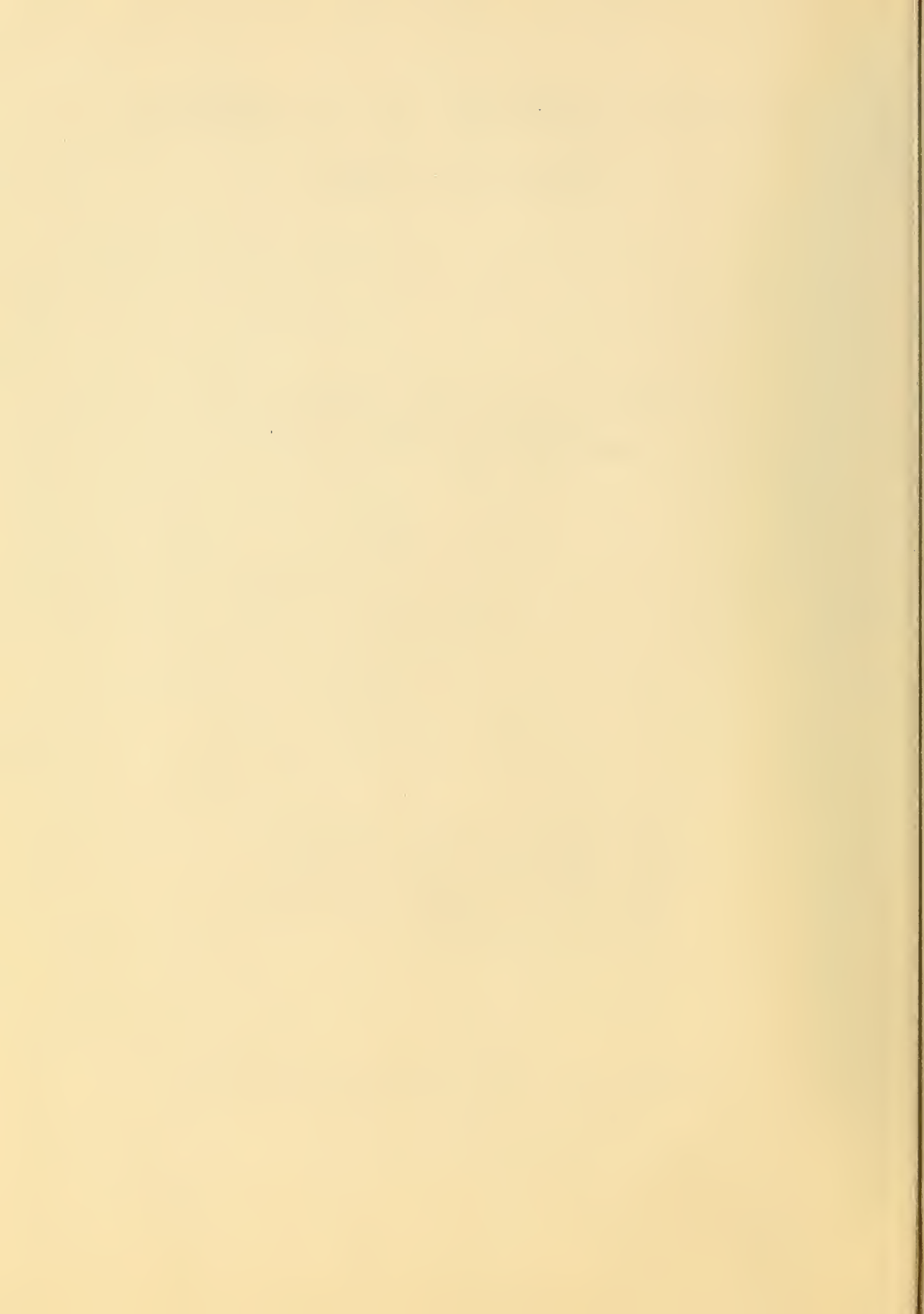
DETAILED TECHNIQUES FOR PREPARING AND USING HARD GALLIUM ALLOYS

George G. Harman

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DETAILED TECHNIQUES FOR PREPARING AND USING HARD GALLIUM ALLOYS

George G. Harman

This report presents an expansion and clarification of techniques for preparing and using dental-amalgam-type gallium alloys for industrial and scientific uses that were previously published in the Review of Scientific Instruments. In addition, new material, such as hardness of the alloys and discussions of the bonding mechanism are presented. A different class of bonding alloys based on the same principals but not incorporating gallium are described, along with application details.

1. Introduction

In the year or so since issuing the various publications, on "Hard Gallium Alloys",^{1,2,3} there have been hundreds of inquiries about the details of alloy mixing techniques, bonding applications and the sources of gallium. Thus it is desirable to discuss in detail the frequently occurring problems in order to assure that the techniques achieve their maximum scientific and industrial usage. From the questions asked it is apparent that many workers are unfamiliar with such procedures as making eutectics, mixing liquid metal with powders, and in general, with the problems and procedures of handling gallium.

Although some new material is presented, this publication is primarily an expansion and clarification of the three preceding ones on the subject^{1,2,3} and reprints of these are available upon request to this author at the National Bureau of Standards, Washington 25, D. C. The first article¹ gave general techniques, listed tables of alloys, gave expansion coefficient curves, and included several inserted "Additional Notes" pages. These notes have been revised twice during the various reprintings of the article. The NBS Technical News Bulletin article² was essentially a summary of the first article and its "Additional Notes". The third article³ was a brief explanation of some problems one may encounter when using the alloys near their maximum useful temperature range and discusses some comments made by another worker.⁴

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1. G. G. Harman, Rev. Sci. Instr. 31 717 (July 1960).
 2. NBS Tech. News Bul. 45 5 (Jan. 1961).
 3. G. G. Harman, Rev. Sci. Instr. 32 465 (April 1961).
 4. H. M. Ferrari, Rev. Sci. Instr. 32 465 (April 1961).

The bonding properties of these alloys which have been of interest to many readers have been investigated only cursorily and as a secondary result of the work and applications described in Reference 1. However, all details and techniques that this writer is familiar with are presented here in an effort to assist readers. Many of the procedures described below are standard metallurgical practices or are normally used in the preparation of dental amalgams. A great deal of cooperation was received from the NBS Dental Research Section and their papers^{5,6} and reports were used as background material in references 1, 2, and 3.

The basic procedure to use the alloys is to mix liquid gallium (or one of its eutectics) with a readily alloying metal powder, then tamp the mixture in holes, or, place it between metal (or some types of ceramic) plates and apply pressure. In time, the mixture hardens by an alloying process similar to that of a dental amalgam, and, depending on various conditions, will produce a bond to the material that will withstand quite high temperatures.

The procedures have been extended to include other, less expensive, materials that require higher hardening temperatures, somewhat similar to that of a single component epoxy resin. These are discussed in Part II.

2. Gallium Based Alloys

2.1 Making the Gallium-Tin (or Indium) Eutectic

One of the most frequent questions received from persons desiring to use gallium alloys is why, how, and when to mix tin (or indium) with the gallium. The purpose of this procedure is to increase the ease of mixing the gallium with other metal powders and to decrease the necessary mixing temperature, thus prolonging the useful working life of the mixed materials. Gallium (Ga) melts at $\sim 30^{\circ}\text{C}$ (86°F) but its melting point may be depressed to $\sim 20^{\circ}\text{C}$ ($\sim 65^{\circ}\text{F}$) by adding 10-12 weight % of tin (Sn) or 20-25% indium (In) to it. Also, by using these Ga + Sn or In mixtures, some lengthening of the working time (pot life) is achieved, as was discussed in the additional notes of Reference I.

Incidentally, it is worth commenting that gallium is available in purities ranging from 99% to 99.9999⁺%. There is no apparent technical advantage in using the higher purities, and they may cost

5. D. L. Smith and J. J. Caul, J. Am. Dental Assoc. 53 315 (Sept.1956)

6. D. L. Smith, H. J. Caul and W. T. Sweeney, J. Am. Dental Assoc.

53 677 (Dec. 1956).

several times the lowest grade. In general, specify the lowest purity available, as long as the lead (Pb) content is not a significant part of the impurity. (Lead has detrimental effects in various mercury-silver alloys and by analogy might also effect gallium alloys.)

The Ga-Sn (or Ga-In) mixture is most easily made by placing solid lumps of tin (not tin powder⁷) or indium in contact with the appropriate amount of gallium. The tin is simply placed in contact with the solid gallium. A little finger pressure will initiate the reaction, which can immediately be seen as bright liquid droplets forming around the edges of the tin. This can then be left overnight to complete the reaction. If the ingredients are heated to $\sim 50^{\circ}\text{C}$ ($\sim 120^{\circ}\text{F}$) or higher, the reaction will occur more rapidly, within minutes. Once formed it will be a liquid (similar in appearance to mercury) above its freezing point, as mentioned previously. This liquid is then used directly in place of the gallium according to the weight percentages given in Table I of Reference 1 (reproduced on the following page).

If desired, a larger amount of Ga-Sn mixture than will be used at one time can be made. Since this mixture freely wets almost anything it touches, some care should be given to the choice of a storage container. A teflon container has proven to be best, but a satisfactory alternative is to coat the inside of a glass bottle with paraffin. Some wetting will take place but usually the entire alloy can be transferred by "dumping" or shaking out.

In order to separate a small portion of the eutectic from a larger quantity, the simplest procedure is to transfer the entire amount onto a piece of paper (it does not freely wet paper) and 'cut' a section of it off with a teflon "policeman" (shown on the extreme right of Figure 2). An ordinary knife or spatula can also be used.

The presently described work utilized the Ga-Sn mixture, but there is no apparent reason why the Ga-In mixture could not be used. Both indium and gallium readily form alloys with the metal powders listed in Table I. Since the lowest melting point mixture (eutectic) incorporates $\sim 25\%$ indium, a significant cost reduction can be achieved. It has been reported that the In-Ga eutectic hydrolizes. This is true if it is stored in 100% humidity but appears to be of no consequence under normal storage conditions. Such mixtures have been used continually in this laboratory for six years (for use as liquid-metal electrodes), stored in small plastic containers that

7. Each tin powder particle is apparently protected by an oxide coat and this severely slows its reaction with the gallium.

TABLE I. Properties of Several Gallium Alloys.^a

Constituents in Weight %	Approx. Hardening Times at 250°C ^b	Maximum Useful Temp. in Air	Expansion Coefficients and Remarks
1. 44% Cu+24% Sn, 32% Ga	24 hr	650°C	$\alpha=23.7 \times 10^{-6}/^{\circ}\text{C}$ after heating
2. 50% Cu+18% Sn, 32% Ga	24 hr	700°C	$\alpha=23.1 \times 10^{-6}/^{\circ}\text{C}$ after heating
3. 66% Cu+34% Ga	4 hr	900°C	$\alpha=19.5 \times 10^{-6}/^{\circ}\text{C}$ after heating
4. 82% Au+18% Ga	5 hr	450°C
5. 66% Au+34% Ga	8 hr	525°C	$\alpha=(15+0.012T)10^{-6}/^{\circ}\text{C}$
6. 59% Au+41% Ga	8 hr	475°C
7. 33% Au+33% Cu+33% Ga	8 hr	650°C
8. 49% Au+21% Ag+30% Ga	2 hr	425°C
9. 65% Ni+35% Ga	48 hr	250°C	Becomes a black powdery mass above this temperature

(4)

10. Au, Ag, Co, Cu, Ni, Sn
 These metals and possibly many others may be added in varying amounts to the gallium alloys to change the setup time and/or the thermal expansion.

a. All of these alloys, except No. 10 expand as they harden, thus locking themselves into the semiconductor cavity. Some other properties of alloys 1, 2, 6, and 9 are discussed in footnote references 5 and 6.

b. These values assume a particle size to pass through \sim 300 mesh screen. Larger particle sizes may take longer. Setup times at higher temperatures will be considerably less. Five or ten minutes will usually suffice at 200°C. At this temperature the Au-Ga mixture produces an exothermic reaction.

were not hermetically sealed, and no adverse effects were observed. Therefore experimentation with this eutectic is recommended.

In addition to indium or tin, other metals might add desirable properties. For the case of dental amalgams, various quantities of zinc, copper and tin are added to the basic mercury-silver composition for such purposes as reducing oxidation, increasing hardening time, controlling expansion, and increasing the hardness. Most likely, similar types of additions will be necessary for the gallium alloys before they will be practical in many applications.

2.2 Selection of the Proper Alloy

The selection of the proper alloy for a particular use is generally based upon the maximum anticipated operating temperature. However, whenever possible a gold-based gallium alloy should be chosen (see Table I). Alloy #5 is probably the most desirable. It is very difficult, even for the beginner, not to succeed in making a proper mixture when using precipitated gold (Au) powder. With gold the problems arising from oxidation, such as with copper and some other powders (discussed in Reference 3), do not exist. Also, the Au alloys all expand significantly upon hardening thus locking themselves into cavities.⁸ The weight percentage of gallium is not critical and it can be varied continuously from about 15% (a very "dry" mixture) up to 41% (a "wet" mixture).

Several workers have had difficulties when making the 41% alloy (#6, Table I). Apparently it has not always hardened properly. The explanation for this trouble is apparent from the phase diagram of Au-Ga, reproduced for convenience in Figure 1a. About 42% Ga results in an Au-Ga intermetallic compound. Additional gallium will not modify this compound, thus leaving free gallium in the interfacial region, resulting in little or no alloy strength. As explained in Reference 3, some metal powder is usually lost before mixing and some more of it is usually not wet with gallium during the mixing. Thus the alloy may end up gallium-rich and never completely harden, or contain pockets of unhardened material in a generally hardened alloy. Also the addition of tin to the gallium may modify the phase diagram. Therefore it is no longer recommended

8. Although gold-gallium alloys may expand 10% upon hardening, this does not necessarily apply high pressure on the walls of a hole. It appears that after filling all voids the expansion pressure is, in part at least, relieved in the upward direction and usually produces a mound at the top of the hole. The "wet" alloys appear to be better in this respect than the "dry" ones. Some "dry" alloys such as #4, Table I, have been observed to crack ceramic tubes while hardening.

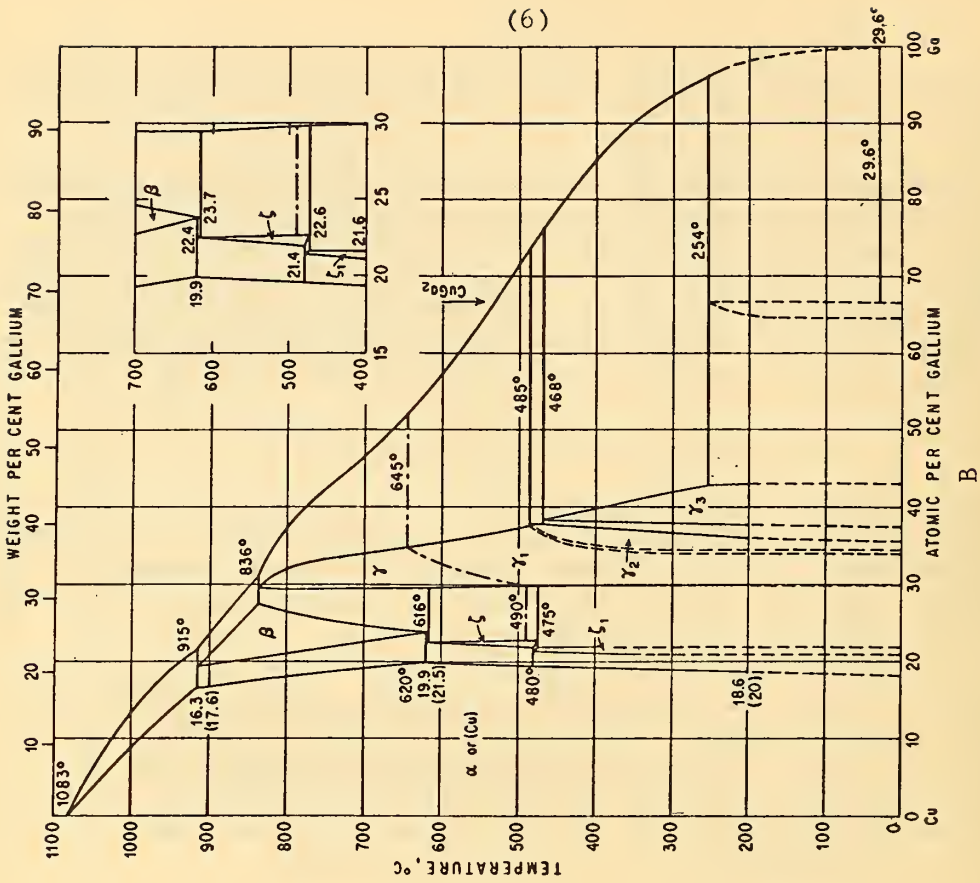
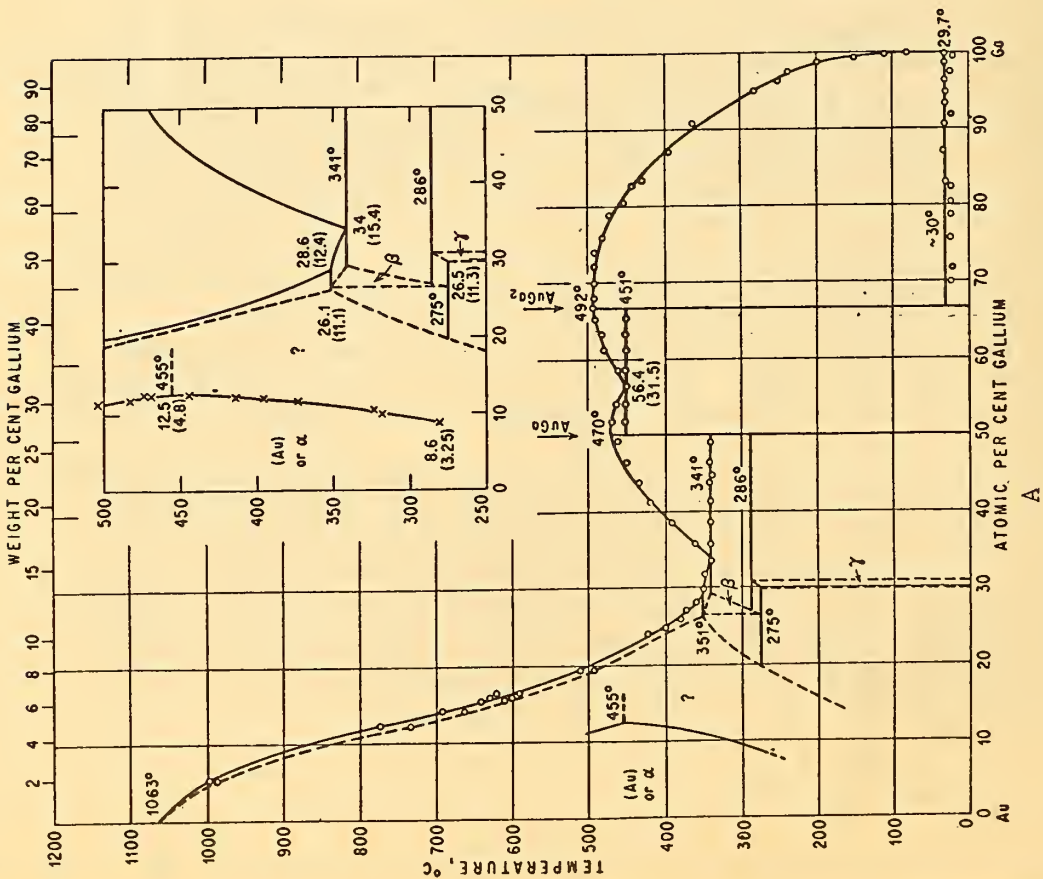


FIGURE 1 - Phase Diagrams for Gallium Alloys. A: Gallium Gold; B: Gallium Copper. (From "The Constitution of Binary Alloys", by Max Hansen, Copyright 1958. McGraw-Hill Book Company, Inc. Used by permission.)

that alloy number 6 (41% Ga + Au) be used unless both the measurement and mixing process are thoroughly controlled. The range of 30-35% of the Ga mixture + Au seems to be the most desirable when using a precipitated Au powder. If the 41% mixture (#6) is used, then any free Ga that is squeezed to the edge (or top) when applying pressure (or packing in holes) should be removed as discussed in Reference 3, thus accomplishing a decrease in the Ga percentage.

There is an additional precaution to be observed when using the Au + Ga (or Ga-Sn mixtures) alloys. Large batches of this mixed material, particularly when containing $\sim 41\%$ of the gallium mixture, may form an exothermic reaction and harden almost immediately upon packing or applying pressure. Smith and Caul (NBS Dental Research Section) measured temperatures as high as 450°C ($\sim 840^{\circ}\text{F}$) during such a reaction on ~ 1 gram pellets of 40% Ga mixture + 60% gold. This reaction is not likely to occur under the normal usage in filling small holes (~ 0.1 gram capacity) or bonding flat pieces of metal together, since there is ample opportunity to conduct away the generated heat.

As a word of caution, one worker reported trouble with a similar exothermic reaction when he mixed his gallium and gold powder in a shaker-type device. The violent shaking apparently generated enough heat to start the reaction. Since no one has reported such a reaction in the copper based alloys, a possible solution would be to use powdered gold-copper alloys. These can be obtained with various percentages of copper (Cu) and are sold as brazing alloys.⁹

Regardless of the chosen metal or the percentage of gallium it is necessary to consider the particle configuration (Precipitated, spherical, or flake type) to arrive at the final properties of the bond. This is discussed more fully under "Pot Life".

2.3 Techniques of Mixing the Alloys

After choosing the desired alloy and weighing the ingredients they must be properly mixed before a reaction can take place. Because gallium wets almost anything it touches, a teflon beaker and stirring rod are preferable but not essential. Figure 2 shows some of the tools used for mixing and applying the alloys.

The beaker is shown in the center and the stirring rod is immediately to its right. Note that the upper end of the stirring

9. Such powders used in present experiments were obtained from Western Gold and Platinum Co., Belmont, California. These powders have a spherical particle configuration.

rod has been cut off flat. This was done since mixing is best accomplished by tamping the gallium into the metal powder with only occasional stirring. Several workers using only stirring, have taken as long as 10 minutes to mix the ingredients. The total time required to hand mix a typical batch (~ 0.5 grams) of Ga + Au powder should be less than one minute for a beginner and $\sim 1/2$ minute after practice, although this will vary with the particle configuration. Gallium + copper powder usually takes about twice this time.

The freshly mixed (tamped) alloy has a silvery appearance, much the same as the original gallium mixture, although gold containing alloys will darken and turn bluish as they harden. The object of mixing is to insure the wetting of each small particle with the liquid metal, much the same way that a piece of copper is tinned with solder. When this wetting is accomplished there is intimate contact between the gallium and powder, and the alloy reaction commences immediately.

Mixing of the ingredients can also be accomplished with a dental type automatic mechanical amalgamator. Smith and Caul⁵ reported that mixing by this means improved some properties that were of dental interest.

When freshly mixed the alloys will be of a granular nature, depending upon the powder particle size, its configuration, and the tendency of the particles to agglomerate. Alloys containing a high Ga mixture ($\sim 40\%$) might be described as being similar to moderately wet cement. Others with $\sim 25\%$ gallium are simply grainy and contain large agglomerates, similar to very dry, freshly mixed cement. There is little tendency even for "wet" mixtures to flow into cracks or voids similar to melted solder and brazing material.

When any of the freshly mixed alloys are packed into cavities a portion of the gallium is squeezed to the top giving the mixture the appearance of being much "wetter" than before packing. Thus, even though a particular mixture appears too "dry" or grainy, it may be completely satisfactory after the packing operation commences. When packing in the cavity has been completed it is usually desirable to scrape away or otherwise remove the excess gallium at the top. This lowers the gallium concentration, which particularly for copper based alloys, raises the melting point. This can be seen from the phase diagram of Figure 1b.

2.4 Pot Life and Metal Powder Configuration

After the components are thoroughly mixed there is a certain amount of working time (pot life) before the mixture is too stiff

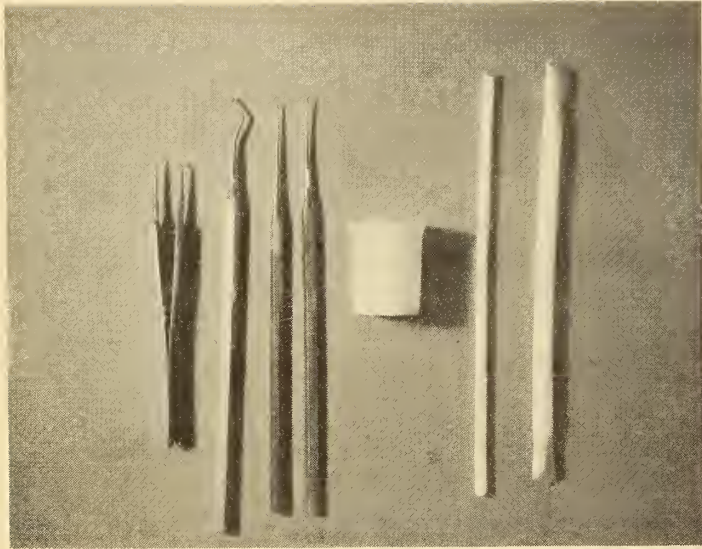


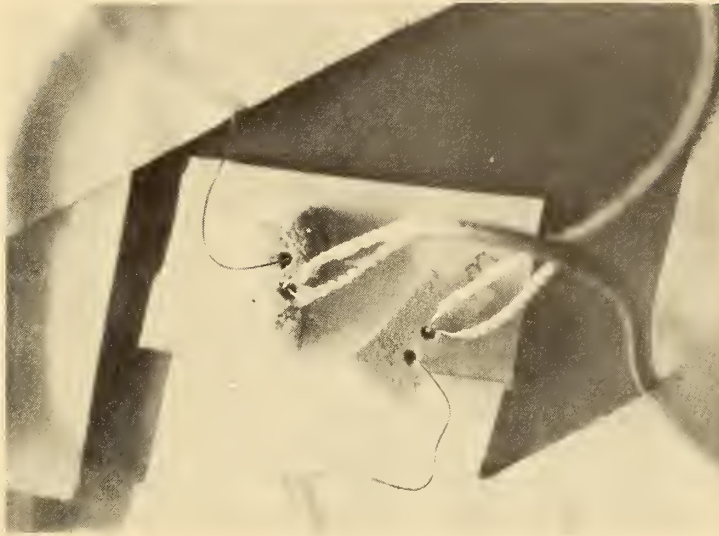
FIGURE 2 - Tools that are frequently used for mixing and packing gallium alloys. From left to right these are tweezers with a bent tip, three standard dental tools, teflon beaker, teflon stirring rod with the top cut off, and a teflon policeman

for further use. For any given mixture this time is an inverse function of temperature. However, each different metal powder (gold, copper, nickel) has a different pot life. Also it appears that powder made either by different processes or by different manufacturers can have a greatly differing pot life. For example, the gold used in the investigations of Reference 1 was a precipitated powder obtained from Fisher Scientific Company. It took about 40 seconds to mix with the gallium (alloy #5) and had a pot life of about 1/2 hour at room temperature. Subsequently, another gold powder⁹, made by a different process, which could be mixed in about 20 seconds (alloy #5) has been tested and gave a pot life of 2 to 3 hours with proportionally extended hardening times. Furthermore, use of the latter material resulted in a satisfactorily "wet" mixture with only 20% of gallium. (With such a mixture no excess gallium squeezed out upon packing and the pot life was about 1/2 hour.) There is a reasonable explanation for this. The conventional type of precipitated powder has a mossy configuration and thus offers a large surface area for a given nominal particle size. The other powders consisted of spherical particles which offer a minimum of surface area. The reader should determine which particle type is best for his particular application. The spherical ones would be best where higher ultimate melting points, longer pot life, or "wetter" mixtures are required. Some manufacturers offer metal (powders) that consist of tiny flakes. If these are not lubricated, they would probably be a good compromise between the precipitated and the spherical powders.

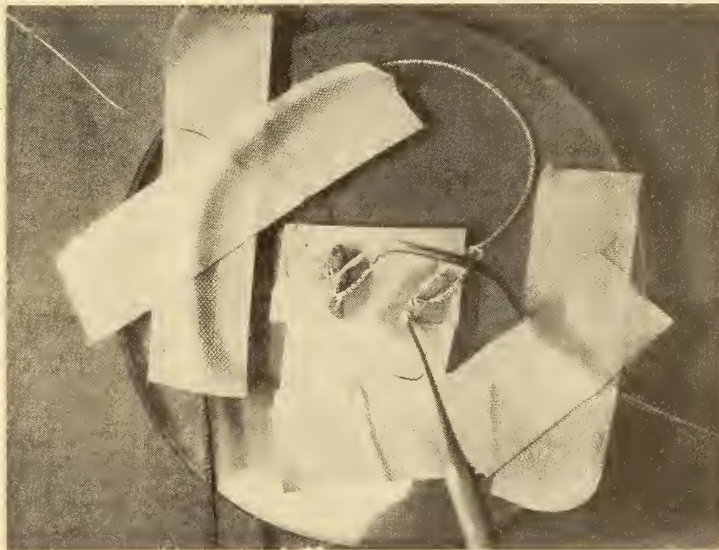
2.5 Packing the Alloys Into Cavities

Normally, portions of the freshly mixed alloys are removed from the beaker (or amalgamator) with tweezers and dropped or pushed into the cavity. Then a pointed metal tool is used to pack the alloy firmly. Dental tools of the type shown in Figure 2, to the left of the beaker, are convenient for this use but any long thin instrument can be used. Some workers have used the shank end of small drill bits. Others have successfully used blunted scribes or small sized jewelers screwdriver blades. Wooden objects, such as toothpicks, have been tried by several persons but without much success.

At times it may be necessary to pack the alloys into delicate samples that are suspended at both ends, such as when mounting samples for thermoelectric measurements. It is rather difficult to support the sample from the back side if ordinary dental tools are used to pack the alloy. A simple and completely satisfactory tool for this purpose can be made by bending one side of a pair of tweezers as shown at the extreme left of Figure 2.



A



B

FIGURE 3 - Method of preparing and mounting crude ceramic and other samples. Figure 3A shows a 2x view of the samples held in position with double-faced-adhesive tape. The wires are placed in holes that were cut with an S. S. White Industrial Abrasive Unit. Figure 3B shows the samples after they have been packed with a gallium-gold mixture. The probe at the bottom of the figure is a dental tool used in packing the alloys.

When planning to imbed wires in cavities, the samples should be completely prepared before mixing the alloys. Figure 3A is a close-up (magnification 2X) of two crude polycrystalline samples prepared for applying the soft alloy. A nickel wire is held in one cavity on each sample and a Chromel-Alumel thermocouple is in the other. The samples are held in place with double-adhesive tape. Figure 3B is an overall view showing final packing of the ingredients. As the alloy hardens, it will expand and lock itself and the wires firmly in the cavities, as discussed previously. The prepared sample can be left for several hours to harden at room temperature or put in an oven at $\sim 100^{\circ}\text{C}$ for several minutes.

2.6 Bonding Surfaces Together

There are two types of bonding for flat surfaces of metals and for some non-metals. The first is for metals that freely alloy with gallium (obtained from Table I.). Of these, silver, copper, and gold have been the most successful. It is possible to obtain good bond strengths between such surfaces. A rough, clean surface produces the best results. The surfaces must be completely wet by the alloy. This is best accomplished by smearing the soft alloy over the surface. A flattened teflon, polyethylene, or other plastic stirring rod (Fig. 2) is quite adequate for this. When properly wet, the surface will have a silvery luster. The surface can also be pre-wet with the gallium-tin mixture alone, if care is taken to wipe off the excess (leaving only a very thin film) before applying the mixed alloy.

The layer of alloy between metal pieces should be moderately thick ($\sim 0.01''$) in order to assure complete coverage. Very thin uniform layers are difficult to obtain. Usually, attempts to bond with such layers produced areas containing numerous air pockets and thus weak bonds.

After the mixed alloy is placed on the metal surfaces they are firmly clamped together with a vice, c-clamp or other means and allowed to harden. The best results (joint strength of 3000 - 4000 lb/sq. in. measured in a tear test) were obtained when joining copper pieces, using a gallium and gold alloy. Heat, (150°C , 300°F) was applied for 24 hours. This was done to facilitate gallium diffusion into the metal surfaces. No tests have been run to determine the optimum time and temperature for sufficient diffusion, and possibly only an hour or so would yield similar results. It is possible that the gallium diffusion into copper follows the usual exponential-time-temperature relationship common with other types of diffusion. This would imply that good results could be obtained at room temperature in an appropriate length of time. See the section on Bonding Mechanism for a further discussion.

High bond strengths do not result when materials that are not readily wet with gallium (e.g., stainless steel and most ceramics) are used. Here the bond is apparently of a mechanical nature and will depend upon such features as surface roughness to obtain adhesion. Abrasion, sandblasting, and etching are customarily used to obtain such surfaces, but even with this the resulting bond strength will probably not exceed 100 or 200 lb/sq. in. in test.

An obvious alternative is to plate the uncooperating surface with gold, copper, or silver. Only a minimum amount of work has been done to verify this, but one precaution is evident. If the plating is very thin (~ 0.1 mil) then there is a possibility that the coat will separate from the substrate during the alloying process. Probably a one or two mil (0.002") coat is safe, but verification experiments should be run at the maximum anticipated operating temperature.

Most non-metals can be treated in the same class with stainless steel. However, both forsterite ceramic and glass-like lithium fluoride crystals developed stronger bonds than anticipated when joined with a gallium-gold alloy. In both cases the samples were heated to 150°C for 24 hours. The forsterite had a rough surface but the lithium fluoride was polished. One test on joining pieces of dense alumina ceramic resulted in very low bond strength.

Many people have inquired about making aluminum-aluminum bonds with gallium alloys. A number of attempts have been made to achieve this result but without any success.

As a general procedure when using more or less brittle bonding agents one should avoid simple butt joints. However, tongue and groove (scarf and landed scarf) are satisfactory. Corner joints should be of the end-lap or mitered joint type with spline. Right angle joints that give rise to either peel or cleavage stress should be made in the 'L' or 'T' design. Cylindrical slip joints (copper plumbing pipes are a good example) are ideal for this type of bonding. Various lap-type joints are satisfactory. The limited number of bond-strength tests have been made with the latter type.

2.7 Hardness of the Alloys

A few hardness tests were made on hand-packed hardened specimens of alloys but at best these are only indicative. Most of the test samples contain discontinuities in sufficient quantity to lower the hardness. (Machine or vice-compressed samples should be better). Also the uneven distribution of gallium throughout a hand-packed sample can result in hardness gradations along the profile. With these qualifications in mind the following table is presented. All

are Vickers hardness values measured with a 5 kg load by W. T. Holshouser.

TABLE II

<u>Alloys</u>	<u>Constituents, Wt %</u>	<u>Approximate Hardness</u>
1	44% Cu + 24% Sn, 32% Ga	68
2	50% Cu + 18% Sn, 32% Ga	58
6	59% Au + 41% Ga	40
7	33% Au + 33% Cu + 33% Ga	40
8	49% Au + 21% Ag + 30% Ga	56
(Footnote 10)	65% Au + 16% Cu + 1% Zn + 18% Ga	128
-	Annealed Copper	73
-	Annealed Yellow Brass	112
-	Annealed Silver	38

The copper, brass and silver (annealed at 450°C, 1/2 hour) are presented for comparison purposes. As an example of the variations encountered, values for alloy No. 6 ranged from 34 to 46, and one anomalously high value (96) was obtained for alloy No. 1. All of the alloys appear at least as hard as brass by the scratch test. This may mean that individual particles are harder and it is the particle boundary that is weakest. Possibly because of this the alloys are usually somewhat brittle; more so than would be indicated from their measured hardness. If this is the case then appropriate heat treatment should improve the ductility.

2.8 Mechanism of Alloying

No studies are known to have been made on the mechanism of gallium alloy binding of the type discussed above. However, a few brief comments can be made, based on the established concepts of liquid phase sintering.



10. This experimental alloy was made by using spherical powders consisting of an alloy of 20% Cu + 80% Au (obtained from Reference 9. These powders were mixed with 20% of a liquid made by mixing 5% Zn and 5% Au in Ga. Probably as a result of the spherical particles the maximum spread in Vickers hardness was only 5%.

This sketch shows two gallium coated gold particles pressed together. The short lines indicate the depth of alloying. The more gallium the greater this depth. Thus, it is apparent that there can be a bond over a wide continuous variation in the amount of gallium present. The interfacial bonding should be the result of (1) a small amount of gold dissolving in the liquid gallium and (2) a crystallization of some of the gold (as a gold-gallium alloy) in the interfacial region, when the majority of the gallium has diffused into, and thus alloyed with, the bulk of the gold particle. Thus a two step process occurs, in which the gallium preferentially diffuses into (and alloys with) the gold particle, leaving behind a gold-rich gallium solution. When the dissolved gold concentration becomes too great, crystallization in the form of a gold-gallium alloy occurs. This nucleates on the particle surface and fills the interfacial region. Assuming this mechanism is correct in the present case, bonds made at elevated temperature should be stronger than those made in the room ambient, because of the greater solubility of gold in gallium at elevated temperatures. Therefore, better more uniform interfacial layers would form and thus the bond strength would be greater. Such crystallization would be primarily dependent upon the maximum temperature rather than time. For a good discussion of such mechanisms see for instance the book Fundamental Principles of Powder Metallurgy by W. D. Jones (1960) Chap. IV, the book Transistors Vol. I, P 28-31 and 112-120, Published by RCA (1956) or other texts on similar subjects.

Assuming this is the correct mechanism for the gallium alloying, then for greatest bond strength the gallium-tin mixture should actually be a gallium-tin-gold mixture containing the maximum amount of gold soluble at room temperature. Also, alloys made from spherical particles, with their longer hardening time, can be raised to higher temperatures before hardening. Therefore, more gold would dissolve in the gallium and a stronger interfacial bond should result.

The above comments may serve to help persons who are not metallurgists to better understand the present alloying processes. The comments apply equally well to the non-gallium containing alloys described in Section II.

2.9 Sources of Gallium

Gallium is a rare, little known element, thus the most frequent question received was for a list of suppliers.

Five grams of gallium is probably the absolute minimum required to evaluate the present techniques and 10 or more is desirable. It is not recommended that 1 gram be purchased for this purpose. Some manufacturers will not sell less than 100 grams and others will sell as little as 5 grams but in general the prices drop significantly for

amounts of 100 grams or more. The following is an alphabetical listing of the manufacturers (or suppliers) of gallium. It represents all of the sources in the United States that this writer is familiar with, although there may be others. Presumably any metal or scientific supply house will obtain gallium for special orders but few have it as a stock item.

AIAG Metals Inc.
9 Rockefeller Plaza
New York 20, New York

Fisher Scientific Company
711 Forbes Avenue,
Pittsburgh 19, Pennsylvania

Aluminum Company of America
2900 Missouri Avenue,
East St. Louis, Illinois

Materials for Electronics, Inc.
152 - 25 138th Avenue,
Jamaica 34, New York

Eagle-Picher
Rare Metals Department
Miami, Oklahoma

United Mineral and Chemical Corp.
Metals Department
16 Hudson Street,
New York 13, New York

2.10 Physiological Properties of Gallium

One of the more frequently asked questions pertains to the physiological properties of gallium metal. Since this is a liquid metal, many people associate it with mercury and assume it to be similarly dangerous. No tests have been performed in this laboratory to verify or contradict this, and it is not our function to do so. However, gallium metal has been used freely without precautions (except perhaps to wash the hands after physical contact) in this laboratory by many persons for over 6 years with no apparent harmful effects. There have been a number of studies on the subject that are more authoritative than uncontrolled personal observations, and the interested reader may refer to them.^{11,12,13,14,15,16}

11. Mineral Yearbook, 1310, (1949).

12. Dudley & Levine, Studies of Acute Toxicity of Gallium, Naval Medical Research Institute Report #3 (1/13/49).

13. Brucer et. al., A study of Gallium 72, Radiology 61 534-613 (1953).

14. Meek, Harrold, and McCord, Toxicity of Gallium, An Exploratory Investigation; Industrial Medicine, 12, 7 (Jan. 1943).

15. J. L. Hartley and N.O. Harris, A Comparative Evaluation of Tissue Tolerance to a Gallium Alloy, Air University, School of Aviation Medicine, USAF, Randolph AFB, Texas: Report #58 - 148, (Nov. 1958).

16. H. C. Dudley and M. D. Levine, Studies of the Toxic Action of Gallium, J. Pharmacology & Experimental Therapeutics V.95, 487 (1949).

3. Alloys That Will Harden in Higher Ambient Temperatures

Since gallium is expensive and its alloys must be mixed immediately before use (or else refrigerated), it is desirable to consider other possibilities, where higher forming temperatures are permitted. In such cases premixed ingredients, which will keep on the shelf for years can be used. These can be in the form of prepared metallic strips and other preformed shapes which can easily be inserted between components, the appropriate pressure and heat applied, and a bond will be formed.

If ambient temperatures up to about 250°C can be tolerated, then a large number of mixtures suggest themselves as capable of being used as the solder. In each case, however, the metals chosen must alloy with one another and one must be liquid and one solid at the chosen bonding temperature. Again, the solid constituent of the bonding materials will be a finely divided powder. For best results, the metals to be bonded should be those which will actually alloy with the liquid constituents of the bonding agent. The following table sets forth some examples of satisfactory bonding materials, where the liquid constituent is in liquid phase at temperatures significantly above room temperature.

TABLE III

	<u>Metals</u>	<u>Useful % Range of Low m.p. Metal</u>	<u>Approximate Hardening Ambient</u>	<u>Approximate Useful Temperature Range</u>
1.	In-Au	53% - 30%	175°C	495° to 350°C
2.	In-Cu	52% - 30%	175°C	700° to 650°C
3.	In-Ag	33% - 30%	175°C	600° to 550°C
4.	Sn-Cu	55% - 30%	250°C	750° to 400°C
5.	Sn-Au	50% - 30%	250°C	600° to 400°C
6.	Sn-Fe	68% - 30%	250°C	900° to 800°C
7.	Sn-Ni	55% - 30%	250°C	1250° to 1150°C

In general the best results are obtained by using combinations in which the low melting component of the bonding agent makes up from 40 to 60% of the entire composition with 30% set as a minimum limit. This is done to assure uniform wetting of both the higher melting powder and the pieces to be fastened. This percentage may possibly be lowered by further experimentation.

Just as with gallium, suitable preparations of indium or tin may be desirable in order to lower the curing temperatures. Typical

examples of this eutectic type depressing of the curing ambient are as follows:

(52% In + 48% Sn) plus Au, Cu or Ni powder cures at about 130°C.

(32% Cd + 68% Sn) + Au, Cu powder cures at about 200°C.

Ternary and quaternary alloys) + appropriate metals.

There are undoubtedly other combinations that may be useful under various circumstances.

The procedure is to mechanically mix the two (or more) components at room temperature. Where indium is used the high melting metal powder may be kneaded into a solid strip of indium, or the powders of indium and other metals may be mixed and pressed into thin strips. Either the strip or the mixed powder is placed between the metals to be bonded. An appropriate low temperature soldering flux (not a brazing flux) is applied. In some cases it may be desirable to "wet" or "tin" the metal pieces with a very thin coating of the low melting point constituent. To insure the best reaction the components are clamped under pressure and the entire unit is placed in an oven at the appropriate temperature for the chosen alloy.

With two exceptions, the above materials have received only cursory tests and therefore additional experimentation would be required before their use. The exception was alloy #1 and by inference alloy #2. Two one-half inch square bars of copper were bonded together using precipitated gold powder which was kneaded into a strip of soft indium metal (50% indium and 50% gold). The resulting strip was placed between the copper bars, which were wet with a soft soldering flux (Division Lead Company flux #335). The bars were held together with a C-clamp and placed in an oven at $\sim 200^{\circ}\text{C}$ overnight. The resulting bond was considerably stronger than 5000 lb/sq. in. and very obviously broke by peel rather than tensile failure since the bars bent in the testing machine. The melting point from the phase diagram (assuming ~ 50 wt% of both In and gold in the bonding alloy and no more than 30% In available for alloying with the copper surfaces would be $\sim 500^{\circ}\text{C}$. Indium has a tensile bond strength of only a hundred or so lb/sq. in. thus it is obvious that both the gold and copper formed hard alloys with the indium resulting in the strong bond. There was no effort to determine the minimum time and temperature possible for forming such a strong bond.

4. Conclusions

This report with Reference 1, 2, 3, and 4 represent all of the published knowledge presently available on industrial and scientific

uses of dental-amalgam-type gallium alloys for bonding purposes. There are undoubtedly many applications where the use of the alloys may not be practical, but for the many others where it is, sufficient details have been presented to allow persons with any type of background to evaluate the use of these alloys in their particular problem. In addition it is hoped that these works will create an interest in fundamental studies of the type of bonding mechanisms involved and result in improved characteristics and simplified techniques. With greater consumption the price of gallium should decrease and make these processes available to a wider range of uses.



U. S. DEPARTMENT OF COMMERCE
Luther H. Hodges, *Secretary*

NATIONAL BUREAU OF STANDARDS
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THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

WASHINGTON, D. C.

Electricity. Resistance and Reactance. Electrochemistry. Electrical Instruments. Magnetic Measurements. Dielectrics. High Voltage.

Metrology. Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Scale. Volumetry and Densimetry.

Heat. Temperature Physics. Heat Measurements. Cryogenic Physics. Equation of State. Statistical Physics. **Radiation Physics.** X-ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. Nucleonic Instrumentation. Neutron Physics.

Analytical and Inorganic Chemistry. Pure Substances. Spectrochemistry. Solution Chemistry. Standard Reference Materials. Applied Analytical Research. Crystal Chemistry.

Mechanics. Sound. Pressure and Vacuum. Fluid Mechanics. Engineering Mechanics. Rheology. Combustion Controls.

Polymers. Macromolecules: Synthesis and Structure. Polymer Chemistry. Polymer Physics. Polymer Characterization. Polymer Evaluation and Testing. Applied Polymer Standards and Research. Dental Research.

Metallurgy. Engineering Metallurgy. Microscopy and Diffraction. Metal Reactions. Metal Physics. Electrolysis and Metal Deposition.

Inorganic Solids. Engineering Ceramics. Glass. Solid State Chemistry. Crystal Growth. Physical Properties. Crystallography.

Building Research. Structural Engineering. Fire Research. Mechanical Systems. Organic Building Materials. Codes and Safety Standards. Heat Transfer. Inorganic Building Materials. Metallic Building Materials.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics. Operations Research.

Data Processing Systems. Components and Techniques. Computer Technology. Measurements Automation. Engineering Applications. Systems Analysis.

Atomic Physics. Spectroscopy. Infrared Spectroscopy. Solid State Physics. Electron Physics. Atomic Physics.

Instrumentation. Engineering Electronics. Electron Devices. Electronic Instrumentation. Mechanical Instruments. Basic Instrumentation.

Physical Chemistry. Thermochemistry. Surface Chemistry. Organic Chemistry. Molecular Spectroscopy. Molecular Kinetics. Mass Spectrometry.

Office of Weights and Measures.

BOULDER, COLO.

Cryogenic Engineering Laboratory. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Cryogenic Technical Services.

CENTRAL RADIO PROPAGATION LABORATORY

Ionosphere Research and Propagation. Low Frequency and Very Low Frequency Research. Ionosphere Research. Prediction Services. Sun-Earth Relationships. Field Engineering. Radio Warning Services. Vertical Soundings Research.

Radio Propagation Engineering. Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation-Terrain Effects. Radio-Meteorology. Lower Atmosphere Physics.

Radio Systems. Applied Electromagnetic Theory. High Frequency and Very High Frequency Research. Modulation Research. Antenna Research. Navigation Systems.

Upper Atmosphere and Space Physics. Upper Atmosphere and Plasma Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.

RADIO STANDARDS LABORATORY

Radio Physics. Radio Broadcast Service. Radio and Microwave Materials. Atomic Frequency and Time-Interval Standards. Millimeter-Wave Research.

Circuit Standards. High Frequency Electrical Standards. Microwave Circuit Standards. Electronic Calibration Center.

