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BRAZING BERYLLIUM BY CAPILLARY FLOW

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TECHNICAL REPORT AFML-TR-67-14, PART II

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Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

FOREWORD

This report was prepared by the Research Laboratories, Solar Division of International Harvester Company, San Diego, California, under Contract AF33(615)-2853. The contract was sponsored by the Metals and Ceramics Division, Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, and is administered under the direction of Mr. R. E. Bowman and Dr. G. E. Metzger, MAMP.

The period covered by this report is 1 January 1967 through 15 June 1968.

Major contributions to this program were made by Dr. A. G. Metcalfe and Mr. R. Bogowitz (brazing studies) assisted by Mr. E. Mack.

The manuscript was released by the authors July 1968 for publication as an AFML technical documentary report. Solar's report number is RDR 1502-9

This technical report has been reviewed and approved.

I. Perlmutter

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Chief, Metals Branch
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ABSTRACT

Six silver-base braze alloys (including some high in copper), with a high tolerance for adverse braze conditions, were developed to give maximum capillary flow in unplated beryllium sheet without flux at 1400°F to avoid loss of base metal wrought properties. In addition, one titanium-base alloy showed promise for brazing beryllium as low as 1400°F.

Silver-base alloys were developed and optimized, by selected additions, for brazing in argon, starting from the silver-copper eutectic. The sequence used in the development and evaluation of braze alloys included:

- Determination of melt-flow temperatures and flow distance on flat plates of beryllium sheet
- Capillary flow over a vertical distance of one inch for isothermal conditions
- Analysis of braze joint structures
- Strength of brazed joints

The tolerance of alloys for changes in braze conditions was studied by varying the argon quality and methods of beryllium surface preparation, and by evaluating the practical application of alloys to beryllium honeycomb. Surface preparation techniques and additions that react unfavorably with beryllium or the atmosphere were found to influence flow considerably. Selected silver-base alloys and typical joint shear strengths at 1000°F are listed:

• Ag-59. 4Cu-9. 5Ge-1. 9Ti-5Mn	8. 6 ksi
• Ag-25. 2Cu-9. 5In-5Mn	6. 7 ksi
• Ag-23. 6Cu-8. 9In-8. 8Pd-2Ti	7. 9 ksi
• Ag-24. 6Cu-9. 5Sn-5Mn	7. 7 ksi
• Ag-33Cu-7Sn-3Mn	8. 4 ksi
• Ag-53Cu-5Zn-0. 2P	7. 3 ksi

Titanium alloys were studied. Compositions based on the titanium-zirconium base system were optimized to braze beryllium below its recrystallization temperature. The composition Ti-46. 6Zr-5. 3Ni-3. 2Ag-4. 5Be exhibited good wetting and capillary flow properties as low as 1400°F. Joint strength was slightly lower than for silver-base alloys.

Aluminum-base braze alloys were also investigated; however, acceptable wetting and flow could not be achieved.

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SECTION I

INTRODUCTION

Application of beryllium in aerospace applications requires reliable methods to join the metal to itself and to other metals. Welding has not proven to be a satisfactory method for joining, because the wrought structure is destroyed and excessive porosity results with present-quality beryllium. Adhesive bonding has been used for low-temperature applications, but shear strengths are limited and joints have high thermal resistance. Therefore, brazing assumes unusual importance for joining beryllium.

However, review of current brazing practices for beryllium shows that little braze alloy flow is expected or achieved in the absence of flux. The use of flux promotes flow but presents the usual problems of entrapment, reduced corrosion resistance in the event of incomplete removal, and general problems of flux removal. In addition, flux causes special problems with beryllium because of the toxicity of the element in certain forms. To achieve adequate wetting in the absence of fluxes, current practice favors preplacement of braze alloys; generally with pressure applied normally to the faying surfaces. This approach is not completely satisfactory because permissible joint designs are limited and reliability is not as high as desired.

Beryllium oxide is the major obstacle to flow. The oxide will form during heating, even in the best attainable atmosphere, so that brazing processes have been developed using fast heating cycles (e.g., by resistance heating) to diminish this problem. Such techniques have been excluded from the scope of this program because they would lead to a severely limited process. The high specific heat and high thermal conductivity of beryllium make fast heating cycles difficult to achieve. The heating rates used in the present program have been compatible with a furnace brazing operation.

The presence of oxide as an inhibitor to braze alloy flow is a typical problem in brazing aluminum, titanium, and stainless steels. Different metallurgical and thermodynamic equilibria are used to solve the problem in each case, but the amounts of oxide involved are limited to films of a few hundred Angstroms (Å) in thickness. A complicating factor enters the picture in the case of beryllium: this factor is the presence of one percent or more of beryllium oxide in typical beryllium metal in the form of a dispersion. Prior experience with attempts to braze oxide dispersion metals, such as SAP and TD Nickel, shows that unusual problems are introduced. It has been shown that oxide in the beryllium was detrimental to braze alloy flow.

SECTION I

INTRODUCTION

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Work reported in AFML-TR-67-14 covered the first year of study (Ref. 1). Silver-base braze alloys were developed for capillary flow on a beryllium substrate at brazing temperatures of 1500 to 1650°F. These alloys exhibited excellent capillary flow and possessed greater tolerance for adverse changes in brazing conditions than most standard braze alloys. This work also showed that developmental titanium-base braze alloys had excellent flow characteristics. Limitations of time and funds did not allow lower flow temperature alloys to be developed to braze wrought beryllium without loss of properties by recrystallization.

A continuation contract was awarded to Solar by the AFML Metals and Ceramics Division to perform second-year studies for the optimization of braze alloys and braze procedures for beryllium. Primary objectives of the second-year work were:

- To develop silver-base and titanium-base alloys for brazing beryllium below the recrystallization temperature

- To study aluminum-base braze alloys

Studies were divided into three major areas of investigation.

- Evaluation of additions to selected base alloys to reduce melt-flow temperatures to 1400°F and develop maximum flow properties.

- Modification of braze alloys to control melt-flow temperatures and the identification of mechanisms to aid wetting and flow.

- Evaluation of promising braze alloys to select the most promising for recommendation.

During initial studies, additions were made to basic braze systems to evaluate their effect on melt-flow temperatures and braze flow properties. These tests were conducted on flat plate beryllium coupons.

In the next phase of study, selected alloys were modified to develop improved wetting and flow properties. Various conditions were investigated that affect braze alloy melt-flow temperatures and flow distance. Both flat plate and capillary T-specimens were used for these tests.

In the final period of study, braze properties of selected alloys were evaluated to aid in selecting the most promising compositions for recommendation. Choices made were based on results for melt properties, capillary flow, joint strength tests, metallographic analysis, and alloy tolerance for changes in braze conditions. Test specimens for these studies included capillary T-specimens, butt- and lap-shear coupons, and simulated honeycomb panels.

Because many of the candidate alloys finally selected exhibit braze properties that are equally good, seven were selected for recommendation; six were silver-base alloys for brazing at 1400°F or above, and one is a titanium-base alloy for brazing at 1400°F or above.

Studies with aluminum-base alloys were discontinued early in the program because of poor results. Acceptable flow occurred only when fluxes were used.

SECTION II

EXPERIMENTAL PROCEDURES

The experimental procedures discussed in this section include braze alloy preparation, preparation of test specimens, and procedures for evaluating program alloys. Braze alloy preparation is divided into two sections; the first section reviews standard procedures and the second section relates to alloys with volatile additions. The preparation of test specimens includes materials, specimen configuration, and surface preparation. The last part of this section deals with test procedures. Equipment for flow studies is described, followed by a discussion of procedures for flow evaluation.

2.1 PREPARATION OF BRAZE ALLOYS

All braze alloys used for this program were prepared in Solar's laboratory. Program alloys that did not contain volatile additions such as cadmium, lithium, phosphorus, and zinc were prepared using the standard arc-melt approach. Alloys containing these additions were prepared using modified melt-sequence techniques. A description of materials and procedures is contained in following paragraphs.

2.1.1 Standard Procedures

All alloying materials used in preparing test alloys were obtained from commercially pure stock. Master melts were generally prepared in either 10.00 or 20.00 gram charges; whereas, test alloy melts were usually made in smaller quantities of from one to three grams. Test alloys showing promise would then be made in larger 5- or 10-gram melts for further evaluation.

Alloying elements for each melt are first weighed separately to the nearest milligram. The total charge is then weighed as a unit to check combined initial weights. After triple melting, the charge button is weighed to detect any loss or gain. Acceptable alloy buttons are then broken open and examined for segregation or unmelted constituents. If defects are noted, the alloy is melted again and re-examined. If defects are still evident, the button is discarded and a new melt is prepared.

FIGURE 1. ARC MELT EQUIPMENT

Earlier studies of alloy preparation (Ref. 1) showed conclusively the advantages of arc melting when compared to induction melting. Therefore, the arc-melting technique was adopted for alloy preparation for this program. Figure 1 shows the arc-melting equipment. The chamber consists of a heavy wall (12 inches high by 6 inches in diameter) Vycor glass cylinder capped at each end by one-inch thick aluminum plates. A water-cooled copper crucible fastened at the center of the base plate holds the melt charge. This charge is melted by an arc that is generated between a nonconsumable tungsten electrode and the charge itself. Manual control of the tungsten electrode is made through an opening in the top plate. Air is prevented from entering the chamber at the electrode by means of a rubber bellows seal and by action of the protective argon gas that is supplied through a tube in the base. Access to the chamber interior is made either through the opening in the top plate or by separating the glass cylinder from the base plate. Power for the arc is developed by a low voltage portable 200 ampere dc generator.

2.1.2 Volatile Additions

Melts with cadmium, zinc, lithium, phosphorus, and titanium generally show characteristic weight losses after standard arc-melting procedures are used. No weight change is noted for silver-copper master melts with additions of indium, germanium, and tin. This is expected considering the high vapor pressure of cadmium, lithium, phosphorus, and zinc, and the relatively lower vapor pressure of indium, germanium, and tin at alloying temperatures. Loss of titanium by oxidation appears most likely.

Three methods of alloy preparation were considered as possible solutions to vaporization losses. They are:

- Alternate Melt. Since weight losses are negligible during preparation of basic silver-copper alloys, any weight change shown after an addition was made was recorded, these data were then used in computing composition for alternate melts. Prior to arc melting, then, the alternate alloy contains an excess addition equal to the amount lost from the original melt. Provided melting procedures are standard, the resultant alloy should be within the acceptable weight range.

- Excess Addition. Assuming there will be losses from melts containing the more sensitive additions, an excess of the addition is added to the charge. The procedure is to make successive remelts and weight checks until the weight that gives the desired composition is reached. The remelts are of short duration so that button weights can be controlled more accurately. Normally, only two to four remelts are required to reach the correct weight.

- Controlled Chamber Pressure. Evaporation of the more volatile components during melting can be minimized by raising chamber pressure to atmospheric pressure or above.

The third approach (controlled chamber pressure) was evaluated first and found to be somewhat limited in effectiveness. Losses as high as 20 percent were encountered. Therefore, this method was unacceptable. The first approach (alternate melt) was evaluated next because it was felt that the remelt frequency for this method would be less than the second approach (excess addition). In practice, this method did not prove satisfactory because losses were not consistent with those determined from the initial test melts. Many alloy buttons exhibited excessive weight changes. This technique was also unacceptable.

The second approach (excess addition) for alloy preparation was evaluated last and the results were acceptable. The desired button weight was usually reached after two or three additional arc-melt passes. This technique was selected for the preparation of braze alloys. A similar technique was used when more than one volatile element was added. The loss of the least volatile element established from prior work on ternary alloys was used as a guide to the excess required in the more complex alloy.

2.1.3 Phosphorus Additions

Although earlier work with phosphorus additions showed that direct alloying with massive phosphorus was satisfactory (provided necessary melting precautions are maintained), more recent work has shown that phosphorus can also be effectively added from a master copper-phosphorus alloy. Chemical analysis of arc-melted commercial copper-phosphorus wire showed only minimal loss. A comparison of the alloy composition before and after arc melting is given below:

Alloy Wire	As Received (%)	After Arc Melting (%)
Phosphorus	8.35	8.20
Copper	91.65	91.80

The special high-purity alloy wire was made for Solar by the Westinghouse Corporation, Alloy Metals Division. It is a eutectic composition with a melt temperature of 1320°F.

2.2 PREPARATION OF BERYLLIUM TEST SPECIMENS

This portion of the report describes the beryllium materials used and includes a discussion on the preparation of test specimens for braze alloy evaluations.

2.2.1 Material

Two grades of beryllium were used for this program - the cross-rolled sheet with up to two percent beryllium oxide and the higher purity ingot sheet with 0.10 percent oxide. Unless otherwise stated, all work was conducted with standard cross-rolled sheet made from compacted powder billet. The ingot sheet beryllium was used only for making honeycomb core. A typical composition for each grade of beryllium is presented in the following tabulation.

	Cross-Rolled Sheet In Accordance With Specification SR200C (%)	Ingot Sheet (%)
Beryllium	Balance	Balance
Beryllium oxide	2.00 max	0.1
Aluminum	0.16 max	0.08
Carbon	0.15 max	0.04
Iron	0.18 max	0.10
Magnesium	0.08 max	0.01
Silicon	0.08 max	0.04
Other metallics	0.04 max	0.02

The beryllium cross-rolled sheet is made from hot-pressed block that has been stress relieved, surface ground, and etched. Surface finish is 63 rms or finer. This sheet was acquired in four thicknesses; 0.020, 0.040, 0.060, and 0.080 inch. The higher purity ingot sheet, selected for use as honeycomb core stock, was in foil thicknesses of 0.005 to 0.006 inch.

When SR200C beryllium is heated above 1350°F, its properties are reduced in relation to the time and temperature conditions applied. This point is shown by data relating to the recrystallization temperatures of cross-rolled sheet presented in Table I and in Reference 2. These data show that beryllium's wrought properties diminish above 1350°F with losses becoming more severe above 1400°F. Therefore, if wrought properties are to be retained, maximum braze temperatures should not exceed 1400°F. In view of this fact, 1400°F has been established as a braze temperature target for the program.

TABLE I

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.020 INCH CROSS-ROLLED SHEET BERYLLIUM (Ref. 3)

	20-Minute Treatment at Temperature (°F)	Test Temperature (°F)	Ultimate Tensile ($\times 10^3$ psi)	Yield Strength 0.2% Offset ($\times 10^3$ psi)	Percent Elongation	Remarks
1	As received	Room	84.1	64.6	15.5	
2	1350	Room	88.2	65.4	16.5	
3	1400	Room	84.6	63.4	10.0	
4	1450	Room	80.5	61.1	7.5	
5	1500	Room	76.2	58.6	5.5	
6	1660	Room	56.2	36.8	3.5	Aged 20 hours at 1350°F

2.2.2 Test Specimens

Development and evaluation of braze alloys was conducted with six different types of specimens:

- Flat plate
- Capillary flow T-specimens
- Tolerance test T-specimens
- Tensile/butt
- Tensile/shear
- Simulated honeycomb

Typical samples of each specimen are shown in Figure 2.

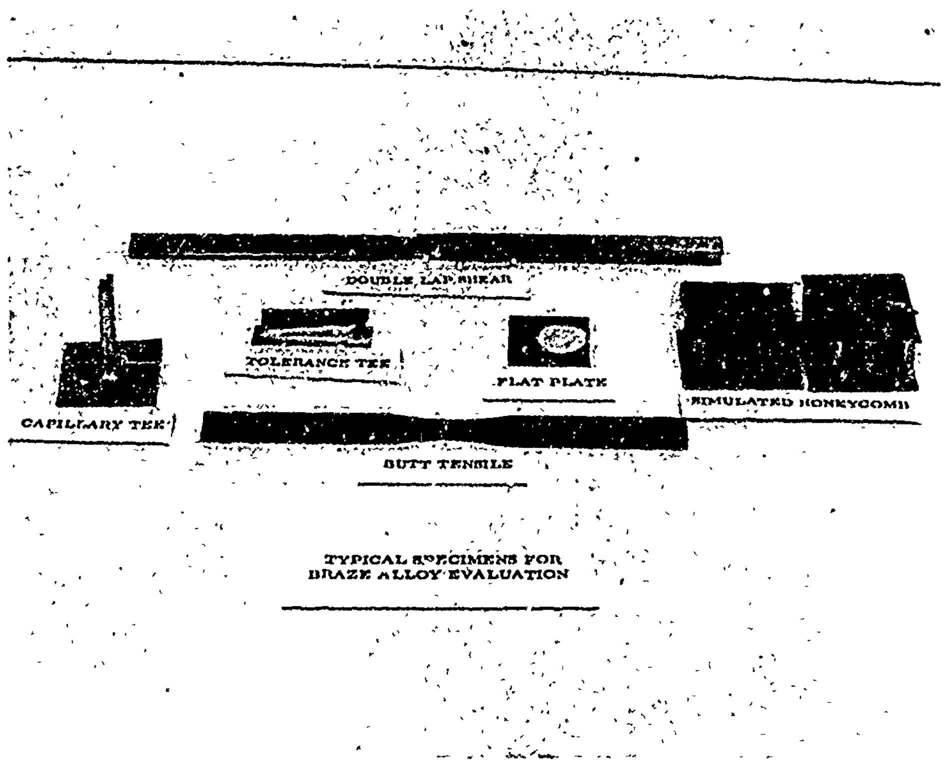


FIGURE 2. BERYLLIUM TEST SPECIMENS FOR BRAZE ALLOY DEVELOPMENT AND SCREENING

Flat Plate

A flat plate coupon was selected to evaluate developmental program alloys, because this type of specimen not only allows braze alloy characteristics to be monitored during the braze cycle, but it also provides samples for comparison of alloy flow distance. Flat plate specimens are 0.75-inch square and are made from 0.020- and 0.040-inch gage stock. Figure 2 shows a typical flat plate coupon with an alloy sample flowed on the surface.

Capillary T-Specimen

Based on prior work, the capillary T-specimen was selected for evaluating capillary flow of program alloys. A standard capillary T-joint is shown in Figure 2. Since the main objectives of this program were to develop braze alloys and braze techniques for brazing beryllium by capillary flow, it is felt that a T-configuration would be a suitable test specimen.

Initially, a 0.002-inch spacing had been selected as clearance between the two vertical members. However, as work progressed, it became apparent that this clearance did not promote reproducible values. A range of gaps between no intentional gap (defined as zero gap) and 0.010 inch were brazed with Ag-28Cu at 1500°F for three minutes to determine the optimum clearance. After brazing, radiographs were made to compare flow for the various gaps.

An examination of the radiographs indicated the zero-gap (net fit) joint was the most reproducible. A comparison between the zero and the standard 0.002-inch clearance is presented in Figure 3. Note the partial flow along the flow path for the standard capillary T-joint (Fig. 3A). Alloy flow preferentially followed the 0.002-inch thick vertical spacer, but did not continue into the adjacent portion of the joint. Although vertical flow for the joint with zero clearance (Fig. 3B) was equal to that shown in the companion specimen, the zero-gap specimen displayed complete coverage for the total width of the joint. Because of the greater reliability shown by the zero-gap specimen, it was selected for evaluating capillary flow of program alloys.

A. 0.002-INCH GAP B. ZERO GAP (nom)

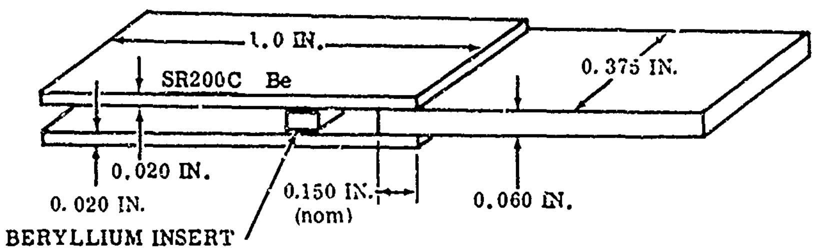
FIGURE 3. RADIOGRAPH SHOWING EFFECT OF JOINT GAP ON FLOW

Tolerance Test T-Sp .cimens

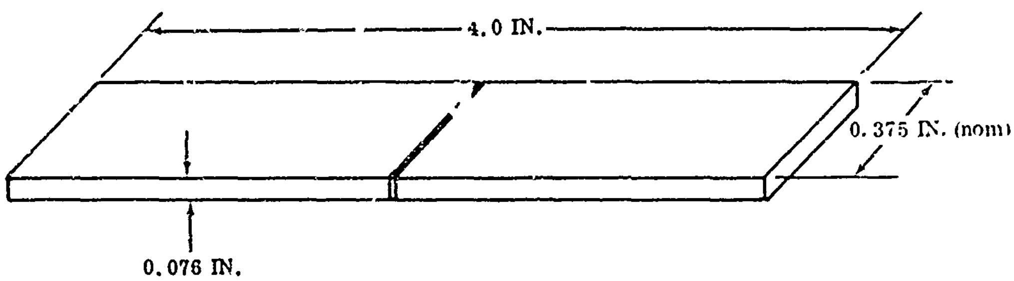
To evaluate the effect of changes in the braze condition on alloy flow, a simple T-joint was adopted. Basically, this specimen was comprised of only two parts, the base and vertical member. A typical specimen is shown in Figure 2. Each member was 1.0 inch long by 0.24 inch wide by 0.030 inch thick. During testing the vertical leg was held upright by a narrow band of titanium foil that spans the top edge and was anchored on each side by spot tacking. Braze alloy flow was monitored visually as wetting progressed along the capillary.

Joint Strength Specimens

Braze joint strength tests were made with two types of specimens - the butt joint and double-lap joint. The butt-type joint (Figure 4) was selected to compare relative strength of braze alloys. This technique was used mainly to aid in screening candidate compositions because stresses developed with this type of joint are transmitted directly into the braze alloy. In this manner, actual strength of the various alloys being studied could be compared, particularly at high temperatures where approach to the melting point causes a rapid diminution of strength. The double-lap joint (Fig. 4) was used in the latter portion of the program to determine shear strengths of promising alloys. Data from the tensile and shear tests were used to rate candidate alloys.



A. DOUBLE-LAP SPECIMEN



B. BUTT JOINT

FIGURE 4. TENSILE SHEAR SPECIMENS

Dimensions for butt and shear specimens are shown in Figure 4. No attempt was made to provide a standard clearance between faying surfaces. Joints were assembled as "net fit", after brazing, the exact clearance measurements were made by using a Scherr-Tumco optical comparator. Typical spacings were generally between 0.0005 and 0.0015 inch and joint overlaps were nominally 0.150 inch.

Coupons for both the lap and butt specimens were cut from SR200C grade beryllium sheet and include all gages of material procured for this program.

Honeycomb Specimens

The beryllium materials used for simulated honeycomb specimens were:

- Core - 0.006-inch gage ingot sheet foil
- Faces - 0.020-inch gage SR200C grade

The core for test specimens was obtained from Reference 3. The core configuration was a 0.25-inch square cell 0.50 inch high. Nodes were joined by resistance spot-tacking. Faying surface edges were precision lapped to ensure complete and and accurate core-face contact. No additional preparation was required for the core and face materials except for final cleaning prior to brazing. This procedure is described in Paragraph 2.2.3. One-inch square portions were cut from both the core and face stock for preparing the simulated honeycomb samples. A typical arrangement for component materials is shown in Figure 2.

2.2.3 Surface Preparation

Surface preparation of beryllium specimens for braze study consisted mainly of etch cleaning and rinsing; no studies were performed with plated surfaces. Fluxes or oxide inhibitors were not used except in one instance where a Solar-developed flux was used to show the correlation between wetting on beryllium with and without flux for aluminum-base braze alloys. Flow results were found to be significantly influenced by rinsing techniques used for beryllium test specimens.

Surface Cleaning

Two etching techniques were used for preparing test coupons:

- Chromic acid bath at 160 to 200°F

  53 grams chromic anhydride

  450 milliliters concentrated orthophosphoric acid

  26.5 milliliters concentrated sulphuric acid

- Ammonium bifluoride and nitric baths at room temperature

Solution 1

10 grams ammonium bifluoride

90 milliliters water

Solution 2

40 percent nitric acid

2 percent hydrofluoric acid

58 percent water

The chromic etch removes approximately 0.002 inch of material in five minutes and leaves a smooth, bright surface. The ammonium bifluoride removes 0.002 inch in approximately 90 seconds, a 60-second dip in the nitric-hydrofluoric etch follows to remove residue left from the initial etching. This treatment leaves a matte finish.

Initial study coupons were cleaned by the chromic acid etch method because prior work showed this approach was preferred to other cleaning techniques. Midway in this program, a study was made to compare flow results for the chromic and ammonium bifluoride etched coupons. Braze alloy flow was evaluated for Ag-27Cu-10Cd at 1550°F. To ensure equal braze conditions, both specimens were fired together. An examination of the test coupons indicated flow was equal for both etchants. In view of these results, the ammonium bifluoride process was adopted because of the reduced time required for complete etching.

Rinse Study

The procedure established at the start of work for rinsing beryllium test coupons after etching consisted of manual washing with deionized water. As work progressed, other rinsing methods were investigated. A standard ultrasonic cleaning method promoted improved wetting and flow properties. A comparison of isothermal flow on flat plates for both manual and ultrasonic cleaning is shown below.

	10-Minute Isothermal Flow at 1400°F (in.)	
Braze Alloy	Manual Rinse	Ultrasonic Cleaning
Ag-26.7Cu-9.9Ge-1Mn	0.22	0.60
Ag-36.2Cu-9.9In-1Mn	0.28	0.70
Ag-26.5Cu-9.6Zn-1Mn	0.20	0.42
Ag-23.6Cu-9.1Sn-9Pd	0.32	0.43

These results show significant flow improvement for all four alloys: especially the first three listed. Since results on flat plates are not always an indication of comparable flow for capillary flow joints, additional isothermal tests were made with standard capillary T-specimens to evaluate the effect of ultrasonic cleaning. The results confirmed that ultrasonic cleaning was beneficial for most braze alloys.

2.3 PROCEDURES FOR FLOW EVALUATION

Flow studies for developmental braze alloys were performed in argon. Earlier work (Ref. 1) showed that outgassing problems related to beryllium metal and braze alloys caused poor wetting and flow in vacuum. Therefore, no braze development work was performed with vacuum during this program.

Although results for argon and hydrogen were found to be similar (Ref. 1), argon atmospheres were favored for this study. A discussion of brazing equipment and flow study procedures is included in this section.

2.3.1 Braze Study Equipment

All test specimens except the simulated honeycomb panels were brazed using the equipment shown in Figure 5. A 20-ampere capacity split tube resistance furnace was used for heating the test chamber because full-scale furnace brazing is easily duplicated. Other characteristics of this process include:

- Observation during operation by incomplete closing of split shell furnace. A high-temperature Vycor tube was used.

- Alternate temperature readings by optical pyrometer or radiation thermometer.

Arrangement of the argon brazing equipment is shown in Figure 5. The Hevi-Duty furnace is controlled with a 20-ampere capacity Variac. A small vacuum pump is used for system evacuation during cycle purging. The three-inch diameter Vycor tube brazing retort incorporates a titanium liner in the heat zone as a precaution to reduce interaction with the Vycor through possible transfer of oxygen as silicon monoxide. This liner also serves as an added argon getter while at elevated temperatures.

High-purity argon is supplied in the following manner: line argon, obtained from a central liquid supply, is directed through a titanium getter operating at 1500°F. Argon entering the braze retort is further cleaned by the additional scrubbing action of the titanium liner, as well as by titanium wool plugs at each end and a titanium support platform and block. Before being exhausted, argon is channeled through a series of filters designed to entrap any beryllium particles or compounds that are generated during the braze cycle.

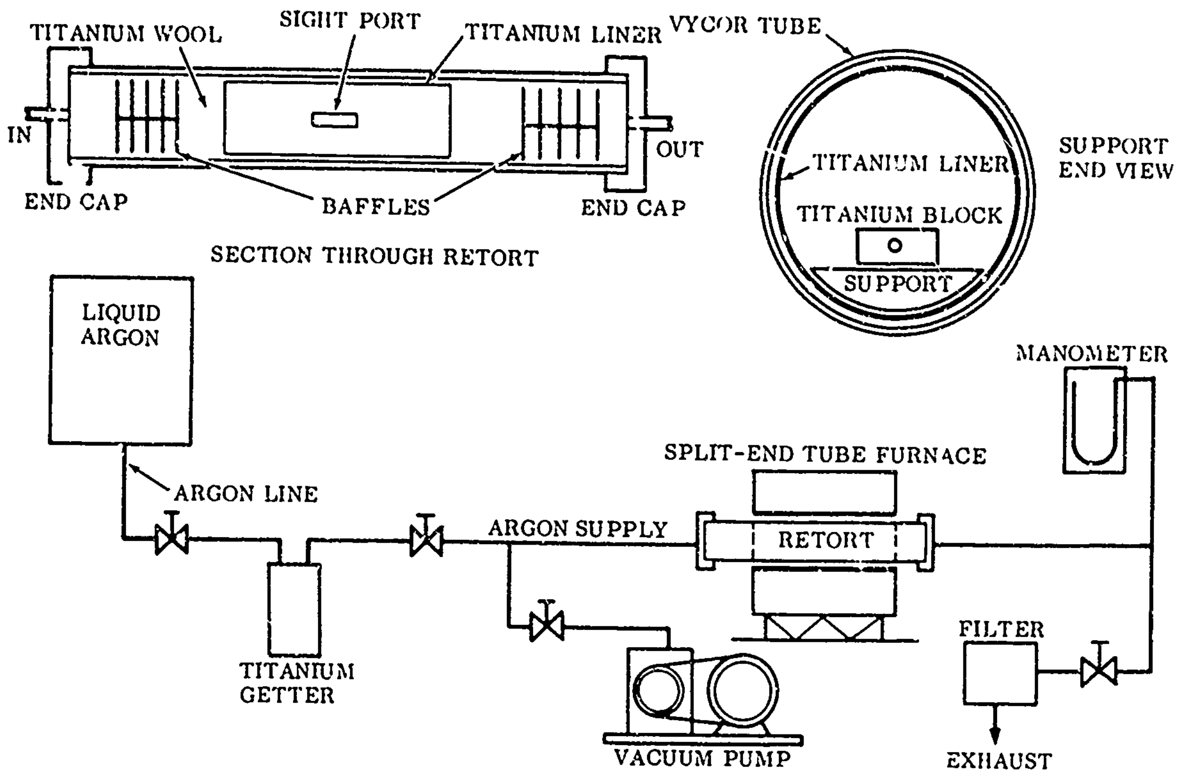


FIGURE 5. BRAZE STUDY EQUIPMENT FOR ARGON

Braze temperatures were monitored with a Honeywell Potentiometer Recorder using a sheathed chromel-alumel thermocouple. The location of the thermocouple was kept within 0.25 inch of the test specimens. This thermocouple was checked for accuracy after each 25 hours of service.

Brazing of the nine simulated honeycomb specimens was performed in one single operation. The arrangement was to use a mild steel envelope for both atmosphere and pressure control during the braze cycle. Figure 6 shows the typical arrangement. The envelope was composed of two 0.018-inch gage mild steel pans that were formed with a lip for edge weld sealing. Two 0.375-inch inlet and exhaust tubes were welded at opposite corners. The subscale test panels were one-inch square by 0.5-inch thick. Titanium core was used as filler surrounding the test specimens. In addition, two titanium slip sheets were used between the specimen face material and envelope; one was 0.002 inch and one was 0.010 inch. An array of thermocouples was attached to the pan faces to monitor temperature and gradients. Reference 3 gives full details of the procedures.

FIGURE 6. BRAZE CONTAINER FOR HONEYCOMB SPECIMENS

An atmosphere control panel (Fig. 7) is used for the braze operation and incorporates a liquid argon atmosphere supply (boil off), vacuum pump, foreline and exhaust-line pressure manometers, titanium getter, control valves, atmosphere quality indicator, and an absolute exhaust filter for biological safety. Brazing the test envelope was performed in an electrical Hevi-Duty furnace (Fig. 8).

2.3.2 Flow Study Procedures

Initial studies for this program were made to investigate the effect of additions on melt, wet and flow temperatures, and flow distance for selected base alloys. These studies were conducted on flat plate coupons. Figure 2 shows a typical flat plate specimen alloy flowed on the surface. Evaluation of braze alloy properties was performed with a group of five different specimens, these included T-joints, joint strength specimens, and simulated honeycomb panels. These specimens are also shown in Figure 2. A discussion of the procedures used for flow study follows.

FIGURE 7. ATMOSPHERE CONTROL PANEL

FIGURE 8. BRAZING HONEYCOMB SPECIMENS

Flat Plate Coupons

The following procedures were adopted for braze flow evaluation on flat plate specimens:

Step 1 - A 0.1 gram sample of alloy was placed at the center of each coupon. The coupon was placed in the retort, the retort was sealed, and a leak check was made.

Step 2 - The system was flushed by five argon-vacuum purges after which the argon flow was maintained at two cfh.

Step 3 - The furnace was preheated to 1650°F before introducing the retort. The glass wall of the retort and the slotted titanium liner permit melt, wet, and flow processes to be visually monitored during the braze cycle. This observation port is also used for optical pyrometer sighting.

Data were recorded on plots showing a temperature-time profile so that the occurrence of significant events could be marked.

Figure 9 shows the appearance of a typical alloy sample at various stages of melt, wet, and flow. At room temperature, prior to firing, angularity of the particle is seen (Fig. 9A). In the next step (Fig. 9B) rounding of the sharp edges indicates the alloy has started to melt. Figure 9C shows wetting has begun to occur at the edges of the alloy.

The remaining views (Fig. 9D, 9E, 9F) show characteristic stages of flow. Although a number of factors affect the extent of flow, the melting ranges of the alloy exert an important controlling influence. Liquation from the partially melted braze alloy particle can be noted in some cases.

Capillary Flow Specimens

Except for a change in the quantity of alloy used for each specimen, the procedures used for flat plates were adopted for capillary flow specimens. Tests made to determine the optimum amount of alloy to use for capillary flow studies indicated a 0.13-gram sample was satisfactory. This amount was selected for the 0.25-inch wide by 1.0-inch high capillary T-joints.

Two approaches were used to determine capillary flow:

- Measurement after cooldown
- A record of flow for isothermal conditions

For isothermal conditions, flow is plotted against time or temperature. As melting progresses, the alloy flows into the joint and travels upward through the capillary. Reference marks on the specimen permit the extent of flow to be monitored visually during the test.

Butt- and Lap-Joint Specimens

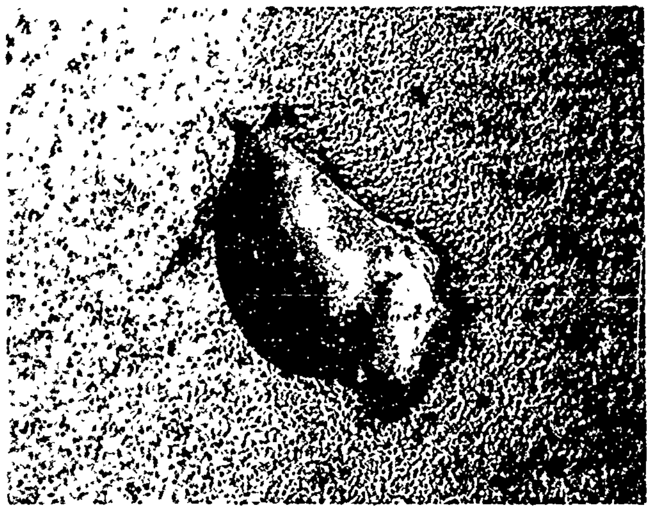
The butt and lap joints were brazed by placing the required amount of alloy at each joint and allowing the alloy to flow into the capillary during the braze cycle. These specimens are brazed in the horizontal position. Figure 2 shows typical as-brazed butt and lap specimens.

Tolerance T-Specimens

The brazing procedure used for these specimens is similar to that used for the capillary T-joints. A 100-milligram sample of alloy to be tested is placed on the base coupon at one end of the vertical member. Flow is monitored by reference points plotted on the specimen.

A. Alloy particle at room temperature

Magnification: 8.5X



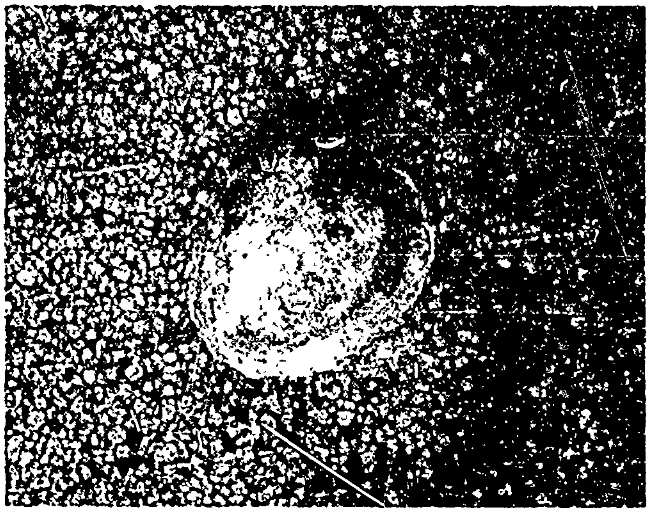
B. Melting. Sharp edges have started to round

Magnification: 8.5X

C. Wetting. Melted alloy beginning to wet beryllium surface. Arrows indicate extent of wetting.

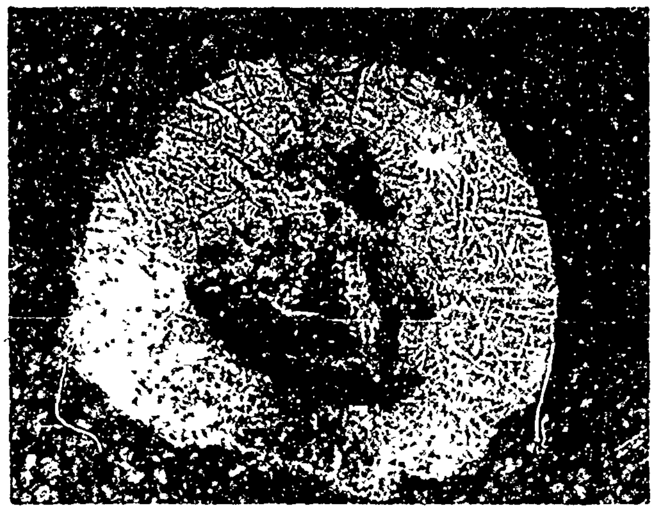
Magnification: 6.5X

FIGURE 9. MELT SEQUENCE FOR A TYPICAL ALLOY (Sheet 1 of 2)



D. Primary stage of flow. Melted portion of alloy has begun to flow on beryllium

Magnification: 8.5X



E. Intermediate flow showing liquation from the partially melted alloy

Magnification: 10X

F. Complete flow. The entire particle has melted and flowed

Magnification: 10X

FIGURE 9. MELT SEQUENCE FOR A TYPICAL ALLOY (Sheet 2 of 2)

Simulated Honeycomb Specimens

The amount of alloy used for honeycomb specimens was based on a weight of 100 to 200 milligrams/square foot. Braze alloy particles, 30 to 100 mesh size, were placed in each core cell. No binder was necessary as the alloy remained "captive" in these cells once the face members are in position.

After the envelope containing the test specimens is weld-sealed, it is checked by mass spectrometer techniques to detect possible leaks. A blanket of Fiberfrax is then placed around the retort to prevent thermal shock during entry into and removal from the furnace. Firing is done with the parts in an edgewise position (Fig. 8).

The braze cycle is essentially a four-step process:

- Atmosphere exchange purge (replacement of all air in cells with argon)
- Outgassing purge (removal of moisture and adsorbed surface gases)
- Braze cycle (under static conditions) at partial pressure of two psi
- Cooling cycle (under static and rarified atmosphere conditions)

Atmosphere quality checks are made frequently during the braze cycle. These checks are sensitive indications of atmosphere conditions. Should the check prove negative during the first or second step, the braze process can be stopped or delayed without damage to the specimen. Braze temperatures are monitored and recorded with a multipoint potentiometer recorder.

SECTION III

SELECTION OF BASIC BRAZE SYSTEMS

The selection of suitable basic braze compositions is restricted because only a small number of metallic and metalloid elements do not form stable beryllides. There are three - aluminum, silicon, and silver, with germanium as a possible fourth.

The aluminum/beryllium system is a simple eutectic, with a eutectic temperature of 1195°F. At the eutectic temperature, the aluminum-rich eutectic liquid is stable over an extremely wide compositional range (Fig. 10). However, if strength at elevated temperatures is required, this system would not be suitable.

The silicon/beryllium system is also a simple eutectic; the eutectic occurring at 39 percent weight beryllium and 1995°F (Fig. 11). The two elements are completely insoluble in each other at all temperatures. The mechanical properties of a mixture of two phases of low ductility do not appear attractive for brazed joints and, in fact, beryllium joints brazed with beryllium/silicon alloys have been demonstrated as being weak and brittle at room temperature.

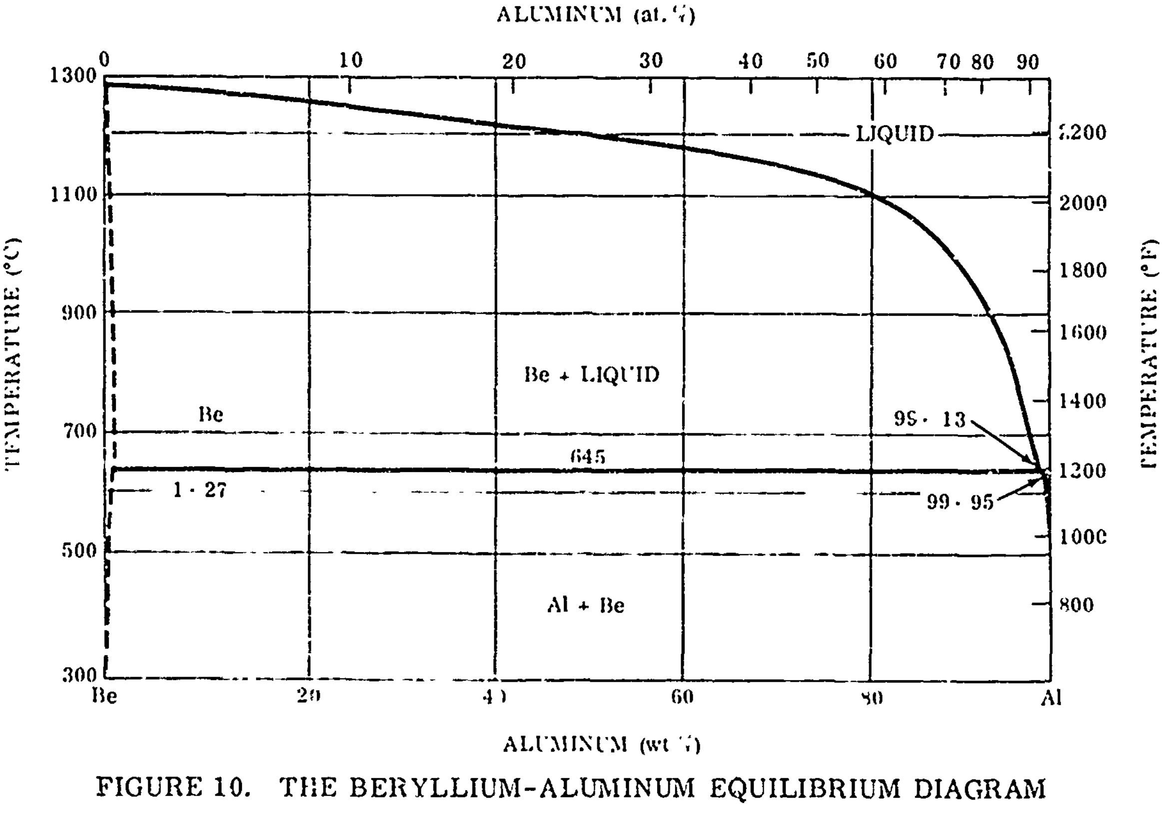


FIGURE 10. THE BERYLLIUM-ALUMINUM EQUILIBRIUM DIAGRAM

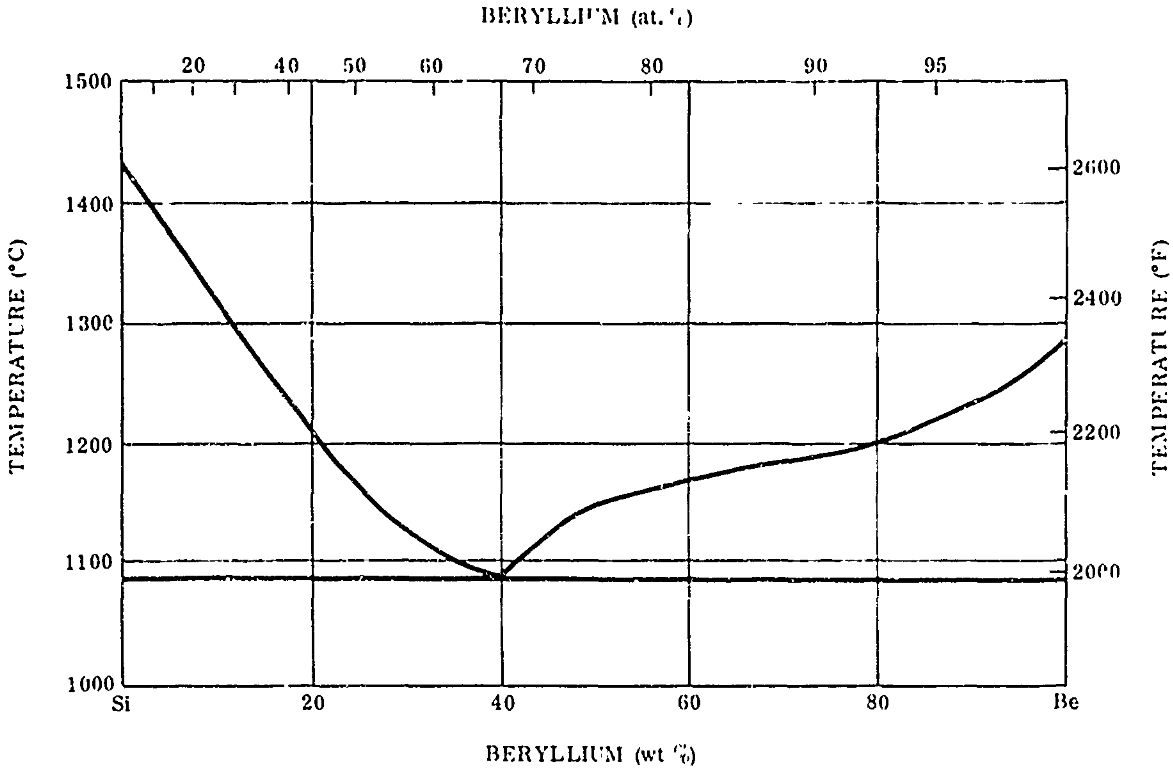


FIGURE 11. THE BERYLLIUM-SILICON EQUILIBRIUM DIAGRAM

The third system, silver/beryllium, shows considerably more promise (Fig. 12). No silver beryllides form below 1400°F. A eutectic between the silver terminal solid solution and silver beryllide (73 atomic percent beryllium) exists at one percent beryllium and 1618°F. Although one of the inherent advantages of silver is to promote a ductile beryllium surface, there are specific problems with silver and its alloys that were studied to help promote maximum joint reliability, strength, and stability to 1000°F.

The effectiveness of the titanium in promoting braze alloy flow has been reported previously by Solar in work on Contract AF33(615)-7249. It was found that one percent titanium additions to Ag-Cu-Ge alloys allowed flow to occur at 1150°F on titanium. The mechanism must relate to the kinetics of the various events occurring at the titanium surface (solution of oxide films in titanium versus growth of films by reaction with atmosphere, concentration of titanium at the surface of the molten braze alloy, and other events). This mechanism led to the analysis presented in Figure 13 that shows pure titanium will reduce BeO until a solid solution is formed containing 3000 ppm of oxygen at 1500°F. Hence, a suitable titanium-base alloy might have good wetting characteristics on beryllium. Braze alloys based on the eutectic between beryllium and titanium or between beryllium and titanium-zirconium were selected for study. Because the alloy could be titanium-base or beryllium-base, two new classes of potential braze alloys were included.

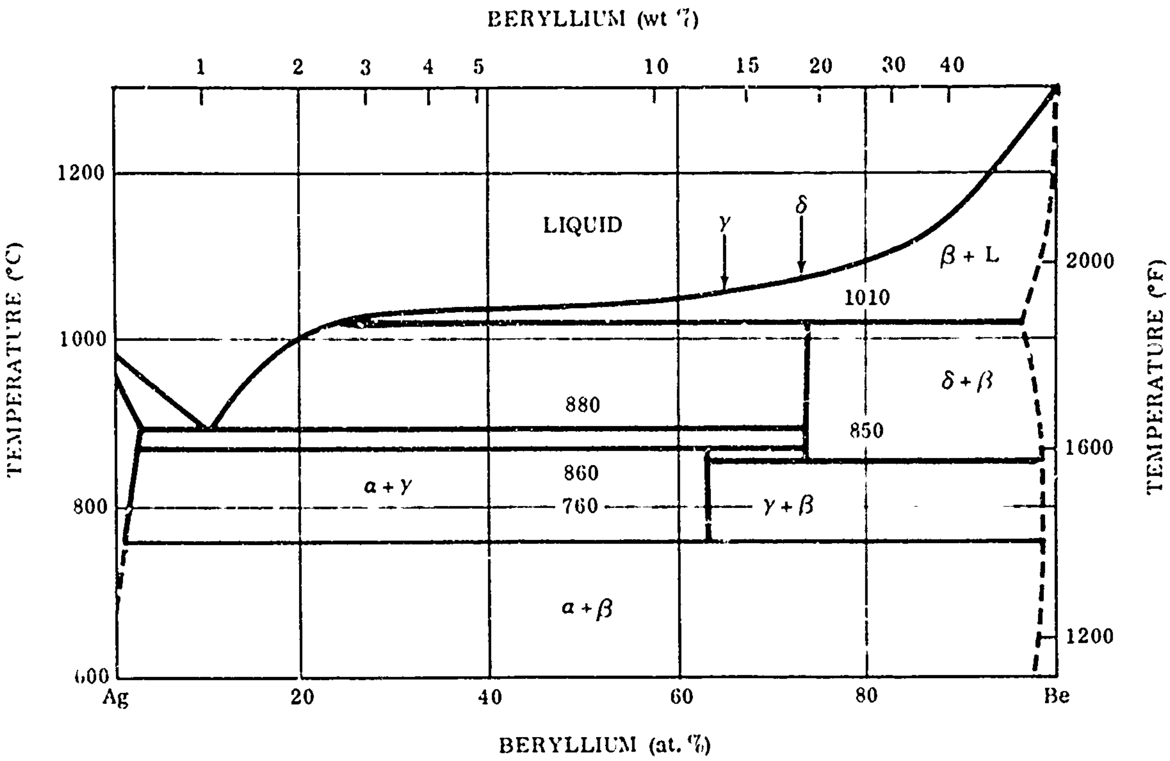


FIGURE 12. THE BERYLLIUM-SILVER EQUILIBRIUM DIAGRAM

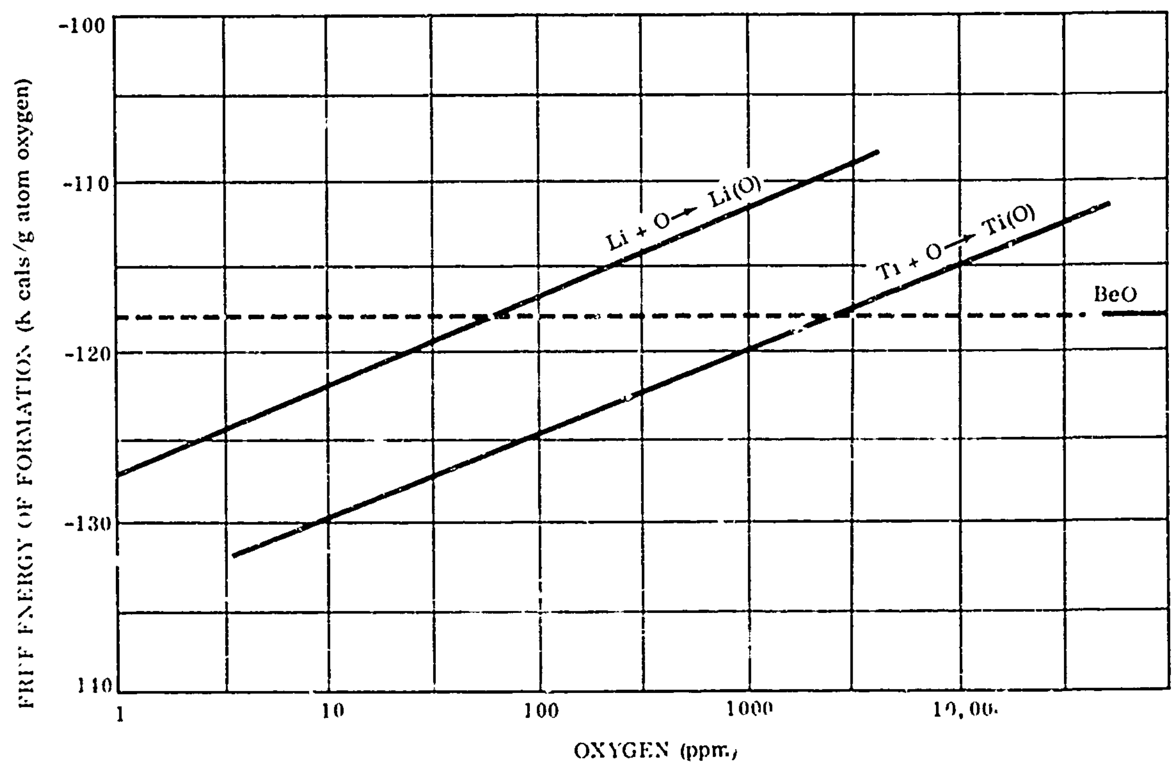


FIGURE 13. FREE ENERGY OF FORMATION OF PHASES AT 1500°F (815°C)

Based on the foregoing discussion, silver, titanium, and beryllium appeared to offer promise as base elements for beryllium braze systems and were selected therefore for development on the earlier programs. Although silicon and aluminum were not used as candidates for base alloys, they were included as additives for alloy development. Other additives included cadmium, copper, lithium, phosphorus, germanium, manganese, beryllium, nickel, zinc, palladium, indium, silver, titanium, and zirconium.

Work reported in AFML TR-67-14 covered the first year of studies to develop braze alloys for beryllium. Silver-base braze alloys were developed for capillary flow at brazing temperatures of 1500 to 1650°F. Beryllium-base alloys were studied but did not show promise and the studies were dropped. Aluminum- and titanium-base alloys were also studied but these systems were not optimized.

In selecting the basic systems for this continuation work, two principal objectives were kept in mind, the retention of beryllium-base metal properties and good capillary flow. From results of the previous year's study for silver-base alloys, it was concluded that those braze systems based on the silver-copper eutectic offered greater opportunities for reduced braze temperatures. If braze temperatures for beryllium do not exceed 1400°F, then base metal properties can be retained.

The braze temperature of 1400°F must be achieved without impairing joint strength at the maximum desired service temperature of 1000°F. The melt temperature of the braze alloy must be appreciably below 1400°F, so that the permissible temperatures for melt, wet, and flow are limited. Therefore, the decision was made to aim at a target having the following parameters:

- A minimum melt point of 1280°F
- A 1400°F braze temperature
- Excellent capillary flow
- High strength to 1000°F
- High tolerance for adverse changes of braze conditions

The silver-copper eutectic composition was adopted as one of the basic alloys for development. Since neither the aluminum- nor titanium-base alloy had been optimized during the earlier program, these two alloys were also included in the group of base alloy selections.

SECTION IV

DEVELOPMENT OF BRAZE SYSTEMS

The combination of braze alloy and brazing technique has been termed the braze system. Development of optimum compositions and processes must proceed hand in hand because the two are interrelated. The procedure for braze alloy development included the following steps:

1. Modification of Ag-28Cu by additions to control melt and flow temperatures. Studies were performed on flat plates using a temperature rise of approximately 50 degrees F/minute above 1200°F.

2. Promising alloys developed in Step 1 were selected for further development. Additions were made to reduce melt-flow temperatures and enhance flow distance. These studies were made with flat plate and capillary T-specimens.

3. Optimization of ternary and quaternary alloys. Based on melt-flow temperatures and flow distance, promising alloys were carried forward for optimization by further modification and higher additions. Related tasks included flow studies to improve braze procedures.

This section contains a discussion of the development of the three basic systems: silver, titanium, and aluminum. The effect of additions on melt, wet, and flow temperatures and flow distance was investigated. Promising alloys were then modified to promote increased wetting and flow. Studies were made to identify mechanisms that would improve braze alloy properties. The selection of promising compositions as candidates for final screening is discussed in Section V.

4.1 DEVELOPMENT OF SILVER-BASE ALLOYS

As indicated in Section III, the silver-copper eutectic composition (28 percent copper) as adopted as a basic alloy for optimization. Initial studies with this binary alloy were primarily concerned with additions to develop lower melting point ternary compositions. Further studies included additions to ternary and quaternary alloys to control melt-flow temperatures and increase capillary flow. Capillary flow tests were made to study the effect of time and temperature on flow. Problems with reproducibility for some alloys were encountered.

All braze tests for this work were performed with the SR200C grade beryllium.

4.1.1 Alloying to Control Melt-Flow Temperatures

Initial studies were primarily concerned with additions to silver-copper alloys at or near the eutectic composition to evaluate the effect on melt-flow temperatures. These additions included cadmium, indium, germanium, lithium, phosphorus, tin, titanium, and zinc. Various silver-to-copper ratios were examined for ternary alloys to study the effect on temperatures.

Additions were made to the silver-copper binary compositions in increments totaling 15 percent for indium and 10 percent for the remaining additions. Repeat tests were made when the test data were considered questionable. Testing was performed on flat plates in argon and the results are presented in Table II. Because early melting procedures resulted in losses by vaporization, some compositions have been corrected to show the approximate amount of addition retained.

Table II shows that significant melt and flow point reductions have been made for all additions except phosphorus and titanium. However, the major advantage for these two additions was expected to be their contribution to improve wetting and flow, rather than control melting points. An interesting aspect of the phosphorus addition is the narrow 60 degree F melt-flow range exhibited for the Ag-43Cu-1.9P alloy. This is 20 degrees F less than that shown by the silver-copper eutectic although the eutectic alloy required a super heat of 80°F to promote flow.

The elements cadmium, indium, germanium, and zinc are highly soluble in silver and copper. They were added in large percentages to effect temperature reductions for the basic binary alloys. Using results for silver-copper eutectic as a basis for comparison, the effect of additions on melt, wet, and flow temperatures for initial tests can be summarized as follows:

- Phosphorus and titanium do not effectively depress melt or flow temperatures
- Cadmium has a mild effect on melt-point reductions
- Germanium, indium, tin, and zinc are moderate to strong melt point depressants
- Lithium has a strong effect on melt and flow point reductions
- Zinc exhibits a mild effect on reducing the flow point while cadmium, germanium, indium, and tin show little influence.

TABLE II

RESULTS FOR ADDITIONS TO Ag-28Cu

Alloy Composition	Temperature (°F)				Notes
	Melt	Wet	Flow	Maximum	
Ag-26.5Cu	1470	1480	1570	1600	
Ag-28.0Cu	1430	1440	1510	1520	
Ag-29.25Cu	1440	1450	1515	1525	
Ag-30.5Cu	1440	1455	1540	1550	
Ag-32.0Cu	1445	1460	1550	1560	
Cadmium					
Ag-27.8Cu-1Cd	1450	1490	1540	1540	
Ag-26.6Cu-5Cd	1440	1465	1545	1575	Average two tests
Ag-25.5Cu-6.7Cd	1430	1470	1530	1600	(1)
Ag-26.2Cu-6.7Cd	1425	1470	1530	1550	(1) Average two tests
Ag-27.0Cu-6.7Cd	1350	1450	1490	1510	(1)
Ag-28.0Cu-6.7Cd	1380	1440	1470	1485	(1)
Ag-24.5Cu-10Cd	1380	1435	1540	1560	(2) Average two tests
Ag-25.2Cu-10Cd	1380	1455	1560	1570	(2) Average two tests
Ag-26.0Cu-10Cd	1400	1460	1550	1560	(2)
Ag-27.0Cu-10Cd	1370	1410	1500	1510	(2)
Ag-29.0Cu-10Cd	1380	1465	1575	1590	(2) Average two tests
Indium					
Ag-27.8Cu-1In	1430	1460	1560	1575	
Ag-24.0Cu-1.5In	1400	1415	1425	1430	Average two tests
Ag-26.6Cu-5.0In	1440	1480	1580	1580	
Ag-24.0Cu-15.0In	1250	1410	1515	1525	
Ag-24.5Cu-10In	1350	1410	1500	1520	
Ag-25.2Cu-10In	1340	1420	1480	1510	
Ag-26.0Cu-10In	1320	1390	1460	1500	
Ag-26.5Cu-10In	1330	1440	1480	1550	Average three tests
Ag-27.0Cu-10In	1320	1385	1470	1500	
Ag-28.0Cu-10In	1330	1440	1510	1590	
Ag-29.0Cu-10In	1335	1425	1500	1560	
Ag-30.5Cu-10In	1360	1440	1490	1500	Average two tests
Ag-31.5Cu-10In	1330	1390	1485	1530	Average two tests
Ag-32.0Cu-10In	1340	1410	1515	1520	
Ag-32.5Cu-10In	1320	1390	1480	1500	
Germanium					
Ag-27.8Cu-1Ge	1450	1500	1550	1570	
Ag-26.6Cu-5Ge	1400	1470	1540	1550	
Ag-22.0Cu-10Ge	1285	1400	1470	1480	
Ag-23.5Cu-10Ge	1300	1475	1550	1560	
Ag-24.5Cu-10Ge	1310	1400	1545	1570	Average two tests
Ag-25.0Cu-10Ge	1350	1410	1450	1460	
Ag-25.2Cu-10Ge	1300	1410	1550	1580	
Ag-26.0Cu-10Ge	1300	1485	1580	1600	
Ag-27.0Cu-10Ge	1285	1335	1480	1530	Average two tests
Ag-30.0Cu-10Ge	1290	1360	1430	1440	

TABLE II (Cont)

RESULTS FOR ADDITIONS TO Ag-28Cu

Alloy Composition	Temperature (°F) Melt	Wet	Flow	Maximum	Notes
Lithium					
Ag-28.0Cu-0.2Li	1400	1430	1450	1500	
Ag-28.0Cu-0.5Li	1300	1380	1475	1485	(1)
Ag-27.5Cu-2.8Li	1120	1250	1325	1600	(1)
Phosphorus					
Ag-27.8Cu-1.0P	1450	1500	1525	1525	(1)
Ag-43.0Cu-1.9P	1430	1450	1490	1490	(1) Average two tests
Ag-27.3Cu-2.6P	1450	1500	1560	1570	(1) Average two tests
Tin					
Ag-27.8Cu-1.0Sn	1420	1480	1540	1540	
Ag-26.6Cu-5.0Sn	1380	1440	1540	1550	
Ag-24.5Cu-10Sn	1300	1405	1475	1480	Average three tests
Ag-25.2Cu-10Sn	1280	1350	1510	1530	
Ag-26.0Cu-10Sn	1280	1370	1410	1430	
Ag-27.0Cu-10Sn	1280	1410	1520	1570	Average two tests
Ag-27.0Cu-10Sn	1280	1340	1410	1430	
Titanium					
Ag-28Cu-0.1Ti	1460	1500	1600	1610	
Ag-27.9Cu-0.5Ti	1450	1510	1590	1600	(1) Average three tests
Ag-27.7Cu-1.8Ti	1450	1490	1530	1550	
Ag-27.4Cu-3.0Ti	1400	1480	1520	1540	
Ag-26.0Cu-8.0Ti	1460	1500	1600	1600	
Zinc					
Ag-27.8Cu-1.0Zn	1425	1470	1530	1540	
Ag-26.7Cu-5.0Zn	1425	1475	1540	1550	
Ag-24.9Cu-8.0Zn	1290	1450	1480	1500	(1)
Ag-25.3Cu-9.0Zn	1280	1405	1460	1500	(1)
Ag-26.5Cu-8.0Zn	1290	1410	1485	1500	(1)
Ag-27.3Cu-8.7Zn	1310	1370	1390	1410	(1)
Ag-27.4Cu-8.6Zn	1360	1420	1500	1500	(1)
Ag-27.0Cu-10.0Zn	1380	1420	1500	1515	(3)
Ag-28.4Cu-8.6Zn	1340	1430	1490	1500	(1)
Ag-28.8Cu-7.0Zn	1400	1480	1520	1550	(1) Average two tests
Ag-29.0Cu-10Zn	1380	1420	1500	1515	(3)
Ag-29.9Cu-7.0Zn	1410	1440	1460	1500	(1)
Ag-30.4Cu-5.0Zn	1400	1425	1430	1450	(1)
Ag-30.8Cu-7.5Zn	1375	1450	1490	1500	(1)

1. Addition content computed on weight loss after arc-melting.
2. Excess cadmium used.
3. Remelt button to obtain predetermined weight.

Modification of Ag-Cu-P Alloy

Work with phosphorus additions to silver-copper binary alloys showed that the melt, wet, and flow temperatures were reduced by phosphorus, but only at copper contents above that of the silver-copper eutectic. The optimum copper content for Ag-Cu-P alloys was determined by evaluating changes in the silver-to-copper ratio at a constant phosphorus content of two percent. The two percent phosphorus alloy was selected because this composition appeared to have the potential to develop a 1400°F braze alloy.

Eight additional compositions were made. Melt, wet, and flow temperatures were determined and compared to the original results. In addition, temperature rechecks were made to verify the original results. The comparison is presented in Table III. Melt, wet, and flow curves were plotted for the Ag-Cu-2P compositions to show the effect of the variations in the silver-to-copper ratio (Fig. 14).

The data in Table III and Figure 14 show dramatically the effect of increased copper additions to Ag-2P. At 50 to 60 percent copper, flow temperatures are the lowest and exhibit the smallest melt-flow range. In addition, results for this 50 to 60 percent copper range appear to be more consistent than for lower percentages of copper. Therefore, these results confirm the premise that a higher copper content may be necessary to achieve the maximum advantage from phosphorus additions.

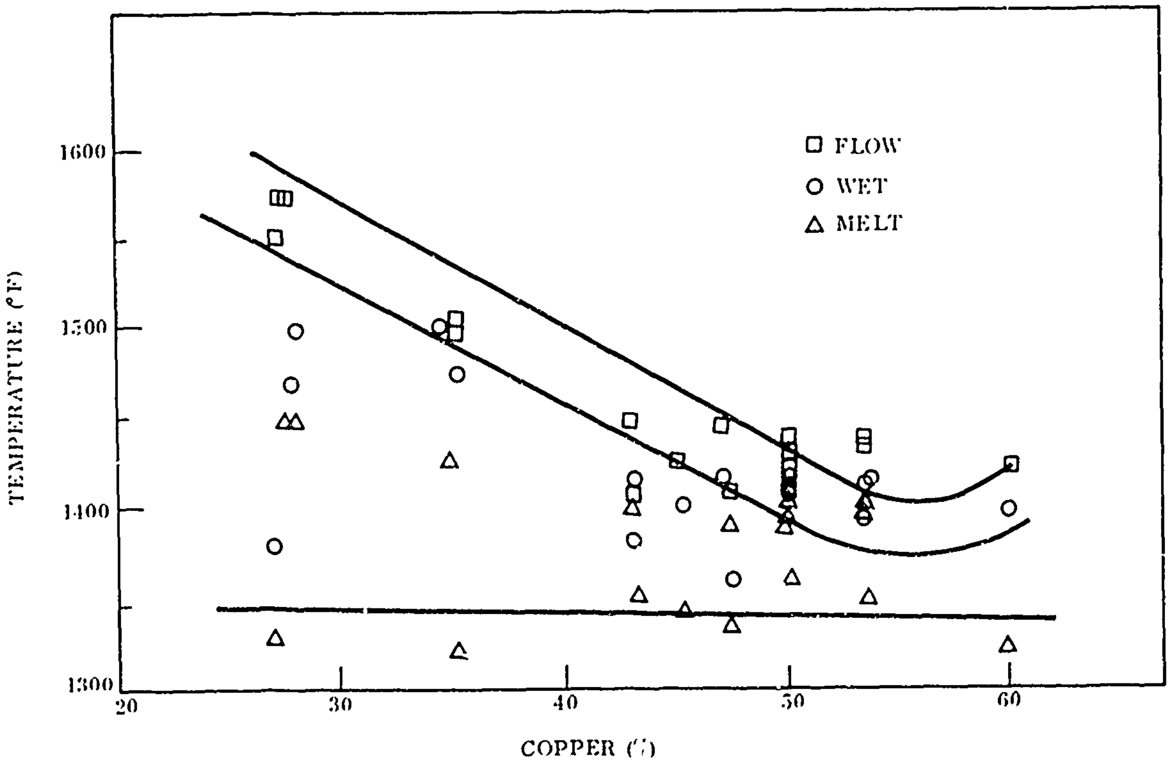


FIGURE 14. EFFECT OF COPPER ON Ag-2.0P

TABLE III

MELT-FLOW TEMPERATURES FOR Ag-Cu-P ALLOYS

Composition (%)			Temperature (°F)				Notes
Ag	Cu	P(nom)	Melt	Wet	Flow	Maximum	
71.4	27.8	0.8	1450	1500	1525	1600	Original alloy
55.5	43.2	1.3	1430	1460	1490	1540	Original alloy
70.3	27.7	2.0	1450	1500	1570	1600	Original alloy
55.0	43.0	2.0	1350	1385	1410	1425	New alloy
			1390	1420	1450	1460	New alloy
63.0	35.0	2.0	1325	1500	1505	1550	New alloy
			1425	1470	1500	1560	New alloy
70.7	27.3	2.0	1325	1385	1550	1565	New alloy
			1450	1470	1570	1570	New alloy
48.0	50.0	2.0	1360	1400	1425	1450	New alloy
			1380	1400	1410	1430	New alloy
			1390	1420	1430	1460	New alloy
			1400	1410	1415	1420	New alloy
50.5	47.5	2.0	1330	1360	1410	1425	New alloy
			1390	1420	1440	1460	New alloy
44.0	54.0	2.0	1360	1390	1440	1450	New alloy
			1390	1420	1430	1460	New alloy
38.0	60.0	2.0	1320	1400	1420	1450	New alloy

Effect of Interaction on Flow Temperatures

Silver-copper braze alloys react with beryllium to form a thin layer of copper beryllide at the interface. With low percentages of copper in the alloy (e. g., sterling silver at 7.5 percent copper), reaction is limited by the amount of copper available, although reaction occurs rapidly at typical brazing temperatures in the temperature range of 1550 to 1560°F. At the silver-copper eutectic, reaction rates would be expected to be higher because the copper content is higher (28 percent), but at the same time, the lower brazing temperatures required (1400 to 1500°F) would tend to reduce reaction. However, a new effect may appear with a eutectic alloy. This is a decrease in the ease of wetting at the edge of the advancing molten braze alloy. This decrease will arise from loss of copper from the molten metal to form a copper beryllide leaving a hypo-eutectic melt (i. e., less than 28 percent copper) at the advancing front. If this effect is significant, then optimum braze alloys should contain somewhat more copper than the eutectic composition. The work described in this section was planned to investigate the magnitude of this effect.

The approach followed was to vary the silver-copper ratio while holding the addition of other elements at a constant level. Variations in the silver-copper ratio were made on each side of the 72Ag-28Cu eutectic ratio. Studies were performed on flat plates to establish melt, wet, and flow temperatures. Curves plotted for these values versus silver-copper ratios indicate reaction by shifting the minimum temperatures from the eutectic composition to one that is hyper-eutectic.

In addition to the Ag-Cu binary, interaction studies were made with the following ternary alloys:

Ag-Cu-10Ge

Ag-Cu-10Sn

Ag-Cu-10Cd

Ag-Cu-10In

Ag-Cu-10Zn

Temperatures were plotted against copper content for each alloy and the curves are presented in Figure 15. Where more than one test was made for an alloy, the average value has been plotted. Salient points for each alloy are contained in following paragraphs.

- Ag-Cu-Binary Alloys. Variations were made on each side of the eutectic alloy, Ag-28Cu, to determine melt, wet, and flow temperatures. Although the minimum temperatures were found for the eutectic composition at 28 percent copper, these temperatures rise rapidly as the copper is reduced below 28 percent. The results show that the best braze alloy should be specified to contain somewhat more than 28 percent copper, and the results support the hypothesis advanced.

- Ag-Cu-10Cd. Data for the silver-copper alloys containing 10 percent cadmium are presented as bands because no trends can be established. The results may reflect the difficulty in preparing alloys with consistent cadmium contents, or the effect of evaporation of cadmium from the braze alloy during brazing.

- Ag-Cu-10Ge. Eight alloys were made containing Ag-10Ge at 22. 0, 23. 5, 24. 5, 25. 0, 25. 2, 26. 0, 27. 0, and 30. 0 percent copper. The melt points are scattered but fairly constant. Inconsistencies in results are evident for wetting and flow temperatures, therefore no curve has been drawn. Additions to improve flow and reduce the wide separation of melt and flow temperatures will be necessary if Ag-Cu-Ge alloys are to become useful.

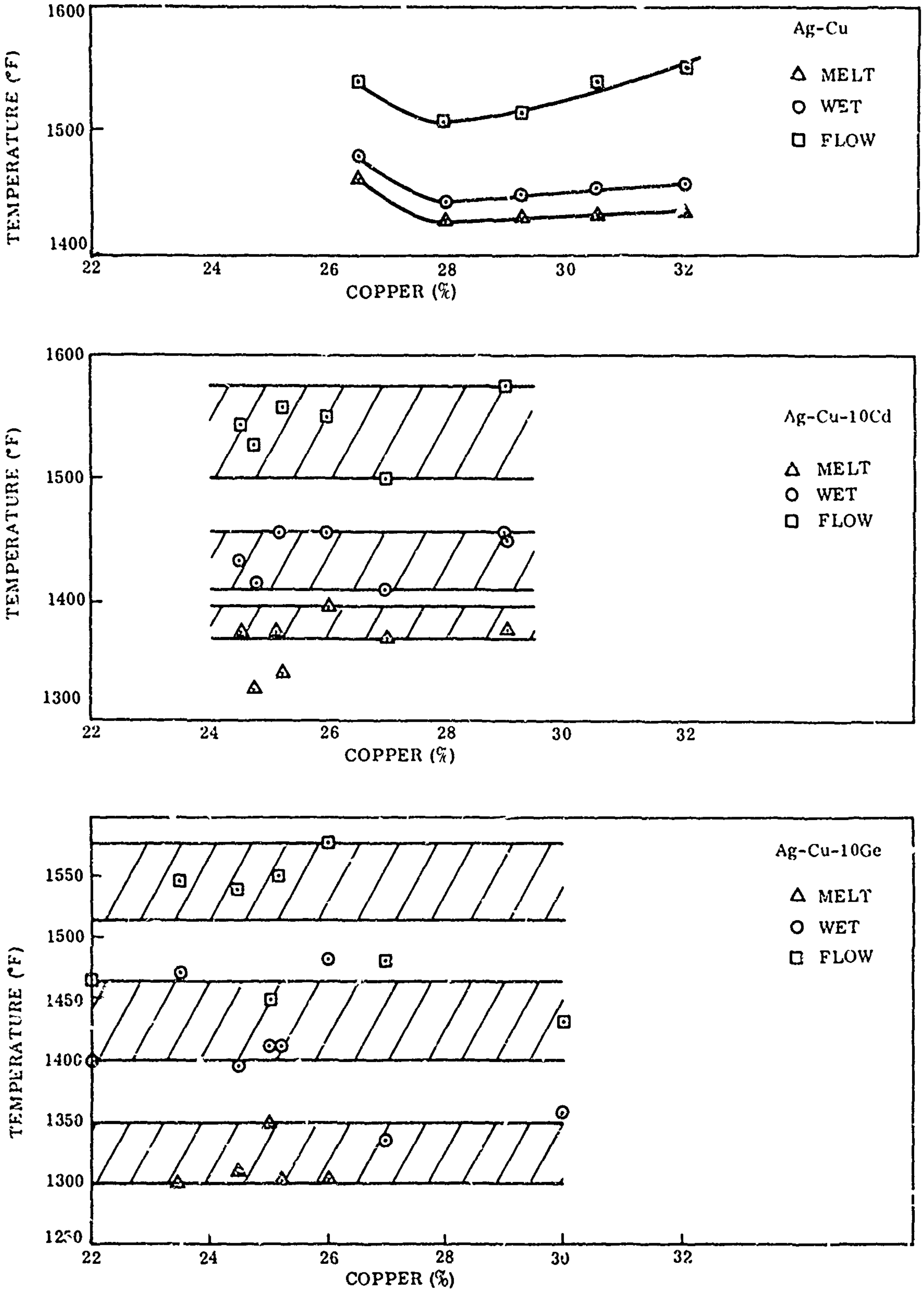


FIGURE 15. REACTION STUDY FOR SILVER-COPPER ALLOYS (Sheet 1 of 2).

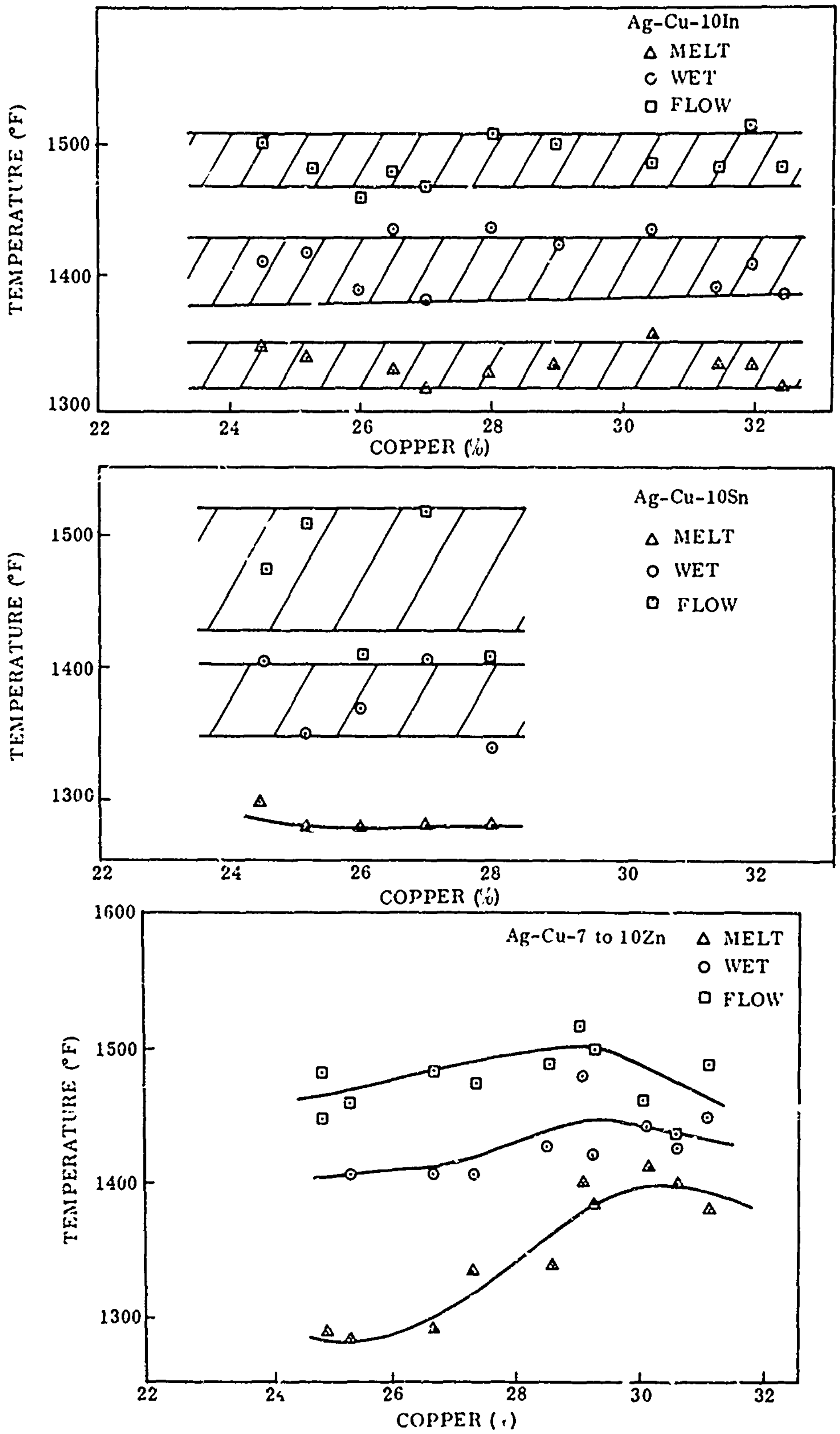


FIGURE 15. REACTION STUDY FOR SILVER-COPPER ALLOYS (Sheet 2 of 2)

- Ag-Cu-10In. Copper contents of 24.5, 25.2, 26.5, 27.0, 28.0, 29.0, 30.5, 31.5, 32.3, and 32.5 percent were studied. As with the Ag-Cu-Ge alloy, the melt temperature curve is fairly constant for all compositions.

- Ag-Cu-10Sn. Melt temperatures are very uniform for these alloys. Wet and flow temperatures are presented as extended areas because of the overlap of temperatures. No definite trend is indicated.

- Ag-Cu-Zn. The zinc content for these test alloys ranged from 7 to 10 percent because all but the two 10 percent zinc alloys used for this combination of elements had been made prior to adoption of the preferred melting technique. The melt, wet, and flow temperature curves in Figure 15 show that copper between 25 and 28 percent reduces melt temperatures, while between 29 and 32 percent the melt-flow differential is narrowed.

4.1.2 Optimization of Flow Distance for Ternary Alloys

Flow studies were performed with ternary alloys that would aid in selecting promising compositions for further development. Tests were performed on flat plates and with capillary T-specimens. Two methods of heating were employed:

- Dynamic (steadily rising temperature)
- Isothermal (holding at a constant temperature)

Measurement of Flow Distance on Flat Plates

Whereas melt, wet, and flow temperatures were used to evaluate developmental braze alloys, measurement of flow distance on flat plates provided another means for evaluating these alloys. Braze alloys, showing promise of flow below 1600°F based on results for melt-flow temperature tests, were selected for evaluation of flow distance.

Total alloy flow was measured on flat plate coupons for steadily rising temperatures. Alloy samples weighing 0.1 gram were used for all specimens. Table IV presents the flow distance measurement and maximum test temperatures for silver-base ternary alloys.

The flow results in Table IV show that most additions have promoted increased flow. Those additions showing the greatest influence are indium, phosphorus, and zinc. Cadmium, lithium, and tin showed moderate influence while titanium and germanium were the least effective.

TABLE IV

FLOW FOR SILVER-BASE TERNARY ALLOYS

Composition	Maximum Temperature (°F)	Flow Spread (in.)
Ag-26.5Cu	1600	0.45
Ag-28Cu	1510	0.21
Ag-29.3Cu	1515	0.17
Ag-30.5Cu	1580	0.16
Ag-32.0Cu	1550	0.22
Ag-24.5Cu-7Cd	1600	0.30
	1540	0.20
Ag-25.2Cu-7Cd	1520	0.40
Ag-26Cu-7Cd	1510	0.25
Ag-27Cu-7Cd	1485	0.40
Ag-24.5Cu-10Cd	1570	0.25
Ag-25.2Cu-10Cd	1570	0.22
Ag-26Cu-10Cd	1550	0.17
Ag-29Cu-10Cd	1600	0.22
Ag-27Cu-10Cd	1510	0.25
Ag-24.5Cu-10In	1520	0.26
Ag-24Cu-15In	1420	0.22
Ag-24Cu-1.5In	1520	0.28
Ag-24Cu-2.6In	1610	0.27
Ag-25.2Cu-10In	1510	0.30
Ag-26Cu-10In	1500	0.30
Ag-26.5Cu-10In	1525	0.35
Ag-26.5Cu-10In	1600	0.28
Ag-27Cu-10In	1500	0.34
Ag-28Cu-10In	1500	0.29
Ag-29Cu-10In	1500	0.36
Ag-30.5Cu-10In	1500	0.30
Ag-30.5Cu-10In	1500	0.18
Ag-31.5Cu-10In	1530	0.33
Ag-32Cu-10In	1515	0.25
Ag-32.5Cu-10In	1500	0.33
Ag-22Cu-10Ge	1480	0.22
Ag-23.5Cu-10Ge	1560	0.22
Ag-24.5Cu-10Ge	1410	0.30
	1540	0.25
	1570	0.20
Ag-25Cu-10Ge	1400	0.23
Ag-25.2Cu-10Ge	1600	0.27
	1580	0.23
	1540	0.20
Ag-26Cu-10Ge	1600	0.275

Composition	Maximum Temperature (°F)	Flow Spread (in.)
Ag-27Cu-10Ge	1530	0.30
	1470	0.21
Ag-30Cu-10Ge	1440	0.25
Ag-28Cu-0.2Li	1500	0.30
Ag-27.5Cu-2.8Li	1600	0.50
Ag-28Cu-0.5Li	1550	0.32
Ag-27.8Cu-1P	1600	0.60
Ag-43.2Cu-1.3P	1540	0.48
Ag-27.5Cu-2P	1600	0.65
Ag-27.3Cu-2P	1565	0.60
Ag-35Cu-2P	1550	0.48
Ag-43Cu-2P	1425	0.37
	1460	0.35
Ag-45Cu-2P	1435	0.35
Ag-47.5Cu-2P	1425	0.38
	1460	0.45
Ag-50Cu-2P	1430	0.40
Ag-24.5Cu-10Sn	1500	0.22
Ag-25.2Cu-10Sn	1510	0.32
Ag-26Cu-10Sn	1430	0.27
Ag-27Cu-10Sn	1570	0.45
Ag-30Cu-10Sn	1520	0.32
Ag-28Cu-0.1Ti	1550	0.37
Ag-28Cu-0.5Ti	1600	0.30
Ag-27.7Cu-1.8Ti	1600	0.37
	1570	0.20
	1550	0.22
Ag-27.4Cu-3Ti	1540	0.22
Ag-26.6Cu-5Zn	1550	0.26
	1470	0.16
Ag-24.9Cu-8Zn	1500	0.28
Ag-25.3Cu-9Zn	1500	0.28
Ag-26.5Cu-8Zn	1500	0.31
Ag-27.3Cu-8.7Zn	1500	0.50
Ag-27.4Cu-8.7Zn	1530	0.26
Ag-28.4Cu-8.6Zn	1500	0.26
Ag-27Cu-10Zn	1500	0.28
Ag-28.8Cu-7Zn	1540	0.31
	1530	0.23
Ag-29Cu-10Zn	1490	0.27
Ag-30.4Cu-5Zn	1450	0.30
Ag-30.8Cu-7.5Zn	1500	0.28

Some compositions exhibit inconsistencies in flow results. For example, Ag-24.5Cu-10Ge shows a 33 percent greater flow at 1410°F than at 1570°F. Also, alloys with nearly equal composition show similar irregularity; e.g., Ag-27.3Cu-8.7Zn shows a flow of 0.5 inch at 1500°F, whereas Ag-27.4Cu-8.7Zn shows a flow of half that amount at 1530°F. It was theorized that these differences were related to undetected inclusions, variations in heating rate, or composition changes resulting from arc-melting techniques for these particular compositions.

Isothermal Flow Tests

Isothermal flow tests were conducted to develop additional data for appraising candidate braze alloys. This approach permits evaluation of alloy flow based on specific time-temperature parameters. Promising silver-base ternary alloys were selected based on melt-flow temperatures and flow distance (Tables II and IV). The isothermal flow tests were made on flat plates at 1450 and 1500°F and in capillary T-joints at 1400°F. Those alloys selected for isothermal flow on flat plates included:

Composition	Temperature/Cycle
Ag-28Cu-0.5Li	1500°F/10 minutes
Ag-27Cu-10Zn	1500°F/10 minutes
Ag-47.5Cu-2P	1500°F/10 minutes
Ag-54Cu-2P	1450°F/10 minutes

The following alloys were selected for isothermal capillary flow tests at 1400°F:

Ag-27.6Cu-2.7Li	Ag-27.4Cu-2.8Li
Ag-47.5Cu-2P	Ag-50Cu-2P
Ag-25.2Cu-10Mn	Ag-26.5Cu-10In
Ag-27Cu-10In	Ag-25.2Cu-10Sn
Ag-26Cu-10Sn	Ag-25.2Cu-9Zn
Ag-26Cu-9Zn	Ag-27.7Cu-0.5Li

Flat plate coupons included 0.75 by 0.75 inch specimens for individual tests, and 0.75 by 3.0 inch specimens for evaluating more than one alloy at a time. Flow results for the 1450 and 1500°F tests are presented in Table V. A comparison of test results shows that flow is nearly equal for all specimens. However, since Ag-54Cu-2P had been fired at 1450°F for five minutes (50 degrees lower and five minutes shorter time than the other three specimens), flow would be expected to be greater than 0.40 inch at 1500°F for a 10-minute braze cycle. Flow results for the two phosphorus alloys (Ag-54Cu-2P and Ag-47.5Cu-2P) show the influence of copper on Ag-2P. This influence was shown earlier where increased copper additions to silver-phosphorus reduced melt, wet, and flow temperatures and also improved flow distance.

TABLE V

ISOTHERMAL FLOW AT 1450 AND 1500°F ON FLAT PLATES

Alloy	Test Temperature (°F)	Time (min)	Flow Distance (in.)
Ag-28Cu-0.5Li	1500	10	0.38
Ag-27Cu-10Zn	1500	10	0.39
Ag-47.5Cu-2P	1500	10	0.35
Ag-54Cu-2P	1450	5	0.40

Capillary flow specimens used for isothermal flow evaluation at 1400°F were of the modified type where gap clearance was maintained at net fit; these specimens are described in Section II. One hundred and fifty milligrams of alloy were used for each test specimen. The procedure used was to hold the specimen at a preselected temperature and monitor capillary flow until either vertical flow ceased or maximum capillary travel was reached within 60 minutes. Curves showing capillary flow for the selected ternary alloys were plotted (Fig. 16). Salient points for each addition are presented in the following paragraphs.

- Ag-Cu-In. Although the three compositions studied vary by only 1.8 percent copper, isothermal flow patterns show appreciable variations. Maximum flow achieved is 0.24 inch in 13 minutes for 25.2 percent copper, 0.60 inch in 50 minutes for 26.5 percent copper, and 0.28 inch in five minutes for 27 percent copper. The results show that 90 percent flow is reached within one minute for the 27 percent copper alloy and 75 percent flow is reached within 15 minutes for the 26.5 percent copper alloy. The most significant feature noted is the continued flow for Ag-26.5Cu-10In well after both other alloys stopped flowing.

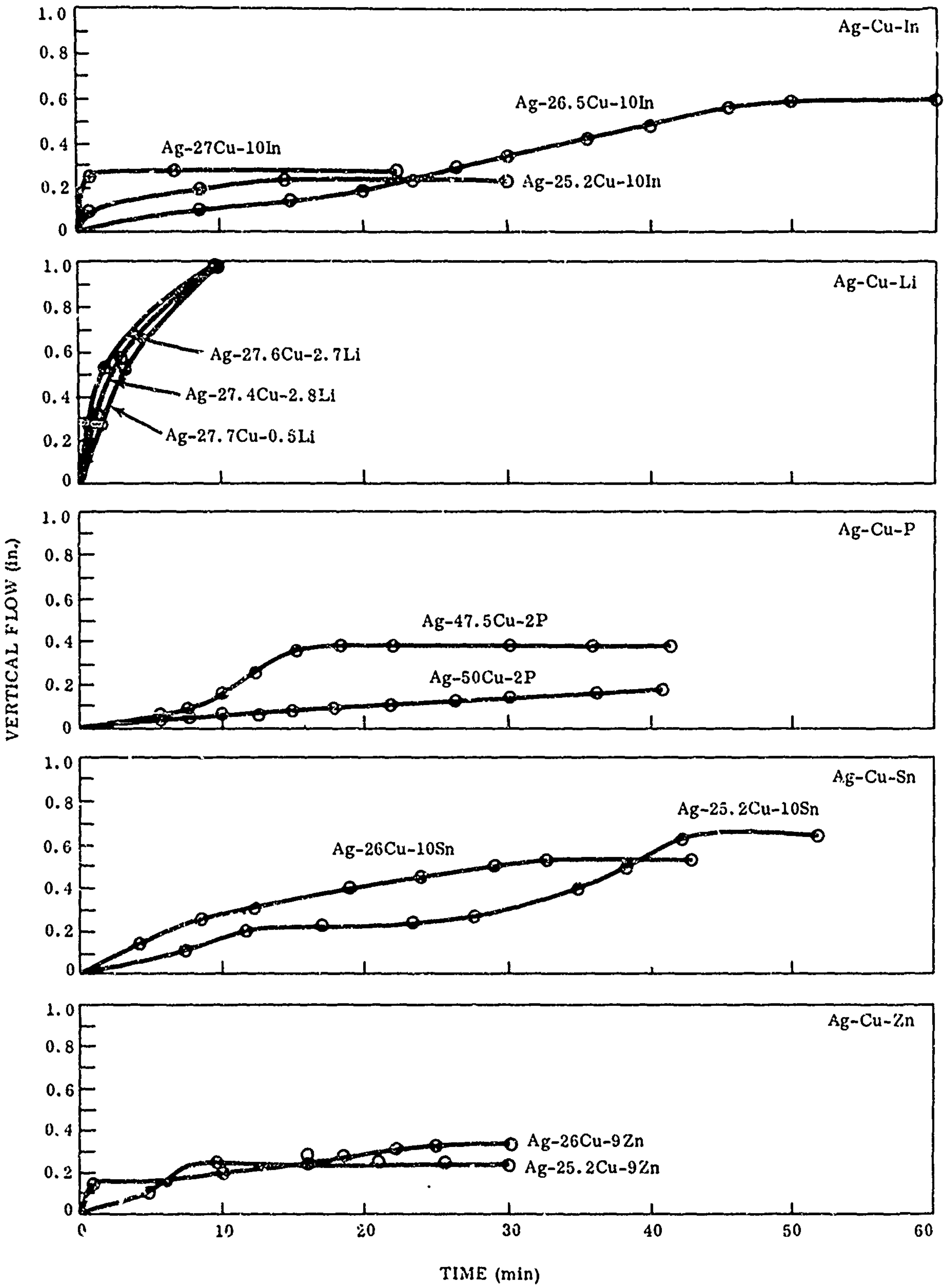


FIGURE 16. ISOTHERMAL FLOW AT 1400°F

- Ag-Cu-Li. The 0.5, 2.7, and 2.8 percent lithium-containing alloys all reached the one-inch maximum flow in 10 minutes for the 1400°F test temperature.

- Ag-Cu-P. These two curves show that copper influenced Ag-P differently than described earlier for flat plate isothermal tests. Although the copper differential is small, Ag-50Cu-2P has reached a maximum flow of 0.38 inch in 18 minutes. For earlier test results, a lower copper content generally showed greater flow and reduced temperatures in comparison to a higher content. This change from previous trends may be attributed to undetected variations in braze control.

- Ag-Cu-Sn. Curves for the two alloys tested show similar capillary flow characteristics. The 25.2 percent alloy reached a maximum flow of 0.52 inch in 30 minutes and the 26 percent copper alloy reached a maximum flow of 0.64 inch in 42 minutes.

- Ag-Cu-Zn. A 0.25 inch capillary flow rise was reached in 10 minutes for the Ag-25.2Cu-9Zn alloy. No further flow occurred for the 25.2 percent copper alloy, while flow for the 26 percent copper alloy continued to a height of 0.33 inch.

Metallographic Studies

Samples for metallographic study included an as-cast braze alloy and alloys that had flowed on flat plate beryllium coupons. This combination permitted a comparison of alloy structures before and after firing. Alloys examined were.

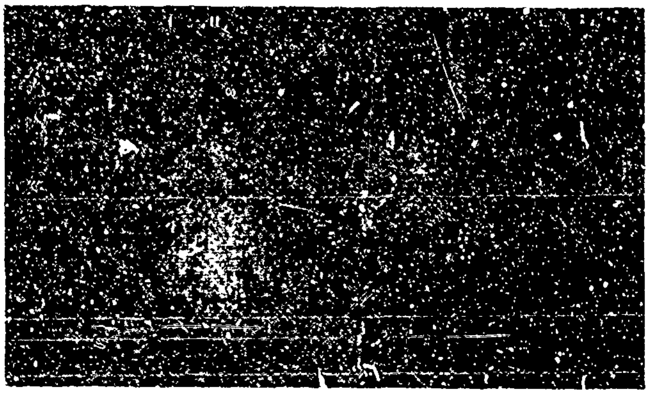
Ag-28Cu

Ag-26Cu-10Sn

Ag-26Cu-10In

Ag-28Cu Alloy. Three samples were prepared to compare results for various treatments. Alloy samples are listed below. Photomicrographs are shown in Figure 17 through 19. Comments on highlights for each structure follow.

- As cast from arc melt
- Brazement on beryllium
- Brazement on nonreactive surface (molybdenum)



Etchant: 1. Ammonium Hydroxide
2. Kroll's

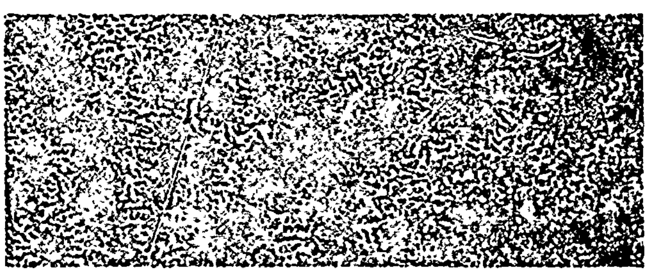
Magnification: 250X

FIGURE 17. SILVER-28 COPPER ARC MET

Etchant: 4% CrO_3
96% H_2O

Magnification: 250X

FIGURE 18. SILVER-28 COPPER FLOWED ON BERYLLIUM



Etchant: Ammonium Bifluoride

Hydrogen Peroxide

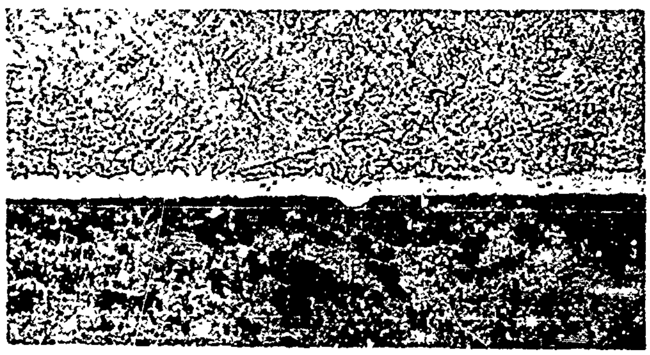
Magnification: 250X

FIGURE 19. SILVER-28 COPPER FLOWED ON NONREACTIVE SURFACE

The structure of the arc melt was a fine, feathery eutectic with no evidence of primary phases (Fig. 17). After flowing on a beryllium coupon (Fig. 18) the amount of eutectic is markedly reduced and a zone of beryllide has formed at the interface. The binary eutectic is at 28 percent copper so that this behavior must be explained by the removal of copper from the alloy to form a copper beryllide at the interface. Calculations show that for a beryllide layer of 0.0005 inch and a braze alloy thickness of 0.005 inch, the braze alloy copper content will be reduced to below 20 percent, and the amount of primary alpha phase (silver rich) should be approximately 40 percent.

This result was confirmed by flowing the same alloy on an essentially non-reactive substrate. Molybdenum was used and the test was performed at 1550°F. Figure 19 shows that the structure of the braze alloy remains largely eutectic.

Ag-26Cu-10Sn. Figure 20 shows the structure after firing on a beryllium surface at 1430°F for two minutes. There is less beryllide than with the binary eutectic, and this must be due, at least partially, to the lower temperature, although the effect of time is unknown on beryllide formation under brazing conditions. Nucleation of the primary phase at the beryllide suggests that the primary phase is silver rich.



Etchant: Kroll's

Magnification: 150X

FIGURE 20. STRUCTURE FOR Ag-Cu-10Sn FLOWED ON BERYLLIUM

Ag-26Cu-10In. Figure 21 shows this braze alloy after a braze cycle of 1500°F for two minutes. The interaction zone is wider than in the case of Ag-26Cu-10Sn (Fig. 20). Two factors will affect this condition:

- The higher brazing temperature (1500 versus 1430°F)
- An increase in reaction rate found in earlier work for Ag-Cu-In alloys (Ref. 1).

Etchant: 1. Ammonium Hydroxide
2. CrO_3
H_2SO_4
H_3PO_4

Magnification: 150X

FIGURE 21. STRUCTURE FOR Ag-Cu-10In FLOWED ON BERYLLIUM

4.1.3 Optimization by Higher Additions to Ternary Alloys

The silver-base ternary alloys developed at this point had melting points suitable for modification to develop a 1400°F braze alloy. Some had deficiencies such as poor wetting so as to cause a flow temperature of 200 degrees F or more above the melting point. Others showed poor flow in the isothermal tests. Therefore, the purpose of subsequent work was to overcome such defects by quaternary and higher additions to increase wetting and flow. Ternary alloys were selected for further development based on favorable characteristics, of which an adequately low melting point (e.g., 1280 to 1340°F) was an essential feature.

Data relating to the silver-copper base alloys were examined for each addition to select the most promising composition for further optimization. Selections were based on characteristics such as melt-flow temperatures, melt-flow temperature differential, flow distance, and reproducibility. Priority in these categories was established by points, those alloys having the greatest number of points were rated as the most promising.

The review showed that seven basic compositions were promising for further development. Two lithium-containing alloys were included to compare results for high- and low-lithium alloys. The selection also included two germanium-containing alloys because of the promising potential indicated for Ag-Cu-Ge at two levels of copper

The compositions are:

- Ag-26.5Cu-10In
- Ag-50Cu-2P
- Ag-26.5Cu-10Zn
- Ag-27Cu-10Ge and Ag-63Cu-10Ge
- Ag-27.8Cu-0.5Li and Ag-27.4Cu-1.5Li
- Ag-26Cu-10Sn

All of these alloys have melting points below 1400°F, covering the range 1280 to 1350°F. Flow temperatures observed on heating were less consistent for the alloys, so that a primary purpose of continued development of these ternary alloys was to obtain consistent flow temperatures of 1400°F or below. Hence, major emphasis has been placed on additions that were expected to improve wetting and flow.

The additions of cadmium and titanium did not appear promising as temperature depressants; consequently, alloys containing these constituents were not included. However, because titanium exhibits the potential to improve wetting, it was included as an additive in the next step in alloy development.

Effect of Additions on Flow Distance and Temperature

Additions to the seven selected ternary alloys included lithium, manganese, nickel, palladium, phosphorus, zinc, and titanium. Test compositions were prepared from elemental materials by additions of elemental materials to the ternary alloys, and by combining master melts with elemental materials or other master melts. Melt, wet, and flow temperature checks were made and recorded together with alloy flow distances. The results of these tests are presented in Table VI. For comparison, results for the basic ternary alloys are included. Tests were performed in argon using standard flat plate coupons. Highlights relating to results are discussed below.

Ag-Cu-In. The effect of additions to the Ag-26.5Cu-10In alloy on melt and flow properties show that all melt temperatures and all but one flow temperature have been increased. The 1480°F flow point and 0.28-inch flow distance for palladium equals that of the basic alloy. Flow distances are increased for lithium and phosphorus addition alloys, but at higher maximum temperatures than for the basic alloy. Manganese and zinc show equal flow distance; nickel leads to a reduced flow distance at higher maximum temperatures.

Ag-Cu-Ge. Two base alloys were studied; one with a high copper content (Ag-63Cu-10Ge) and one with a lower copper content (Ag-27Cu-10Ge). Although the 27 percent copper alloy was selected for continued development, the higher copper composition was included because other work indicated improved properties were gained with increased copper.

The results for Ag-27Cu-10Ge in Table VI show that none of the additions were effective in reducing melt or flow temperatures. Alloy flow distance was reduced except for the manganese addition where a slight increase in flow has occurred from liquation of the alloy fragment. A major portion of the alloy remained unmelted.

TABLE VI

RESULTS FOR QUATERNARY ALLOYS

Composition	Temperature (°F) Melt	Wet	Flow	Flow Distance (in./deg F)
Ag-26.5Cu-10In[1]	1325	1410	1480	0.30/1500
Ag-26.3Cu-9.5In-0.6Li	1400	1460	1560	0.35/1580
Ag-25.2Cu-9.5In-5Mn	1385	1470	1590	0.30/1600
Ag-25.2Cu-9.5In-5Ni	1390	1440	1610	0.25/1625
Ag-26Cu-9.8In-2.25P	1390	1590	1650	0.41/1660
Ag-24.1Cu-9.1In-9Pd	1450	1465	1480	0.28/1500
Ag-24.9Cu-9.4In-6Zn	1410	1510	1620	0.30/1620
Ag-27Cu-10Ge[1]	1285	1335	1480	0.30/1530
Ag-25.6Cu-9.5Ge-5Mn	1375	1480	1540	0.33/1545
Ag-24.6Cu-9.1Ge-9Pd	1375	1500	1660	0.27/1670
Ag-25.6Cu-9.5Ge-5Ni	1400	1450	1585	0.25/1590
Ag-25.4Cu-9.4Ge-6Zn	1370	1560	1640	0.28/1650
Ag-26.7Cu-9.9Ge-1Li	1420	1530	1650	0.25/1660
Ag-26.8Cu-10Ge-0.5Ti	1475	1550	>1800	Incipient melt at 1800 maximum
Ag-63Cu-10Ge[1]	1430	1500	1530	0.35/1540
Ag-60Cu-9.5Ge-5Mn	1420	1500	1575	0.42/1650
Ag-57.2Cu-9.1Ge-9Pd	1450	1470	1530	0.44/1650
Ag-60Cu-9.5Ge-5Ni	1450	1480	1570	0.44/1650
Ag-59Cu-9.4Ge-6Zn	1425	1480	1540	0.40/1600
Ag-62.5Cu-9.9Ge-1Li	1520	1540	1550	0.40/1600
Ag-61.5Cu-9.7Ge-2.4P	1340	>1850	>1850	None/1850 maximum
Ag-60.5Cu-9.6Ge-4Ti	1500	1590	1700	0.32/1850 residue
Ag-62.6Cu-10Ge-0.5Ti	1440	1460	1500	0.35/1510
Ag-27.7Cu-0.5Li[1]	1300	1380	1475	0.32/1550
Ag-26.4Cu-0.4Li-5Mn	1360	1400	1410	0.36/1420
Ag-26.4Cu-0.5Li-5Ni	1390	1450	1540	0.27/1550 residue
Ag-25.2Cu-0.5Li-9Pd	1290	1380	1425	0.31/1430
Ag-26.1Cu-0.5Li-6Zn	1310	1435	1510	0.33/1520
Ag-26.6Cu-0.5Li-4Ti	1320	1450	1500	0.26/1510 residue
Ag-27.6Cu-1.5Li-0.25Ti	1300	1340	1450	0.30/1460
Ag-50Cu-2P[1]	1385	1410	1420	0.35 to 0.45/1420
Ag-47.5Cu-1.9P-5Mn	1340	1400	1410	0.50/1475
Ag-49.5Cu-1.95P-1Li	1425	1460	1510	0.58/1520
Ag-47.5Cu-1.9P-5Ni	1350	1425	1435	0.70/1540
Ag-45.5Cu-1.8P-9Pd	1425	1435	1445	0.45/1475
Ag-48Cu-1.9P-4Ti	1500	1525	1850	0.50/1850 residue
Ag-47Cu-1.9P-6Zn	1400	1420	1450	0.60/1540
Ag-26Cu-10Sn[1]	1280	1390	1410	0.60/1480
Ag-26.7Cu-9.9Sn-1Li	1390	1470	1520	0.24/1530
Ag-24.6Cu-9.5Sn-5Mn	1325	1425	1540	0.35/1575
Ag-24.6Cu-9.5Sn-5Ni	1490	1540	1660	0.40/1750
Ag-23.6Cu-9.1Sn-9Pd	1400	1475	1575	0.35/1650
Ag-25.4Cu-9.6Sn-2.2P	1300	1625	1630	0.32/1750
Ag-25Cu-9.5Sn-4Ti	1440	1550	1625	0.20/1650 residue
Ag-26Cu-9.9Sn-0.5Ti	1340	1475	1550	0.27/1560
Ag-23.6Cu-9.1Sn-9Zn	1400	1470	1625	0.60/1700
Ag-26.5Cu-10Zn[1]	1300	1410	1485	0.21/1485
Ag-24.6Cu-9.5Zn-5Ni	1330	1400	1450	0.42/1450
Ag-24.1Cu-9.1Zn-9Pd	1350	1450	1600	0.38/1600
Ag-25.9Cu-9.9Zn-1Ti	1385	1450	1550	0.31/1560
Ag-26.5Cu-9.9Zn-1Ti	1340	1460	1550	0.35/1560
Ag-25.4Cu-9.6Zn-4Ti	1380	1430	1460	0.27/1640
Ag-30.1Cu-6.7Zn-2.6P	1450	1700	>1850	None to 1850

1. Basic ternary alloy

Additions to the Ag-63Cu-10Ge alloy show a general narrowing of the melt-flow range when compared to results for Ag-27Cu-10Ge. An improvement in flow distance is noted for additions of titanium, lithium, zinc, and nickel.

Ag-Cu-Li. Additions to the ternary alloy, Ag-27.7Cu-0.5Li, show that melt points are increased for manganese and nickel, but that manganese and palladium additions have reduced flow temperatures. The reduced flow temperature for Ag-Cu-1.5Li-0.25Ti may be influenced by the increased lithium. Increased flow distance is noted for manganese, palladium, and zinc additions.

Ag-Cu-P. Additions of manganese and nickel to the Ag-50Cu-2P alloy have reduced the melt temperatures while only manganese has reduced flow temperatures. At 1420°F, the maximum test temperature for Ag-50Cu-2P, greater flow distance is indicated for all alloys except Ag-48Cu-1.9P-4Ti.

Ag-Cu-Sn. None of the additions made to the Ag-26Cu-10Sn alloy have reduced melt-flow temperatures or improved wetting as shown by the reduced flow distance for higher maximum temperatures.

Ag-Cu-Zn. The 1300°F melt temperature for the Ag-26Cu-10Zn alloy was not reduced with the additions shown in Table VI. Nickel and titanium additions have lowered the flow temperature. The 0.42-inch flow distance at 1450°F for the nickel addition is a considerable increase over 0.31 inch at 1485°F for the basic alloy. A comparison of titanium additions at one and four percent show better flow at 1560°F for the one percent alloy than at 1640°F for the four percent alloy, even though the higher titanium alloy has a flow point 90 degrees F lower than the one percent titanium alloy.

Modification of Selected Alloys to Control Melt-Flow Point

To reduce both the melt-flow temperature differential and the braze temperature of developmental braze alloys, additional work was performed with alloy selections based on data shown in Table VI. Those exhibiting promising melt-flow temperatures and flow distance were carried through for these tests. None of the higher copper compositions for the Ag-Cu-Ge alloys were included in this selection because those with the lower copper content appeared to be brighter prospects based on melt-flow temperatures. However, the higher content copper alloys were included in later tests because of significant wetting and flow properties.

Additions to the selected alloys included germanium, lithium, manganese, nickel, phosphorus, palladium, titanium, tin, and zinc. Quantities from a minimum of 0.1 percent to a maximum of 10 percent were used. Tests were performed with standard flat plate coupons in argon to determine melt, wet, and flow temperatures.

TABLE VII

EFFECT OF ADDITIONS ON MELT-FLOW DIFFERENTIAL

Base Alloys	Addition (%)	Temperature (°F) Melt(1)	Wet(1)	Flow(1)	Melt Point Change(2)	Melt-Flow Differential (°F)
Ag-27Cu-10Ge	None	1285	1335	1480	-	200(2)
Ag-25.6Cu-9.9Ge	0.1Li				+ 50	230
Ag-26.6Cu-9.9Ge	1.0Li				+ 20	230
Ag-26.7Cu-9.9Ge	1.0Mn				- 80	150
Ag-25.6Cu-9.9Ge	5.0Mn				- 25	165
Ag-26.7Cu-9.9Ge	1.0Pd				- 25	200
Ag-24.6Cu-9.1Ge	9.0Pd				- 30	240
Ag-25.6Cu-9.5Ge	5.0Ni				0	185
Ag-27Cu-10Ge	0.2P				+ 50	100
Ag-27Cu-10Ge	0.1Ti				+ 75	125
Ag-26.8Cu-9.9Ge	0.5Ti				+ 75	>150
Ag-26.6Cu-9.8Ge	1.5Sn				+ 95	80
Ag-27.6Cu-9.9Ge	1.0Zn				- 80	230
Ag-25.4Cu-9.4Ge	6.0Zn				- 30	260
Ag-26.5Cu-10In	None	1325	1410	1480	-	110(2)
Ag-26.5Cu-9.9In	0.1Li				- 65	60
Ag-26.3Cu-9.5In	0.6Li				- 40	160
Ag-26.2Cu-9.9In	1.0Mn				- 80	190
Ag-25.2Cu-9.5In	5.0Mn				- 55	200
Ag-26.2Cu-9.9In	1.0Pd				- 70	180
Ag-24.1Cu-9.1In	9.0Pd				+ 10	30
Ag-25.2Cu-9.5In	5.0Ni				- 50	220
Ag-26.5Cu-10In	0.2P				-100	180
Ag-26Cu-9.8In	2.0P				- 50	260
Ag-26.5Cu-10In	0.1Ti				- 65	175
Ag-26.5Cu-10In	0.5Ti				- 15	125
Ag-25.8Cu-9.8In	2.0Ti				+ 35	115
Ag-26.1Cu-9.8In	1.5Sn				- 40	130
Ag-26.2Cu-9.8In	1.0Zn				- 40	150
Ag-24.0Cu-9.4In	6.0Zn				- 30	210
Ag-27.7Cu-0.5Li	None	1300	1380	1475	-	130(2)
Ag-27.5Cu-0.5Li	1.0Mn				+140	90
Ag-24.6Cu-0.5Li	5.0Mn				+ 20	50

TABLE VII

EFFECT OF ADDITIONS ON MELT-FLOW DIFFERENTIAL

Base Alloys	Addition (%)	Temperature (°F)				Melt-Flow Differential (°F)
		Melt(1)	Wet(1)	Flow(1)	Melt Point Change(2)	
Ag-27Cu-10Ge	None	1285	1335	1480	-	200(2)
Ag-25.6Cu-9.9Ge	0.1Li				+ 50	230
Ag-26.6Cu-9.9Ge	1.0Li				+ 20	230
Ag-26.7Cu-9.9Ge	1.0Mn				- 80	150
Ag-25.6Cu-9.9Ge	5.0Mn				- 25	165
Ag-26.7Cu-9.9Ge	1.0Pd				- 25	200
Ag-24.6Cu-9.1Ge	9.0Pd				- 30	240
Ag-25.6Cu-9.5Ge	5.0Ni				0	185
Ag-27Cu-10Ge	0.2P				+ 50	100
Ag-27Cu-10Ge	0.1Ti				+ 75	125
Ag-26.8Cu-9.9Ge	0.5Ti				+ 75	>150
Ag-26.6Cu-9.8Ge	1.5Sn				+ 95	80
Ag-27.6Cu-9.9Ge	1.0Zn				- 80	230
Ag-25.4Cu-9.4Ge	6.0Zn				- 30	260
Ag-26.5Cu-10In	None	1325	1410	1480	-	110(2)
Ag-26.5Cu-9.9In	0.1Li				- 65	60
Ag-26.3Cu-9.5In	0.6Li				- 40	160
Ag-26.2Cu-9.9In	1.0Mn				- 80	190
Ag-25.2Cu-9.5In	5.0Mn				- 55	200
Ag-26.2Cu-9.9In	1.0Pd				- 70	180
Ag-24.1Cu-9.1In	9.0Pd				+ 10	30
Ag-25.2Cu-9.5In	5.0Ni				- 50	220
Ag-26.5Cu-10In	0.2P				-100	180
Ag-26Cu-9.8In	2.0P				- 50	260
Ag-26.5Cu-10In	0.1Ti				- 65	175
Ag-26.5Cu-10In	0.5Ti				- 15	125
Ag-25.8Cu-9.8In	2.0Ti				+ 35	115
Ag-26.1Cu-9.8In	1.5Sn				- 40	130
Ag-26.2Cu-9.8In	1.0Zn				- 40	150
Ag-24.0Cu-9.4In	6.0Zn				- 30	210
Ag-27.7Cu-0.5Li	None	1300	1380	1475	-	130(2)
Ag-27.5Cu-0.5Li	1.0Mn				+140	90
Ag-24.6Cu-0.5Li	5.0Mn				+ 20	50

TABLE VII (Cont)

EFFECT OF ADDITIONS ON MELT-FLOW DIFFERENTIAL

Base Alloys	Addition (%)	Temperature (°F) Melt[1]	Wet[1]	Flow[1]	Melt Point Change[2]	Melt-Flow Differential (°F)
Ag-26.4Cu-0.4Li	5.0Ni				+ 50	150
Ag-27.5Cu-0.5Li	1.0Pd				+ 90	140
Ag-25.2Cu-0.5Li	9.0Pd				- 50	135
Ag-27.7Cu-0.5Li	0.2P				+160	>100
Ag-27.7Cu-0.5Li	0.1Ti				+150	60
Ag-27.6Cu-1.5Li	0.2Ti				- 20	150
Ag-26.6Cu-0.5Li	4.0Ti				- 40	180
Ag-27.5Cu-0.5Li	1.5Sn				+ 60	190
Ag-26.7Cu-0.5Li	9.9Sn				+ 50	220
Ag-27.5Cu-0.5Li	1.0Zn				+ 35	100
Ag-26.1Cu-0.5Li	6.0Zn				- 30	200
Ag-60Cu-2P[3]	None	1320	1400	1420	-	65
Ag-50Cu-2P[4]	None				-	50
Ag-60Cu-2P	0.1Li				+110	180
Ag-49.5Cu-1.9P	1.0Li				+ 15	85
Ag-59.4Cu-2P	1.0Mn				+ 90	50
Ag-47.5Cu-1.9P	5.0Mn				- 70	70
Ag-47.5Cu-1.9P	5.0Ni				- 10	85
Ag-59.4Cu-2P	1.0Pd				- 20	120
Ag-45.5Cu-1.8P	9.0Pd				+ 15	120
Ag-60Cu-2P	0.1Ti				- 10	160
Ag-48Cu-1.9P	4.0Ti				+ 90	200
Ag-59.1Cu-2P	1.5Sn				- 40	130
Ag-25.5Cu-2.2P	9.6Sn				-110	200
Ag-59.4Cu-2P	1.0Zn				0	90
Ag-47Cu-1.9P	6.0Zn				- 10	50
Ag-26Cu-10Sn	None	1280	1390	1410	-	145
Ag-26Cu-10Sn	0.1Li				- 50	210
Ag-26.7Cu-9.9Sn	1.0Li				- 50	130
Ag-25.7Cu-10Sn	1.0Mn				- 60	110
Ag-24.6Cu-9.5Sn	5.0Mn				-115	215
Ag-23.6Cu-9.1Sn	5.0Ni				+ 70	170

TABLE VII (Cont)

EFFECT OF ADDITIONS ON MELT-FLOW DIFFERENTIAL

Base Alloys	Addition (%)	Temperature (°F) Melt[1]	Wet[1]	Flow[1]	Melt Point Change[2]	Melt-Flow Differential (°F)
Ag-25.7Cu-10Sn	1.0Pd				- 10	140
Ag-23.6Cu-9.1Sn	9.0Pd				- 40	175
Ag-25.7Cu-10Sn	0.2P				+ 10	140
Ag-25.4Cu-9.6Sn	2.2P				-140	>250
Ag-26Cu-10Sn	0.1Ti				- 40	150
Ag-26Cu-9.9Sn	0.5Ti				-100	210
Ag-26Cu-9.5Sn	4.0Ti				0	185
Ag-25.7Cu-10Sn	1.0Zn				+ 20	140
Ag-23.7Cu-9.0Zn					- 60	190
Ag-26.5Cu-10Zn	None	1300	1410	1485	-	130
Ag-26.3Cu-10Zn	0.1Li				+ 70	100
Ag-26Cu-6Zn	0.5Li				-100	200
Ag-26Cu-9.9Zn	1.0Li				-120	210
Ag-26.5Cu-9.9Zn	1.0Mn				+ 80	90
Ag-24.6Cu-9.5Zn	5.0Mn				-170	300
Ag-24.6Cu-9.5Zn	5.0Ni				- 80	120
Ag-26.5Cu-9.9Zn	1.0Pd				+ 40	100
Ag-24.1Cu-9.1Zn	9.0Pd				- 60	>250
Ag-26.5Cu-10Zn	0.2P				+ 50	140
Ag-30.1Cu-6.7Zn	2.6Pd				+ 40	>250
Ag-26.5Cu-10Zn	0.1Ti				+ 20	130
Ag-26.5Cu-9.9Zn	1.0Ti				- 70	200
Ag-25.4Cu-9.6Zn	4.0Ti				- 10	80
Ag-26.1Cu-9.8Zn	1.5Sn				+ 30	140
Ag-23.6Cu-9.0Zn	9.0Sn				- 10	200

1. Values based on initial development work (Table I).
2. Based on modified temperatures; + = increase, - = decrease.
3. Based on Ag-Cu-P with lowest melt point.
4. Included for comparison with the 50Cu alloys.

Ag-Cu-P. Significant melt point reductions are shown by the additions 5.0 percent manganese and 9.6 percent tin. Considerable temperature increase is shown for 0.1 percent lithium, 1.0 percent manganese, and 4.0 percent titanium. Flow temperature improvements, noted by melt-flow differentials, are indicated for manganese and zinc. The other additions show flow temperatures have been increased.

The effect of titanium on Ag-Cu-P alloys with 0.1 percent phosphorus was studied. Two percent titanium additions were made to the Ag-55Cu-0.1P and Ag-28Cu-0.1P alloys to determine melt-flow properties. A comparison of results for these alloys with base alloys shows that titanium offers no advantage. Both the melt-flow temperatures and flow distance were not improved.

Ag-Cu-Sn. All additions except nickel have depressed melt temperatures for the Ag-Cu-Sn alloy. Reductions up to 140 degrees are shown. The lower phosphorus and zinc additions show minor increases of 10 and 20 degrees F, respectively. A 70-degree increase is noted for nickel. Favorable flow temperature reductions were made with lithium and manganese. No significant flow temperature changes are seen for the remaining additions.

Ag-Cu-Zn. Except for Ag-Cu-Zn-P, melt point reductions are exhibited by all the larger quantity additions. The smaller quantity additions do not appear promising for the Ag-Cu-Zn alloy. Although five percent manganese has reduced the melt point by 170 degrees F, the extensive 300-degree melt-flow differential annuls any gains with respect to brazing temperatures. Five percent nickel and four percent titanium appear to be favorable additions for temperature control.

Isothermal Flow of Quaternary Alloys

Isothermal flow studies were performed to develop additional data that would aid in screening quaternary alloys. Alloy selections were based on results of melt-flow temperature and flow distance tests. Flow evaluations were conducted at 1450°F for time periods of 5 and 10 minutes. Flat plate test coupons, large enough to accommodate all alloy samples with the same base composition, were used to ensure identical braze conditions for all alloys within a particular grouping.

The alloy selections and their flow distance measurements are presented in Table VIII. Results for the ternary alloy, Ag-54Cu-2P, are included with the Ag-Cu-P base quaternary alloys for comparison.

The results in Table VIII compared to flow results for quaternary alloys (Table VI) show that flow distances for some compositions are improved by time at braze temperature. The Ag-Cu-Sn-Pd alloy, for instance, exhibits a flow of 0.32 inch at 1450°F for the 5.0-minute braze while at 1650°F the 0.5-minute braze cycle exhibits a flow of 0.35 inch. The Ag-Cu-Sn-Mn and Ag-Cu-Sn-Zn alloys exhibit a flow that is 55 percent less than that shown by the Ag-Cu-Sn-Pd alloy.

TABLE VIII

ISOTHERMAL FLOW FOR QUATERNARY ALLOYS

Composition	Flow Distance (in.)
Braze Cycle - 1450°F/5 Minutes	
Ag-23.6Cu-9.1Sn-9Pd	0.32
Ag-25.6Cu-9.5Sn-5Mn	0.18
Ag-23.6Cu-9.1Sn-9Zn	0.18
Ag-54Cu-2P	0.40
Ag-49.5Cu-2.0P-1Li	0.20
Ag-47.5Cu-1.9P-5Mn	0.60
Ag-47.5Cu-1.9P-5Ni	0.48
Ag-45.5Cu-1.8P-9Pd	0.37
Ag-47.3Cu-1.8P-6Zn	0.39
Braze Cycle - 1450°F/10 Minutes	
Ag-26.4Cu-0.5Li-5Mn	0.42
Ag-26.1Cu-0.5Li-9Pd	0.46
Ag-27.6Cu-0.5Li-4Ti	0.27 (Residue)
Ag-27.6Cu-1.5Li-0.3Ti	0.37

Microprobe Analysis

An examination of flow for the quaternary alloy, Ag-25.4Cu-9.6Zn-4Ti, on beryllium showed that a pattern of segregation had developed. This flow pattern is of special interest because that portion showing maximum flow exhibits promising wetting characteristics. A drawing showing the flow pattern for this alloy on beryllium is shown in Figure 22. This drawing shows the braze alloy has separated into an inner island of residue and into an outer peripheral band exhibiting excellent wetting. The exceptional wetting properties of this outer band is indicated by measurements of its thickness (less than 0.0002 inch) and extensive horizontal travel beyond the remaining higher

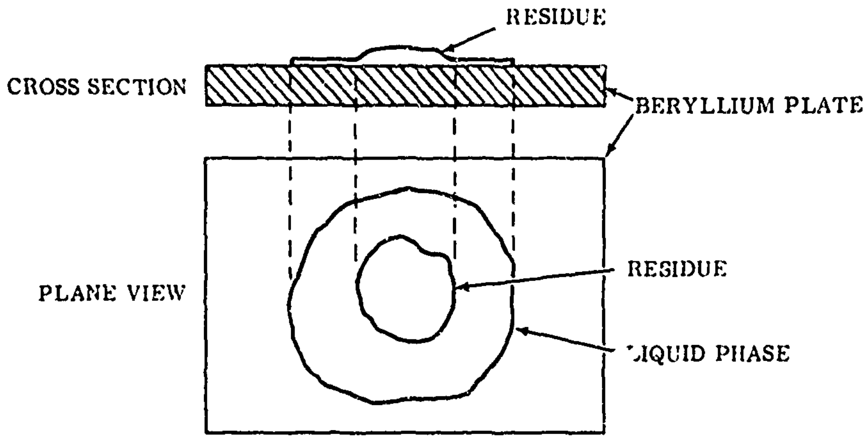


FIGURE 22. ILLUSTRATION OF FLOW FOR Ag-Cu-Zn-Ti ON BERYLLIUM

melting portion. Because of the promising wetting and flow properties of this outer alloy ring, attempts to determine its composition were made by using microprobe analysis techniques. A sample of the basic alloy was used as a standard for comparison. Test results are presented in the following listing.

Element	Original Alloy Composition (%)	Outer Band (%)
Silver	61.0	85.4
Copper	25.4	14.0
Zinc	9.6	0.6
Titanium	4.0	--

These results show that the titanium addition appears to be responsible for lack of flow of this composition because no titanium is present in the melt phase. No further work was done by the microprobe to optimize silver-base braze alloy compositions. However, in subsequent work microprobe analysis was developed for optimization of titanium-base alloys.

Summary of Results for Additions to Ternary Alloys

Up to this point in the development of silver-base braze alloys, additions have been made to promising ternary alloys to promote the following properties:

- A reduction in melt-flow temperatures
- Narrowed melt-flow temperature differentials
- Good flow properties

Some of the more significant improvements realized by additions to ternary alloys that were selected for continued development are presented in Table IX. Ternary base alloys are included for comparison.

The data in Table IX show that in many cases the melt point is still above the desired braze temperature of 1400°F even though selected ternary alloys, with the exception of Ag-63Cu-10Ge, have melting points between 1280 and 1350°F. Many of the alloys studied in this preliminary series have melting points above the 1400°F temperature. In addition, melt-flow temperature differentials have not been changed appreciably by any of the additions. However, other properties such as wetting and flow may be sufficiently attractive to overshadow undesirable characteristics.

4.1.4 Optimization of Quaternary Alloys

The principal requirement in further work was to reduce braze alloy flow temperatures to 1400°F. The work reported in Paragraph 4.1.3 was based on the approach that additions to improve wetting would narrow the melt-flow range without markedly increasing the melting points of the ternary alloys that were used as basis for quaternary development. However, as discussed in the summary to this section, it was not possible to realize this goal. In many cases, where the melt-flow differential was narrowed, the melting point was raised so that flow temperatures were greater than the preferred value of 1400°F (Table IX). Hence, the first step in this continued optimization work was to secure the needed reduction in flow temperature.

As for previous silver-base alloys, the approach followed was to make additions to or modification of promising alloys to improve wetting and promote braze temperatures of 1400°F or less. Associated studies included isothermal flow tests, and an evaluation of the effect of time on flow properties.

TABLE IX

COMPARISON OF RESULTS FOR QUATERNARY ALLOYS

Selected Alloy	Additions	Melt-Flow Temperature Difference (°F)	Melt Point (°F)	Flow Distance (in./deg F)
Ag-26.5Cu-10In	None	155	1325	0.30/1500
	0.6Li	160	1400	0.35/1580
	9.0Pd	30	1450	0.28/1500
	8.5Pd-5Mn	140	1380	0.28/1530
	8.8Pd-2Li	125	1350	0.28/1480
Ag-63Cu-10Ge	None	100	1430	0.35/1540
	5Mn	155	1420	0.42/1530
	5Pd	80	1450	0.44/1530
	6Zn	115	1425	0.40/1540
	1Li	30	1520	0.40/1550
	0.5Ti-5Mn	200	1340	0.40/1550
	0.5Ti-5Pd	115	1395	0.42/1515
Ag-27Cu-10Ge	None	190	1285	0.30/1530
	5Mn	165	1375	0.33/1540
Ag-26.5Cu-10Zn	None	185	1300	0.31/1485
	5Ni	120	1330	0.43/1480
	4Ti	80	1380	0.45/1640 (Residue)
	2Ti-5Mn	100	1400	0.34/1505
Ag-50Cu-2P	None	35	1385	0.40/1420
	5Mn	70	1340	0.50/1475
	5Ni	50	1350	0.70/1540
	6Zn	50	1400	0.60/1540
	9Pd	20	1425	0.45/1475
Ag-26Cu-10Sn	None	130	1280	0.60/1480
	5Mn	215	1325	0.35/1575
	1Li	130	1390	0.42/1530
	1.9Li-5Pd	185	1250	0.32/1480
	1.9Li-5Mn	100	1480	0.33/1480
	4.9Pd-5Mn	170	1340	0.33/1520
Ag-26.4Cu-0.5Li	None	175	1300	0.32/1550
	5Mn	50	1360	0.37/1420
	9Pd	135	1290	0.33/1430
	9Pd-5Mn	400	1100	0.38/1500
Ag-25.6Cu-1Li	4.8Mn-1Ti	200	1290	0.33/1490

Additions to Reduce Braze Temperatures

Alloy selections for further optimization were based on a survey of test data for ternary and quaternary alloys. Those showing the most promising melt-flow temperatures and flow distance results for both dynamic and static heating conditions were selected.

Alloy selections were modified in two ways, by changes or substitutions in composition or through further additions. These substitutions or additions were made with lithium, manganese, palladium, nickel, titanium, and zinc. Tests were conducted in argon on flat plates. Melt, wet, and flow determinations were made under conditions of steadily rising temperatures. Table X presents these data. Results for basic alloys have been included for comparison. Comments regarding the effect of these modifications follow.

Ag-Cu-Ge-Ti. The high content copper base was selected at this time because prior results indicated this alloy possessed promising wetting and flow properties. Additions included manganese, palladium, and zinc.

A comparison with results for the Ag-Cu-Ge alloy shows that melt temperatures have been reduced but that flow temperatures are nearly equal. Palladium has improved the flow distance slightly. The 0.36-inch flow at 1480°F for Ag-63Cu-9.5Ge-0.5Ti alloy appears best for this group.

Ag-Cu-In-Pd. Lithium, manganese, and titanium additions were made to this base alloy. Test results show that all three elements have reduced the melt temperature; however, flow temperatures remain equal for the lithium and have increased for the titanium and manganese. Flow distance results show only a slight improvement for the lithium addition. In comparison with the basic Ag-Cu-In alloy, no significant improvement is seen for any of the additions.

Ag-Cu-Li-Mn. Although results for a nine percent palladium addition to this base alloy show considerable melt point reduction, the flow temperature has increased by 90 degrees F. Also, flow distance has not been improved.

Ag-Cu-Li-Ti. Lithium concentrations for these alloys had been increased from 0.5 to 1.0 percent. The effect for five percent manganese shows favorable melt but somewhat high flow. The alloy with palladium exhibits a melt temperature of only 1175°F and may have poor strength at 1000°F, but the flow temperature is approaching the 1400°F maximum target. Flow distance is somewhat less than for other Ag-Cu-Li alloys.

TABLE X

RESULTS FOR MODIFIED QUATERNARY ALLOYS

Base Composition	Addition	Temperature (°F)				Flow(1) (in./deg F)
		Melt	Wet	Flow	Maximum	
Ag-24.1Cu-9.1In-9Pd(2)	None	1450	1465	1480	1500	0.28/1500
Ag-23Cu-8.6In-8.5Pd	5Mn	1330	1425	1520	1530	0.28/1530
Ag-23.6Cu-8.9In-8.8Pd	2Ti	1320	1525	1600	1610	0.23/1610
Ag-23.6Cu-8.9In-8.8Pd	2Li	1350	1450	1475	1480	0.28/1480
Ag-63Cu-10Ge(2)	None	1430	1500	1530	1540	0.36/1540
Ag-63Cu-10Ge(2)	0.5Ti(3)	1390	1425	1470	[illegible]	0.36/1480
Ag-59.4Cu-9.5Ge-1.9Ti	5Mn	1340	1480	1540	1550	0.40/1550
Ag-59.4Cu-9.5Ge-1.9Ti	5Pd	1395	1450	1510	1515	0.42/1515
Ag-56.5Cu-9Ge-1.8Ti	10Zn	1375	1500	1540	1545	0.32/1545
Ag-26.1Cu-0.5Li-5Mn(2)	None	1360	1400	1410	1420	0.37/1420
Ag-24Cu-0.5Li-5Mn	9Pd	1100	1335	1500	1505	0.38/1505
Ag-25.6Cu-1Li-2Ti	5Mn	1290	1350	1480	1490	0.33/1490
Ag-25.6Cu-1Li-2Ti	5Pd	1175	1370	1445	1500	0.28/1500
Ag-24.6Cu-9.5Sn-2Li(2)	None	1360	1520	1550	1555	0.30/1555
Ag-24Cu-9.3Sn-1.9Li	5Pd	1290	1410	1475	1480	0.30/1480
Ag-24Cu-9.3Sn-1.9Li	5Mn	1400	1440	1490	1495	0.30/1495
Ag-23.6Cu-9.1Sn-9Pd(2)	None	1400	1475	1575	1650	0.38/1650
Ag-23.4Cu-9Sn-4.8Pd	5Mn	1340	1470	1510	1520	0.33/1520
Ag-24.2Cu-9.3Sn-4.9Pd	2Ti	1380	1475	1550	1560	0.27/1560
Ag-25.2Cu-9.5Zn-5Ni(2)	None	1330	1400	1450	1480	0.43/1480
Ag-22.8Cu-9Zn-4.7Ni	5Mn	1360	1430	1500	1520	0.33/1520
Ag-25.2Cu-9.6Zn-4Ti(2)	None	1380	1430	1460	1640	0.42/1640
Ag-24.7Cu-9.2Zn-2Ti	5Mn	1400	1440	1500	1505	0.34/1505
Ag-24.7Cu-9.2Zn-2Ti	5Pd	1350	1495	1540	1545	0.25/1545
Ag-25.6Cu-9.6Zn-2Ti	1Li	1430	1520	1550	1555	0.33/1555

1. Inches/maximum temperature (°F)
2. Base alloy
3. From earlier values

Ag-Cu-Sn-Li. Manganese and palladium additions were made to this base alloy. Palladium showed advantage in lowered melt temperatures and increased flow distance. Manganese was effective in narrowing the melt-flow range, reducing the flow temperature and increasing flow distance.

Ag-Cu-Sn-Pd. Melt and flow temperatures for this base alloy were effectively reduced by manganese and titanium. The 0.33-inch flow distance for manganese can be considered an improvement over base alloy flow. Undoubtedly the titanium alloy would also exhibit improved flow distance for a 1650°F maximum.

Ag-Cu-Zn-Ni. A manganese addition of five percent shows no advantage. Temperatures are increased and flow distance is reduced.

Ag-Cu-Zn-Ti. The only apparent advantage shown by additions of lithium, manganese, and palladium is a reduction in melt temperature by palladium. All other melt-flow temperatures were increased. Because of high maximum temperatures for the Ag-Cu-Zn-Ti alloy, reasonable flow distance comparisons could not be made. However, from the data presented, it could be assumed that the three additions have increased flow distance.

In summary, the results in Table X show that melt temperatures for many of the base alloys have been depressed favorably and remain within the initial 1285 to 1350°F range. However, all flow temperatures are above the 1400°F value that was established as the desired maximum. Experience has shown (Ref. 1) that flow temperatures are invariably much higher for the continuous heating experiments than are obtained under isothermal conditions with a dwell of 10 minutes at temperature. The relation between the two heating conditions is discussed in the next section.

Effect of Time on Flow Properties

An interesting aspect of braze alloy performance is seen by the comparison of flow for dynamic and static temperature conditions. For isothermal flow (static braze conditions where the temperature is maintained at a constant level), many alloys tend to exhibit flow equal to or greater than flow for dynamic heating rates where maximum temperatures are considerably higher. A comparison of flow distance on flat plates for typical developmental alloys for static (isothermal) and dynamic (steadily rising) temperature conditions is shown in Table XI.

A dwell at 1400°F is capable of promoting a greater flow distance than are steadily increasing temperatures (Table XI). The Ag-Cu-In-Pd-Mn alloy, for instance, has more than twice the flow at 1400°F for static conditions than at 1530°F for dynamic conditions. Although the Ag-Cu-In-Pd-Ti alloy and others show less flow for isothermal conditions, maximum temperatures (super heat) must be considered.

The significance of these results is that heating rate and time at a particular temperature will influence melt-flow points and, subsequently, braze temperatures. This influence is brought out by results shown for isothermal flow tests discussed in the following section.

TABLE XI

FLOW FOR STATIC AND DYNAMIC TEMPERATURE CONDITIONS

Alloy	Flow (in.)	
	Static[1]	Dynamic[2] (in. /deg F)
Ag-Cu-Ge-Ti-Mn	0.28	0.40/1550
Ag-Cu-Ge-Ti-Pd	0.41	0.42/1515
Ag-Cu-In-Pd	0.30	0.28/1550
Ag-Cu-In-Pd-Mn	0.60	0.28/1530
Ag-Cu-In-Pd-Ti	0.15	0.23/1610
Ag-Cu-Li-Mn	0.37	0.37/1420
Ag-Cu-Li-Mn-Ti	0.33	0.33/1490
Ag-Cu-Li-Pd-Ti	0.27	0.28/1500
Ag-Cu-Sn-Li	0.42	0.30/1555
Ag-Cu-Sn-Mn-Pd	0.25	0.33/1520
Ag-Cu-Sn-Mn-Li	0.50	0.30/1495
Ag-Cu-Zn-Li	0.34	0.35/1490
Ag-Cu-Zn-Ti-Mn	0.32	0.34/1505
Ag-Cu-Zn-Ti-Pd	0.30	0.25/1545

1. 1400°F/ten minutes
2. For steadily increasing temperatures

Isothermal Flow at 1400°F

The melt, wet, and flow temperatures as well as flow distance, reported earlier, were determined under conditions of steadily rising temperatures. Flow occurs at lower temperatures under isothermal conditions and such conditions represent the final step in a practical brazing cycle. The flat plate coupons were used as they offer a rapid method to determine isothermal flow. Tests were performed similarly to melt-flow temperature checks except that the alloy was maintained at a constant temperature for a definite time period. Flow distance measurements were then taken after completion of the cycle.

Tests were conducted at 1400°F. The decision was made to adopt a time period of 10 minutes at braze temperature. This interval was selected because larger scale beryllium assemblies normally require from 5 to 15 minutes at braze temperature. Braze temperature variations of no greater than ±10 degrees F were considered acceptable.

Data from melt-flow temperature tests and flow distance results were used as criteria in the selection of promising alloys for these tests. Compositions selected for evaluation were based on Ag-Cu-Ge, Ag-Cu-In, Ag-Cu-Li, Ag-Cu-P, Ag-Cu-Sn, and Ag-Cu-Zn alloys. These alloys included both the high and low germanium and phosphorus additions. Flow results are presented in Table XII. Results for basic ternary alloys have been included for comparison. Comments on results for each system follow.

Ag-Cu-Ge. In comparison to the basic alloy, Ag-27Cu-10Ge, results for the Ag-Cu-Ge system show improved flow for five of the eleven alloys tested. Where two levels of addition were made, the higher level alloys exhibit greater flow.

The favorable flow (0.45 inch) for the Ag-63Cu-10Ge alloy was not improved by additions of titanium or titanium-manganese, titanium-palladium, and titanium-zirconium. Since no wetting had occurred for Ag-Cu-Ge-Ti, it could be expected that titanium would also impede flow for the Ag-Cu-Ge-Pd alloy. Poorer results exhibited for the Ag-Cu-Ge-Pd alloy may verify this probability even though a difference of four percent palladium exists. This expectation is supported by the fact that flow for the Ag-Cu-Ge-Mn and Ag-Cu-Ge-Zn alloys is also reduced when titanium is present. The strong interaction of titanium and germanium (e. g., Ti_5Ge_3) is believed to account for this effect that has been noted previously (Ref. 1). Where flow occurred, the lower level additions generally showed the least promise.

Ag-Cu-In. Table XII shows that flow is improved for this base alloy by additions of lithium, manganese, palladium, and titanium. Palladium-manganese and palladium-lithium in combination appear to offer more promise than the individual additions. However, this is not true for palladium-titanium where greater flow is seen for the individual elements.

The most effective additions appear to be palladium, manganese, and minor amounts of lithium. Palladium in combination with lithium or manganese is quite effective whereas titanium additions to the Ag-Cu-Ge-Pd alloy impede flow. For singular titanium additions, the 0.1 amount is most promising. Phosphorus, tin, and zinc were not promising.

Ag-Cu-Li. Two basic ternary alloys with variations in the amount of lithium show that greater flow is developed with the lower addition. Improved flow occurs with the additions of manganese, palladium, nickel, titanium, tin, and zinc. Phosphorus at 0.2 percent and titanium at 4.0 percent were not beneficial. Although base alloys with manganese and palladium exhibit improved flow, these additions in combination are not advantageous. Titanium appears to reduce the properties of the Ag-Cu-Li-Pd alloy and improve those of the Ag-Cu-Li-Mn alloy.

TABLE XII

ISOTHERMAL FLOW AT 1400°F

Braze Composition	Flow Distance (in.)
Ag-Cu-Ge	
Ag-27Cu-10Ge	0.27(1)
Ag-26.7Cu-9.9Ge-1Li	0.28(1)
Ag-26.7Cu-9.9Ge-1Mn	0.22
Ag-25.6Cu-9.5Ge-5Mn	0.31
Ag-26.5Cu-9.5Ge-5Ni	0.28
Ag-26.7Cu-9.9Ge-1Pd	0.22
Ag-24.6Cu-9.1Ge-9Pd	0.53
Ag-27Cu-10Ge-0.2P	0.27 (residue)
Ag-26.9Cu-9.9Ge-0.5Ti	None
Ag-26.7Cu-9.9Ge-1Zn	0.25
Ag-25.4Cu-9.1Ge-6Zn	0.30
Ag-63Cu-10Ge	0.45
Ag-63Cu-9.9Ge-0.5Ti	0.43
Ag-59.4Cu-9.5Ge-1.9Ti-5Mn	0.28
Ag-59.4Cu-9.5Ge-1.9Ti-5Pd	0.41
Ag-56.5Cu-9Ge-1.8Ti-10Zn	0.23
Ag-Cu-In	
Ag-26.5Cu-10In	0.24
Ag-26.5Cu-9.9In-0.1Li	0.35
Ag-26.3Cu-9.5In-0.6Li	0.40
Ag-26Cu-10In-1.5Li	0.21
Ag-25.8Cu-9.8In-2Li	0.33
Ag-26.2Cu-9.9In-1Mn	0.28
Ag-25.2Cu-9.5In-5Mn	0.32
Ag-26.2Cu-9.9In-1Pd	0.28
Ag-24.1Cu-9.1In-9Pd	0.30
Ag-26.5Cu-10In-0.2P	0.24
Ag-26.1Cu-9.8In-1.5Sn	0.22
Ag-Cu-In (Cont)	
Ag-26Cu-10In-0.1Ti	0.30
Ag-26Cu-10In-0.5Ti	0.22 (residue)
Ag-25.8Cu-9.8In-2Ti	0.20 (residue)
Ag-26.2Cu-9.9In-1Zn	0.20
Ag-24.9Cu-9.4In-6Zn	0.20
Ag-23.6Cu-8.9In-8.8Pd-2Li	0.42
Ag-23.6Cu-8.9In-8.8Pd-2Ti	0.15
Ag-23Cu-8.6In-8.5Pd-5Mn	0.60
Ag-Cu-Li	
Ag-29Cu-0.5Li	0.32
Ag-27.7Cu-1Li	0.26
Ag-27.5Cu-0.5Li-1Mn	0.36
Ag-26.1Cu-0.5Li-5Mn	0.37
Ag-24.6Cu-0.5Li-5Ni	0.40
Ag-27.5Cu-0.5Li-1Pd	0.40
Ag-25.2Cu-0.5Li-9Pd	0.50
Ag-27.7Cu-0.5Li-0.2P	0.20
Ag-27.7Cu-0.5Li-0.2Ti	0.37
Ag-26.6Cu-0.5Li-4Ti	0.20
Ag-27.6Cu-1.5Li-0.1Ti	0.42
Ag-27.5Cu-0.5Li-1.5Sn	0.42
Ag-27.7Cu-0.5Li-9.9Sn	0.37
Ag-27.5Cu-0.5Li-1Zn	0.37
Ag-26Cu-0.5Li-6Zn	0.34
Ag-24Cu-0.5Li-4.8Mn-9Pd	0.30
Ag-25.6Cu-1Li-4.8Mn-2Ti	0.45(1)
Ag-25.6Cu-1Li-2Ti-5Mn	0.45
Ag-25.6Cu-1Li-2Ti-5Pd	0.27

1. Revision based on average results.

TABLE XII (Cont)

ISOTHERMAL FLOW AT 1400°F

Braze Composition	Flow Distance (in.)	Braze Composition	Flow Distance (in.)
Ag-Cu-P		Ag-Cu-Sn (Cont)	
Ag-50Cu-2P	0.35	Ag-26Cu-10Sn-0.1Ti	0.32
Ag-54Cu-2P	0.30	Ag-26Cu-9.9Sn-0.5Ti	0.35
Ag-60Cu-2P	0.35	Ag-26Cu-9.5Sn-4Ti	0.20
Ag-49.5Cu-1.9P-1Li	Incomplete melt	Ag-25.7Cu-10Sn-1Zn	0.27
	Heavy oxide	Ag-23.6Cu-9.1Sn-9Zn	0.21
Ag-59.4Cu-2P-1Mn	0.36	Ag-23.4Cu-9Sn-4.8Pd-5Mn	0.25
Ag-47.5Cu-1.9P-5Mn	0.42	Ag-24.2Cu-9.3Sn-4.9Pd-2Ti	0.37
Ag-47.5Cu-1.9P-5Ni	0.37[1]	Ag-24Cu-9.3Sn-1.9Li-5Mn	0.50
Ag-59.4Cu-2P-1Pd	0.38	Ag-24Cu-9.3Sn-1.9Li-5Pd	0.44
Ag-45.5Cu-1.8P-9Pd	0.30		
Ag-59.1Cu-2P-1.5Sn	0.45	Ag-Cu-Zn	
Ag-25.3Cu-2.2P-9.6Sn	Balled up		
	Did not wet	Ag-26.4Cu-10Zn	0.27[1]
Ag-60Cu-2P-0.1Ti	0.35	Ag-26.1Cu-6Zn-0.5Li	0.34
Ag-47Cu-0.3P-6Zn	1.00	Ag-26.5Cu-9.9Zn-1Li	0.30
Ag-25.4Cu-2P-6Zn	None	Ag-26.5Cu-9.9Zn-1Mn	0.17
Ag-59.4Cu-2P-1Zn	0.40	Ag-24.6Cu-9.5Zn-5Mn	0.28
Ag-47Cu-1.8P-6Zn	1.00	Ag-25.2Cu-9.5Zn-5Ni	0.30
		Ag-26.5Cu-10Zn-0.2P	0.22
Ag-Cu-Sn		Ag-26.5Cu-9.9Zn-1Pd	0.15
		Ag-24.1Cu-9.1Zn-9Pd	0.32
Ag-26Cu-10Sn	0.22	Ag-26.1Cu-9.8Zn-1.5Sn	0.22
Ag-26Cu-10Sn-0.1Li	0.40	Ag-23.6Cu-9Zn-9Sn	0.25
Ag-23.6Cu-9.9Sn-1Li	0.42	Ag-26.5Cu-10Zn-0.1Ti	0.45
Ag-24.6Cu-9.5Sn-2Li	0.33	Ag-25.9Cu-10Zn-1Ti	0.16
Ag-33Cu-7Sn-3Mn	0.47	Ag-25.2Cu-9.6Zn-4Ti	0.35
Ag-25.7Cu-10Sn-1Mn	0.40	Ag-22.8Cu-9Zn-4.7Ni-5Mn	0.40
Ag-24.6Cu-9.5Sn-5Mn	0.38	Ag-20.5Cu-7.2Zn-4.5Pd-10Ge	0.30
Ag-24.6Cu-9.5Sn-5Ni	0.25	Ag-23Cu-8Zn-0.2P-5Pd	0.30
Ag-25.7Cu-10Sn-1Pd	0.29	Ag-25.6Cu-9.6Zn-2Ti-1Li	0.27
Ag-23.6Cu-9.1Sn-9Pd	0.26	Ag-24.7Cu-9.2Zn-2Ti-5Mn	0.32
Ag-25.7Cu-10Sn-0.2P	0.23	Ag-24.7Cu-9.2Zn-2Ti-5Pd	0.30
Ag-25.4Cu-9.6Sn-2.2P	Balled up		

1. Revision based on average results.

Ag-Cu-P. Lithium, manganese, palladium, titanium, tin, and zinc were evaluated for their effect on isothermal flow for the Ag-Cu-P alloy. The one inch flow for zinc at 0.3 and 1.8 percent phosphorus indicates exceptional promise for this addition. Flow for the lower content zinc alloy was considerably less. Five percent manganese and 1.5 percent tin have improved base alloy properties while palladium, nickel, and titanium show little effect. Tin above two percent appears to reduce flow.

Ag-Cu-Sn. Additions showing improved flow for the Ag-Cu-Sn alloy include lithium, manganese, palladium, and titanium. Again, the minor lithium addition shows greater flow. The composition Ag-33Cu-7Sn-3Mn shows maximum flow for all alloys in this group. This alloy has increased copper and reduced tin in relation to the other basic Ag-Cu-Sn alloys.

Phosphorus does not appear beneficial and palladium only mildly. Small titanium additions promote greater flow than large additions. Little change is noted for zinc additions.

Quinary compositions show that lithium-manganese, lithium-palladium, and palladium-titanium additions are beneficial while the combination manganese-palladium has little effect.

Ag-Cu-Zn. Additions to this base alloy included lithium, manganese, nickel, phosphorus, palladium, titanium, germanium, and tin. Based on the data in Table XII, the greatest improvement was promoted with titanium at 0.1 percent and nickel-manganese at 4.7 and 3.0 percent. Manganese, palladium, and titanium at one percent each exhibited the poorest flow. Other additions of lithium, palladium, manganese, nickel, and titanium, either singularly or in combination, develop flow distance measurements between 0.22 and 0.40 inch.

4.1.5 Summary of Silver-Base Braze Alloy Development

The work with silver-base braze alloys presented in this section pertains principally to the development and optimization of promising alloys based on Ag-28Cu. Melt, wet, and flow temperature tests and flow distance measurements were made with flat plates and capillary T-joints. In the course of development, compositions were optimized by additions and modification to produce good capillary flow at 1400°F. The braze time-temperature relation and interaction were found to influence alloy wetting and flow. Silver-base braze alloy selections as candidates for final evaluation are discussed in Section V.

4.2 TITANIUM BASE ALLOYS

Earlier work (Ref. 1) indicated various titanium-base alloys appeared promising for brazing beryllium. The alloys studied exhibited excellent wetting and flow properties; however, joint strength and braze temperatures were not optimized. One of the major interests during this program was to reduce melt-flow temperatures to the target of 1400°F, and also to increase joint strength by matching expansion rates of beryllium and braze alloy more closely.

Based on both earlier work and a literature survey of titanium alloy phase relationships, the binary, Ti-5.6Be, was selected for initial study. The effect of additions and modifications on temperature control and flow was investigated. Test alloys were evaluated by comparison of flow on flat plates and in capillary T-joints.

4.2.1 Alloying to Reduce Melt and Flow Temperatures

Previous work (Ref. 1) established that low melting point alloys could be developed in the Ti-Cu-Be, Ti-Ni-Be, and Ti-Zr-Be systems. Preliminary work was performed to determine if the Ti-Ag-Be and Ti-Mn-Be systems held promise, and also to examine the Ti-Cu-Be system in more detail because the previous work had been somewhat cursory.

Preliminary Work on Melt-Flow Temperatures of Ternary Alloys

The approach in this preliminary work was to investigate melt, wet, and flow characteristics of Ti-13Mn-Be, Ti-10Cu-Be, and Ti-(35 to 47.5)Ag-Be at various beryllium additions on each side of the content of the binary eutectic alloy, Ti-5.6Be. In the next step, promising alloys were modified at the optimum beryllium content by further additions of the ternary element. Tests were made on flat beryllium plates 0.020 inch thick so that contraction stresses could be estimated from any distortion of the sheet. Results are presented in Table XIII and are discussed individually below.

Ti-Mn-Be. Additions of 5.0, 5.6, and 6.5 percent beryllium were made to the Ti-13Mn base alloy to determine the composition with the minimum braze temperature. Test results show little difference for these compositions. An examination of the test specimens indicated flow was slightly greater for the 5.6 percent addition; therefore, this composition was selected for further study.

The Ti-Mn-5.6Be alloys were prepared with manganese additions up to 40 percent. Results of these additions show that temperatures remained relatively unchanged with up to 25 percent manganese. Above 25 percent, the melt point increased. A five percent addition of nickel to the Ti-25Mn-4.2Be alloy reduced the melt-flow temperature by 50 degrees F.

TABLE XIII

RESULTS FOR TITANIUM-BASE ALLOYS

Composition	Temperature (°F)			
	Melt	Wet	Flow	Maximum
Ti-35. 0Ag-5. 0Be	>1825			1825
Ti-34. 8Ag-5. 6Be	>1825			1825
Ti-34. 6Ag-6. 2Be	>1825			1825
Ti-47. 5Ag-5. 0Be	>1825			1825
Ti-47. 2Ag-5. 6Be	>1825			1825
Ti-46. 5Ag-6. 6Be	>1825			1825
Ti-8. 9Cu-6. 7Be	1800	1810	1820	1820
Ti-9. 2Cu-5. 6Be	1795	1810	1820	1820
Ti-9. 4Cu-5. 0Be	1805	1820	1820	1820
Ti-15Cu-4. 8Be	1650	1710	1715	1725
Ti-20Cu-4. 5Be	1590	1630	1650	1660
Ti-30Cu-4. 0Be	1600	1615	1620	1630
Ti-40Cu-3. 4Be	1635	1645	1650	1660
Ti-12. 3Mn-5. 0Be	1795	1800	1805	1810
Ti-12. 2Mn-5. 6Be	1800	1805	1810	1815
Ti-12. 1Mn-6. 5Be	1800	1810	1815	1820
Ti-15. 0Mn-4. 9Be	1790	1795	1800	1800
Ti-25. 0Mn-4. 2Be	1780	1790	1795	1800
Ti-40. 0Mn-3. 4Be	>1825			1825
Ti-24. 0Mn-4. 1Be-5. 0Ni	1730	1735	1740	1750

Ti-Cu-Be. The Ti-10Cu base alloy was alloyed with 5. 0, 5. 6, and 6. 7 percent beryllium. Results of melt, wet, and flow tests show that the 5. 6 percent addition develops minimum temperatures.

The Ti-Cu-5. 6Be alloy was then modified with increased copper additions. An examination of flow results in Table XIII shows that the melt and flow temperatures for the 20 and 30 percent copper alloys have been lowered by 200 degrees F. The melt-flow range for the 20 percent composition has expanded to 60 degrees F; whereas, the 30 percent alloy has retained the characteristically narrow 20 degree F range.

Ti-Ag-Be. An alloy of 50 percent titanium and 50 percent silver was modified with beryllium additions of 5. 0, 5. 6, and 6. 2 percent. As noted in Table XIII, these alloys had a melting point in excess of 1825°F. No additional work was done with these compositions because of the high temperatures.

Further Work on Melt-Flow Temperatures of Ternary Alloys

Studies were made to determine the effect of copper, nickel, and zirconium additions on melt-flow temperatures and on flow distance for titanium at 5. 6 beryllium. In one series of alloys, titanium was replaced by the alloying element so that the beryllium remained constant at 5. 6 percent; whereas, in the second series the Ti-5. 6Be alloy was diluted by the addition.

Tests were made on flat plates and test results are presented in Table XIV. Results for several Ti-Cu-Be alloys from Table XIII are included to show the relation between melt-flow points and flow distance.

The impressive effect of copper is shown in Figure 23. Temperatures are reduced rapidly from 9. 2 to 20 percent copper for both alloy series. Above approximately 20 percent copper, the behavior of alloys from the two series differs. Alloys with beryllium maintained at 5. 6 percent show a sharp rise of temperature from 10 to 24 percent copper and then a gradual decrease in temperature from 24 to 38 percent copper. From this, it appears that dilution of the beryllium content is the most effective method to reduce alloy melt-flow temperatures.

Nickel additions of 10 to 40 percent were made to titanium at 5. 6 beryllium. The results in Table XIV show that complete melting had not occurred for the five alloys.

Ti-5. 6Be-20Ni, with a minor amount of flow at 1760°F, had the least amount of unmelted alloy (residue) remaining. The data in Table XIV also show that 20 percent nickel is the most effective addition for reducing melt-flow temperatures of the

TABLE XIV

RESULTS FOR MODIFIED TITANIUM ALLOYS

Composition	Temperature (°F)				Flow Distance (in.)
	Melt	Wet	Flow	Maximum	
Ti-9. 2Cu-5. 6Be	1735	1775	1780	1790	0. 50
Ti-15Cu-4. 8Be	1650	1710	1715	1725	0. 37
Ti-20Cu-4. 5Be	1590	1630	1650	1660	0. 37
Ti-30Cu-4Be	1600	1615	1620	1630	0. 40
Ti-40Cu-3. 4Be	1635	1640	1650	1660	0. 42
Ti-18. 9Cu-5. 6Be	1600	1650	1675	1700	0. 45
Ti-23. 6Cu-5. 6Be	1650	1690	1700	1700	0. 32
Ti-28. 3Cu-5. 6Be	1660	1675	1690	1700	0. 27
Ti-37. 8Cu-5. 6Be	1640	1660	1680	1700	0. 27
Ti-5. 6Be-10Ni	1740	1770	>1820	1845	0. 30
Ti-5. 6Be-20Ni	1675	1700	>1760	1840	0. 50
Ti-5. 6Be-25Ni	1675	1725	>1850	1850	0. 50
Ti-5. 6Be-30Ni	1690	1780	>1810	1850	0. 27
Ti-5. 6Be-40Ni	1770	1850	>1850	1850	0. 27
Ti-18. 9Zr-5. 6Be	1670	1700	1740	1750	0. 35
Ti-28. 4Zr-5. 6Be	1630	1650	1690	1700	0. 37
Ti-37. 9Zr-5. 6Be	1530	1610	1650	1660	0. 30
Ti-47. 2Zr-5. 6Be	1525	1535	1610	1620	0. 32
Ti-47. 2Zr-5. 6Be	1525	1550	1570	1580	0. 27
Ti-50Zr-5. 6Be	1540	1555	1600	1610	0. 30
Ti-60Zr-5. 6Be	1500	1525	1640	1660	0. 28

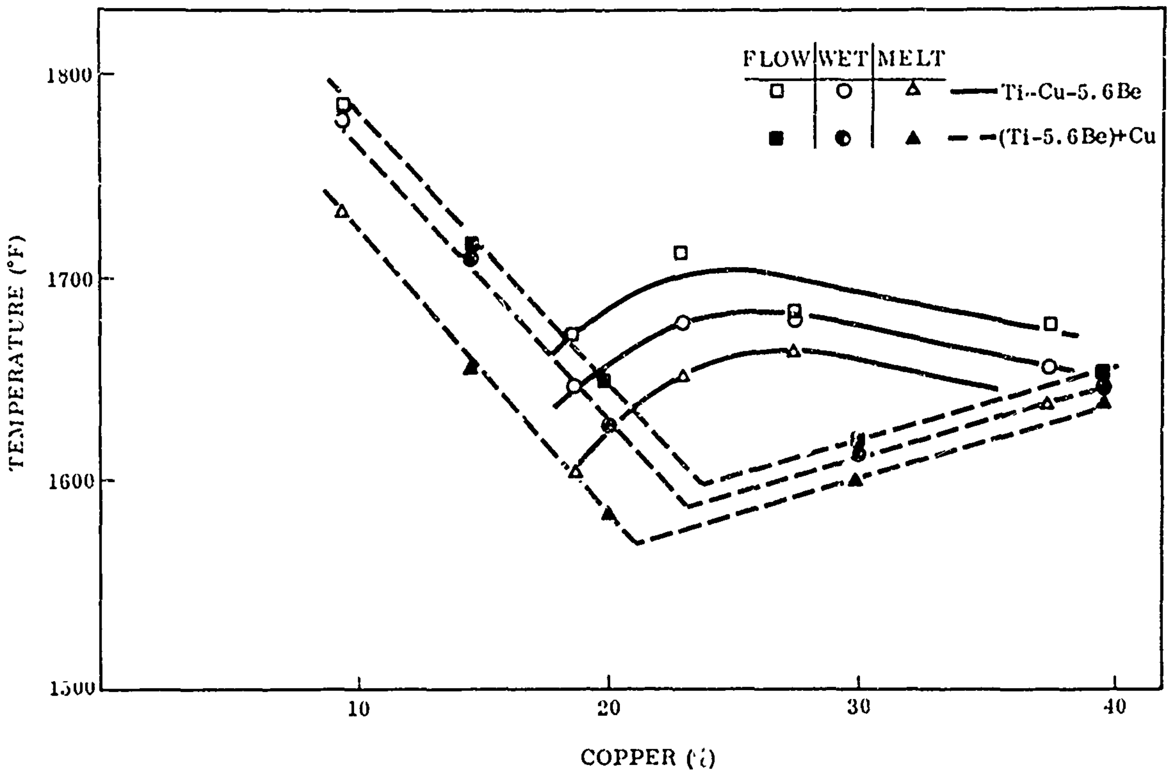


FIGURE 23. EFFECT OF COPPER ON TITANIUM-BERYLLIUM

compositions tested. Although the 25 percent addition shows the same melt temperature as for 20 percent nickel, flow was not complete at 1850°F. The 0.50-inch flow distance for both the 20 and 25 percent nickel alloys indicates greater wetting by the 20 percent nickel.

Zirconium appears to be very effective in reducing melt-flow temperatures of Ti-5.6Be. Melt, wet, and flow curves were plotted for these alloys and are shown in Figure 24. Since the melt temperature of Ti-5.6Be is approximately 1850°F, melt temperatures have been reduced 350 degrees F by zirconium. Reductions appear to be most effective at 45 to 60 percent zirconium.

Isothermal Flow of Selected Alloys

In view of the established differences between melt and flow temperatures of alloys on heating and isothermal flow (Ref. 1), certain promising compositions were

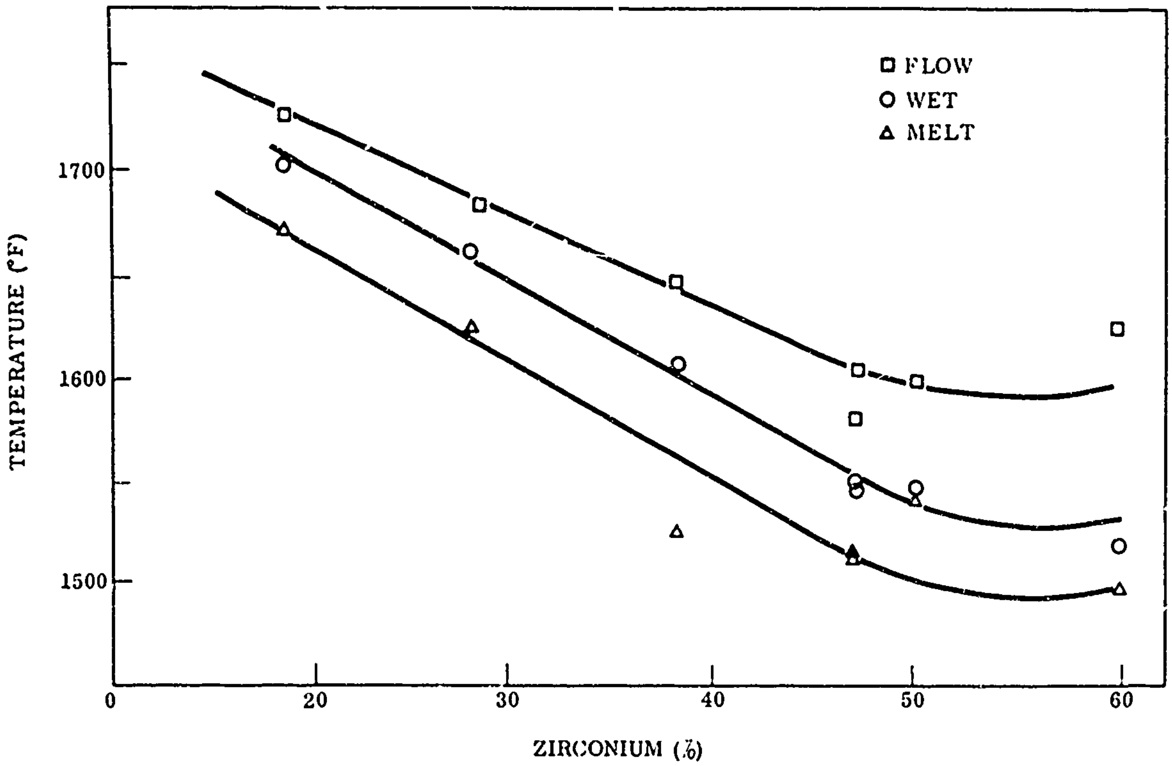


FIGURE 24. EFFECT OF ZIRCONIUM ON Ti-5.6Be

selected for isothermal flow tests on flat plates. The alloys selected for further study included:

- Ti-24Mn-4Be-5Ni
- Ti-47.2Zr-5.6Be
- Ti-30Cu-4Be
- Ti-19Cu-5.6Be
- Ti-20Cu-4.5Be

Braze alloy particle weights of 50 milligrams were used for titanium-base alloys compared to the 100 milligrams for the more dense silver-base alloys. Flat plate isothermal results are presented in Table XV. Some of the braze alloys caused exfoliation of the beryllium sheet because of differential contraction (Table XV). The Ti-Mn-Be-Ni alloy produces excellent flow at a temperature that is within 50 degrees F of the melt point. At a temperature 200 degrees F lower than the 1750°F for Ti-Mn-Be-Ni, Ti-Zr-Be exhibits a flow that is 60 percent less. A comparison of results for Ti-Cu-Be compositions shows that Ti-30Cu-4Be is the only alloy to exhibit flow at

1600°F. Absence of spalling by the Ti-Mn-Be-Ni alloy indicates that additions of manganese and/or nickel to titanium-beryllium may be beneficial in reducing interface stress.

TABLE XV

ISOTHERMAL FLOW FOR SELECTED TITANIUM-BASE ALLOYS

Alloy	Test Temperature (°F/min)	Flow Distance (in.)	Remarks
Ti-24Mn-4Be-5Ni	1700/10	-	Did not melt
Ti-24Mn-4Be-5Ni	1750/10	0.50	Did not exfoliate
Ti-47Zr-5.6Be	1500/10	-	Did not melt
Ti-47Zr-5.6Be	1550/10	0.20	Exfoliated
Ti-30Cu-4Be	1600/10	0.35	Exfoliated
Ti-20Cu-4.5Be	1600/10	-	Did not melt
Ti-18.9Cu-5.6Be	1600/10	-	Did not melt

4.2.2 Optimization of Ti-Zr-Be Alloys

It was determined (para 4.2.1) that certain Ti-Zr-Be braze alloys were the most promising based on melt-flow temperatures, flow distance, and thermal expansion properties. Therefore, studies to optimize these promising alloys were continued. This work included additions to base compositions and also changes in the beryllium content to further reduce braze temperatures and improve wetting and thermal expansion properties.

Additions to Reduce Melt Flow Temperatures

Additions to selected Ti-Zr-Be base alloys included manganese, palladium, copper, nickel, silver, and additions of multiple elements. Melt, wet, and flow results, together with earlier data, are presented in Table XVI. Two series of alloys were made: in the first, the beryllium was held constant at 5.6 percent and the addition element replaced Ti+Zr; in the second, the additional element diluted the original alloy so that the beryllium content decreased. In some cases where a beneficial trend was noted, other alloys were made to explore this trend.

TABLE XVI

EFFECT OF ADDITIONS TO Ti-Zr-Be ON MELT-WET-FLOW[1]

Addition	Temperature (°F) on CRS Beryllium			Remarks
	Melt	Wet	Flow	
Ti-47.2Zr-5.6Be (Base)	1520	1550	1575	Good flow
Nickel				
Ti-46Zr-5.5Be-2Ni	1445	1490	1525	Restrained flow
Ti-44.5Zr-5.3Be-5Ni	1450	1480	1525	Restrained flow
Ti-42.3Zr-5.05Be-10Ni	1370	1435	1525	Restrained flow
Ti-42.7Zr-4.5Be-10Ni	1475	1500	1560	Restrained flow
Ti-42.2Zr-5.6Be-10Ni	1340	1375	1450	Restrained flow
Manganese				
Ti-47.2Zr-5.6Be-5Mn	1480	1510	1550	Restrained flow
Ti-42.2Zr-5.6Be-10Mn	>1700	-	-	-
Ti-45Zr-5Be-5Mn	1470	1510	1570	Restrained flow
Copper				
Ti-46Zr-5.5Be-2Cu	1420	1470	1540	Restrained flow
Ti-44.5Zr-5.3Be-5Cu	1420	1500	1550	Restrained flow
Ti-42.3Zr-5.05Be-10Cu	1390	1420	1490	Restrained flow
Ti-42.2Zr-5.6Be-10Cu	1390	1425	1500	Restrained flow
Silver				
Ti-44.5Zr-5.3Be-5Ag	1460	1500	1600	Freer flowing and wetting
Ti-42.2Zr-5.6Be-10Ag	1450	1490	1540	Restrained flow
Palladium				
Ti-44.5Zr-5.3Be-5Pd	1400	1470	1540	Restrained flow
Ti-45.2Zr-4.5Be-5Pd	1420	1475	1500	Restrained flow
Ti-44.7Zr-5.6Be-5Pd	1410	1465	1550	Restrained flow
Ti-42.2Zr-5.05Be-10Pd	1445	1580	1630	Restrained flow
Ni-Mn-Cu				
Ti-45Zr-5.3Be+(1Ni-2.8Mn-1Cu)	1420	1490	1525	Restrained flow
Ti-43Zr-5.05Be+(2Ni-5.6Mn-2Cu)	1425	1490	1510	Restrained flow
Ti-41Zr-4.5Be+(4Ni-11.2Mn-4Cu)	1385	1460	1510	Restrained flow
Cu-Mn-Ag				
Ti-45Zr-5.3Be+(1Cu-1.7Mn-2.3Ag)	1450	1480	1500	Restrained flow
Ti-40Zr-4.8Be+(3Cu-5.2Mn-7Ag)	1475	1485	1520	Restrained flow
Ti-35Zr-4.2Be+(5Cu-8.8Mn-10Ag)	1470	1495	1515	Restrained flow

1. Flat plate results using standard cycle, i.e., 50 degrees F/minute to melt point, 10 to 12 minutes total cycle.

The date in Table XVI were examined and salient points for additions and modifications are presented.

Nickel Additions. Greatest temperature reductions were developed with 10 percent nickel at beryllium contents of 5. 05 and 5. 6 percent. Of these two, Ti-Zr-5. 6Be-10Ni is most significant because this composition exhibits a melt and flow point 30 and 75 degrees F lower, respectively, than the Ti-Zr-5. 05Be-10Ni alloy.

Manganese Additions. An interesting aspect of manganese additions is the dramatic change in melt temperatures between 5 and 10 percent of the element. Results for the Ti-Zr-5Be-5Mn alloy are similar to those shown for the Ti-Zr-5Mn-5. 6Be. This similarity indicates the beryllium content is not as critical as with Ti-Zr-Be-Ni compositions.

Copper Additions. Data for the four copper alloys indicate that the best results are obtained at 10 percent copper and 5. 0 to 5. 6 percent beryllium. As with manganese-addition alloys, the beryllium content does not affect temperatures as markedly as for Ti-Zr-10Ag-5. 6Be.

Silver Additions. The Ti-Zr-10Ag-5. 6Be alloy shows nearly equal melt temperature for considerably lower flow than Ti-Zr-5Ag-5. 3Be. The 1600°F flow point is of interest in that this is the only alloy in Table XVI that exhibits the more extensive wetting that is characteristic of earlier alloys with higher maximum temperatures. As melt and flow temperatures have been reduced, wetting capabilities have receded correspondingly.

Palladium Additions. Five percent palladium at 5. 3 and 4. 5 beryllium appears to offer greater temperature reductions than the 5. 0 percent palladium at 5. 6 percent beryllium and 10 percent palladium at 5. 05 percent beryllium. The 5. 3 percent beryllium alloy possesses a lower melt point and the 4. 5 percent beryllium a lower flow point for this group of alloys.

Ni-Mn-Cu and Cu-Mn-Ag Additions. Only one of the six alloys studied showed promise - the Ti-Zr-4. 5Be-4. 4Ni-4. 4Cu-11. 2Mn alloy with a melt point of 1385°F and a flow point of 1510°F. However, as with most other alloys in Table XVI, wetting was restricted.

Isothermal Flow for Selected Alloys

Most of the initial titanium-base alloys, with melt, wet, and flow temperatures in the range of 1700 to 1800°F, exhibited excellent wetting and flow distance (Ref. 1). Reduction of melt and flow temperatures (para 4. 1) has led to an unwelcome side effect, namely a reduction in wetting characteristics. Most of the alloys reported in Table XVI exhibit restrained and inhibited wetting. Because braze alloys are more reactive at the higher braze temperatures, it follows that the lower braze temperature alloys may be time-sensitive and require longer braze cycles to promote equal flow. To study this possibility, certain alloys were selected for evaluation of flow at various temperatures. The selected alloys were chosen from Table XVI or were new alloys suggested by the results presented in that table. The alloys and test temperatures are contained in the following list.

Alloy Composition	Test Temperature (°F)
Ti-47.2Zr-5.6Be	1475, 1525
Ti-40Zr-4.5Be-6.7Ni-10Ag	1375, 1435
Ti-42.3Zr-5.6Be-10Ni	1300, 1325
Ti-45.2Zr-4.5Be-5Pd	1350, 1450, 1475
Ti-47Zr-5.6Be+20Cu-Ni-Mn	1350, 1460, 1485
Ti-42.3Zr-5.1Be-10Cu	1350, 1400

The procedure used was to start at a temperature somewhat below the probable melt point to determine if melting and wetting would occur within a time period of ten minutes. If melting did not occur after ten minutes, the temperature was gradually increased until melting was observed. This temperature was then held for at least 15 minutes before either another temperature increase was made or before the test was terminated. The data from these tests were plotted graphically based on time-flow distance values. Figure 25 presents these data. Remarks regarding significant occurrences follow.

Maximum flow for any one test temperature:

- Was reached within four minutes from the time of reaching that temperature
- Did not increase as long as that temperature was maintained
- Increased only as the temperature was increased

The results in Figure 25 indicate that these titanium-base alloys are extremely sensitive to temperature. Isothermal flow occurs within the first few minutes at temperature and then ceases. Only when temperatures are increased does flow recommence. Again, this additional flow ceases after the first few minutes.

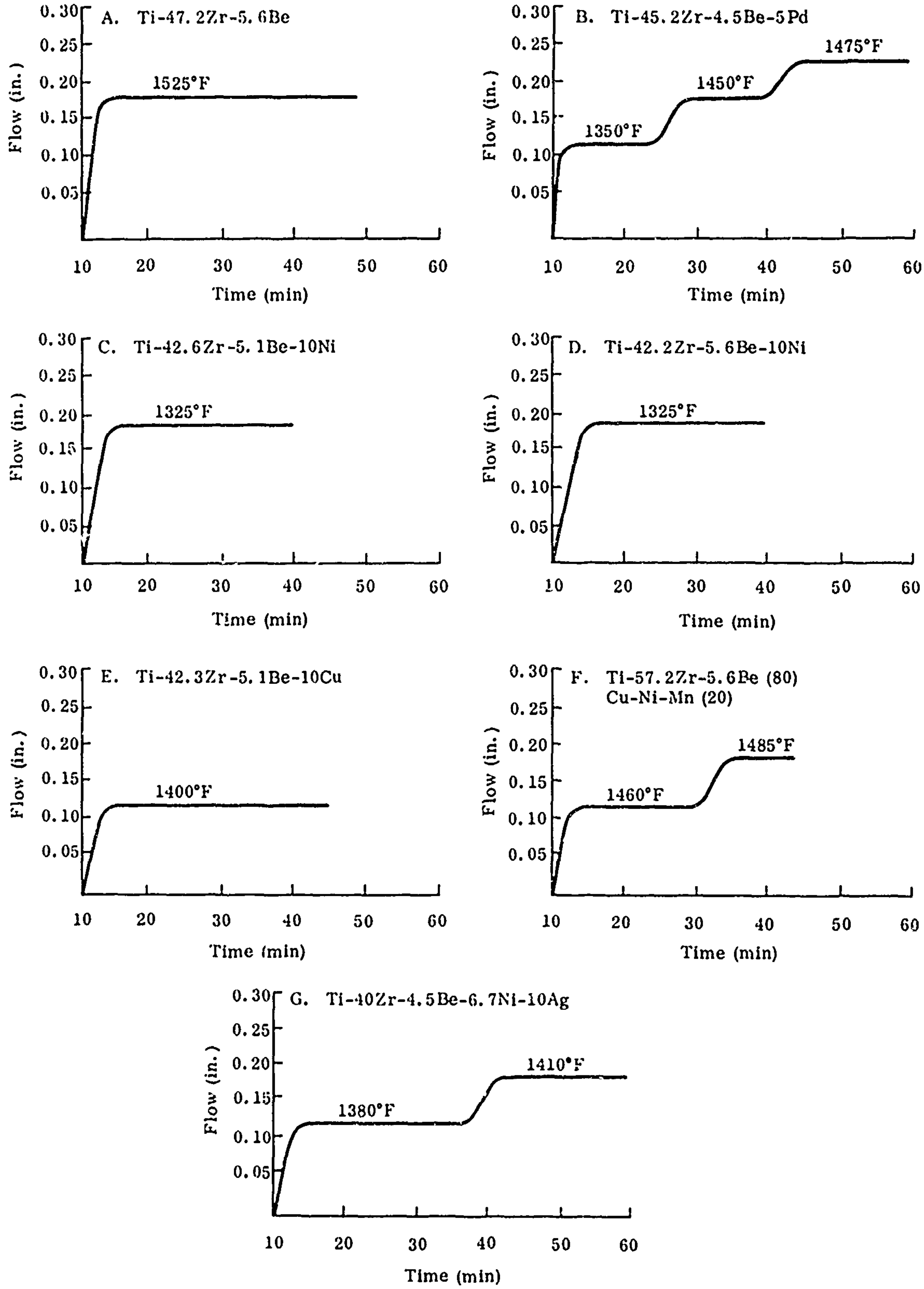


FIGURE 25. EFFECT OF TIME ON ISOTHERMAL FLOW

Formulations Based on Electron Microprobe Analysis

The most promising alloys, based on the data presented in Figure 25, are those in the Ti-Zr-Ni-Be series. The palladium-containing alloys begin to wet beryllium at 1350°F, but flow increases to a very limited extent when the temperature is increased 100 degrees F. The Ti-Zr-Cu-Be alloys do not begin flow until 1400°F versus 1325°F for the nickel-containing alloys. Two of the Ti-Zr-Ni-Be alloys contain additional elements (Ag or Cu-Mn). The six-component alloy was dropped because flow does not begin until 1460°F.

The approach planned for the further optimization of titanium-base alloys was to be based on liquation at set temperatures followed by analysis of the low-melting fraction. Because of the characteristics of this selection method, the Ti-Zr-Ni-Ag-Be alloy was selected rather than the lower melting Ti-Zr-Ni-Be alloys. It was reasoned that if silver were undesirable in the optimum braze alloy, then this undesirable quality would become evident as the successive liquations would contain progressively less silver. On the other hand, if silver were a desirable element, then this desirable quality could be found only by starting with the initially less desirable Ti-Zr-Ni-Ag-Be alloy.

The alloy was heated on flat plates of beryllium at two intermediate temperatures between melt and flow to cause liquation of the lower melting phase, and to leave the higher melting portion as residue. Composition of the liquate portion is then determined by microprobe analysis techniques. Based on these analyses, new compositions were compounded and evaluated for isothermal flow at appropriate temperatures. The liquate was again processed in the same manner described above. This procedure was repeated twice and was quite effective.

The titanium-silver and zirconium-silver phase diagrams are characterized by wide gaps between liquidus and solidus at any temperature. This gap approaches 100 percent for the nickel-silver alloys usually regarded as immiscible or insoluble. Hence, segregation of silver was recognized as a possible problem.

The first microprobe analysis traces showed evidence of such a segregation, so that high and low silver regions were found in the liquate obtained from the Ti-Zr-6.7Ni-10Ag-4.5Be alloy. Two average compositions are given in Table XVII corresponding to these regions. It was assumed in computing the analysis that the beryllium had remained at 4.5 percent. Five compositions were melted; three were at the low silver content of 7.7 percent, but with 4.0, 4.5, and 5.0 percent beryllium to check for the shift of the optimum composition away from 4.5 percent; the other two contained the high silver content to check whether or not one was the lower melting point composition. The alloy Ti-46.6Zr-6.1Ni-7.7Ag-4.0Be was selected for additional liquation experiments.

TABLE XVII

MICROPROBE ANALYSIS AND FLOW RESULTS BASED ON
Zr-38.8Ti-4.5Be-6.7Ni-10Ag ALLOY

Liquate Composition by Microprobe Analysis					Arc-Melted Compositions for Liquation Tests					Isothermal Flow Inches (1)	
Zr	Ti	Be	Ni	Ag	Zr	Ti	Be	Ni	Ag	1400°F	1450°F
44	38	Bal	6.2	7.8							
56	17	Bal	3.2	19.9							
					43.8	37.9	4.5	6.1	7.7	0.28	0.33
					44.0	38.2	4.0	6.1	7.7 (2)	0.27	0.36
					43.6	37.6	5.0	6.1	7.7	0.27	0.30
					56.0	17.0	4.5	3.0	19.5	Did not melt	
					50.0	25.0	4.5	3.5	17.0	Did not melt	
48	29	Bal	4.5	14							
48.9	42.2	Bal	5.5	3.3							
					48	29	4.5	4.5	14.0	None	
					47.5	29	5.0	4.5	14.0	0.50	
					48.5	29	4.0	4.4	14.0	0.33	
					46.6	40.5	4.5	5.25	3.15	0.90	
					46.4	40	5.0	5.2	3.1	0.80	

1. Flat plates/10 minute cycle.
2. Selected for further study.

Again, the microprobe analysis showed high silver analyses in places, but with low silver contents throughout most of the liquate. Five alloys were prepared. Results showed that the high silver content alloy (14.0 percent) would flow at 1400°F in some cases but that the low silver content alloy had optimum flow. The changes of optimum alloy composition with each step are listed below:

Initial	Zr-38. 4Ti-6. 7Ni-10Ag-4. 5Be
Liquate I	Zr-38Ti-6. 2Ni-7. 8Ag-4. 5Be
Optimum melt based on Liquate I	Zr-38. 2Ti-6. 1Ni-7. 7Ag-4. 0Be
Liquate II	Zr-42Ti-5. 5Ni-3. 3Ag-4. 5Be
Optimum melt based on Liquate II	Zr-40. 5Ti -5. 3Ni-3. 2Ag-4. 5Be

The silver content has been drastically reduced at each step, but the nickel content has decreased slightly as the optimum was reached.

Merits of this approach are readily seen by the comparison of isothermal flow for selected alloys at the different levels of optimization (Fig. 26). Temperatures at which initial flow occurred were reduced by 50 degrees F while temperatures for maximum capillary flow show a reduction of 140 degrees F.

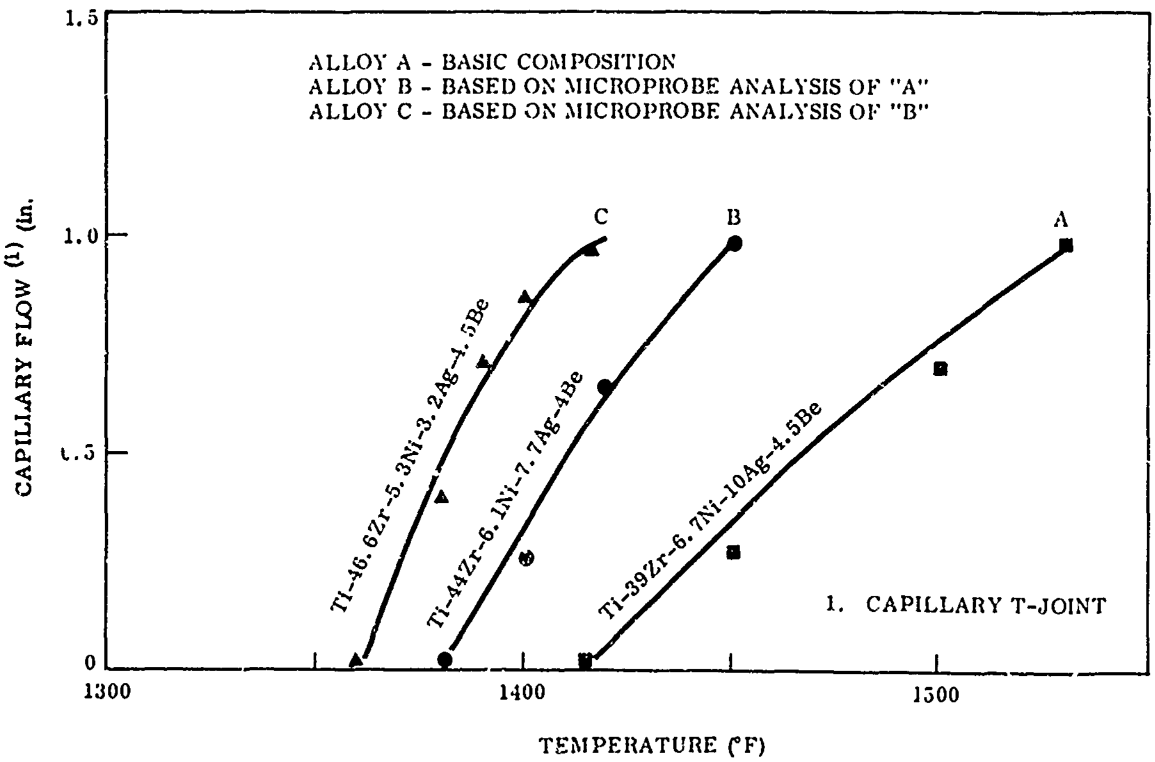


FIGURE 26. CAPILLARY FLOW UNDER ISOTHERMAL CONDITIONS FOR Ti-Zr BASE BRAZE ALLOYS

4.3 ALUMINUM-BASE ALLOYS

The brazing of beryllium with aluminum-base alloys is difficult because stable refractory oxides that resist flow are readily generated. During earlier studies (Ref. 1), it became apparent that both beryllia (BeO) and alumina (Al_2O_3) were major deterrents to wetting and flow of aluminum-base alloys on beryllium. The relative ease with which these stable compounds develop would require great efforts and elaborate equipment to prevent their formation. In addition, removal or reduction of these oxides present on the alloy or faying surfaces during brazing cannot be accomplished without use of fluxes. This problem, then, would indicate the need for concurrent development of complete braze systems rather than braze alloy development that is performed independently of supporting work.

Preliminary studies were made to evaluate additions for their ability to develope and promote wetting of beryllium surfaces. Melt, wet, and flow temperatures were obtained and alloy flow distance was measured for flat plate specimens for both dynamic and static heating conditions.

4.3.1 Study to Develop Basic Aluminum Alloys

Preliminary studies were made to evaluate additions to aluminum for their ability to develop and promote wetting. The additions included copper, lithium, phosphorus, silicon, and zinc. Test results are presented in Table XVIII.

TABLE XVIII

RESULTS FOR ADDITIONS TO ALUMINUM

Alloy Composition	Temperature (°F)			
	Melt	Wet	Flow	Maximum
Al-12Si	1340	1500	-	1700
Al-1P	1275	1735	-	1810
Al-33Cu	1190	1560	-	1800
Al-1Li	1325	1575	-	1800
Al-5Zn	1385	1700	-	1850
Al-10Zn	1425	1640	-	1850
Al-25Zn	1350	1680	-	1850
Al-45Zn	1350	1700	-	1850
Al-75Zn	1320	1640	-	1850

The results in Table XVIII show that none of the compositions studied were successful in promoting flow below 1700°F. Although wetting had occurred, all samples exhibited high alloy-base metal contact angles (55 to 75 degrees), an indication of restricted wetting. Melt temperatures are generally 100 to 300 degrees F above that for unalloyed aluminum.

Additions to Al-Cu to Reduce Melt-Flow Points

Since Al-33Cu showed the lowest melt and wetting temperatures and the smallest contact angle for initial test alloys, this alloy was selected for continued development work. Additions of titanium, lithium, manganese, palladium, and phosphorus were made to evaluate their effect on braze temperatures and flow properties. Test results are shown in Table XIX. Results for the basic binaries are included for comparison.

TABLE XIX

EFFECT OF ADDITIONS TO ALUMINUM-BASE BINARY ALLOYS

Alloy Composition	Temperature (°F)				Flow Spread (in.)	Notes
	Melt	Wet	Flow	Maximum		
Al-33Cu	1190	1560	-	1800	-	
Al-32.7Cu-1Ti	1150	1390	1750	1800	0.22	
Al-32.9Cu-2Ti	1390	1600	1750	1800	0.32	Residue
Al-31.4Cu-5Ti	1350	1425	1690	1775	0.32	
Al-29.5Cu-10Ti	1460	1675	>1750	1750	0.20	Residue
Al-32.7Cu-2Li	1400	-	-	1850	-	
Al-31.4Cu-5Pd	1350	1660	1780	1850	0.29	
Al-32.9Cu-2P	1300	1600	1780	1850	0.27	
Al-33Cu-3P	1650	1700	>1850	1850	-	
Al-31.4Cu-5Ni	1360	1550	1700	1850	0.35	

The data in Table XIX show that all additions with the exception of 2.0 lithium and 3.0 phosphorus have increased flow, however, flow temperatures remain well above the desired 1250 to 1400°F range.

4.3.2 Optimization Studies for Ternary Alloys

Based on results obtained from additions to the basic alloy, Al-Cu, the Al-Cu-Ti and Al-Cu-P compositions were selected for further study. The elements manganese and zinc were added to study their effect on melt-flow temperatures and flow properties of aluminum-base braze alloys. A five percent manganese addition to Al-33Cu-2Li and a seven percent zinc addition to Al-33Cu-3P were evaluated for melt-flow temperatures and flow distance. Test results are presented below.

Alloy	Temperature (°F)				Flow Distance (in.)
	Melt	Wet	Flow	Maximum	
Al-30.7Cu-2Li-5Mn	1610	1640	1660	1675	0.34
Al-30.1Cu-2.6P-6.7Zn	1310	1700	1850	1850	0.22 (residue)

These results are similar to those for the ternary alloys shown in Table XIX where flow is promoted, but maximum flow temperatures remain high. The Al-30.7Cu-2.0Li-5Mn alloy is of interest because characteristics such as flow distance, an apparently narrow melt-flow differential, and a low contact angle (15 degrees) make this alloy a possible candidate for further development.

Isothermal Flow

Only limited isothermal tests were made because of the high braze temperatures required for most aluminum alloys. Based on flow temperatures and flow distance, two ternary alloys were selected to determine flow under isothermal conditions. The alloys, Al-31.4Cu-5Ti and Al-31.4Cu-5Ni, were tested at 1450°F for ten minutes. Since no wetting occurred at this temperature, the temperature was increased to 1500°F and held for an additional ten minutes before termination. An examination of the coupons showed that only initial stages of wetting occurred for both alloys.

4.3.3 Discussion of Results for Aluminum-Base Alloys

Initial work with aluminum alloys, to establish base compositions for further development, showed that although most of the binary systems that were evaluated melted between 1200 and 1400°F, none had flowed. Based on initial test properties, the basic alloys, Al-33Cu and Al-10Zn, were selected for continued investigation. Test results for additions to these two brazing alloys showed that titanium, lithium, palladium, phosphorus, and nickel had permitted flow between 1610 and 1800°F (Table XIX). Further additions to two of the ternary alloys were not successful in developing melt and flow temperatures within the 1100 to 1300°F range.

Isothermal flow tests performed with two promising ternary compositions to study flow at lower temperatures for longer braze cycles showed that little flow was achieved at 1500°F for a 10-minute braze. Although melting occurred, flow was restricted considerably.

An analysis of these results indicated certain conditions were present in aluminum-base alloys to prevent wetting that cannot be overcome as with silver-base alloys. The four principal factors that control wetting and flow on beryllium are:

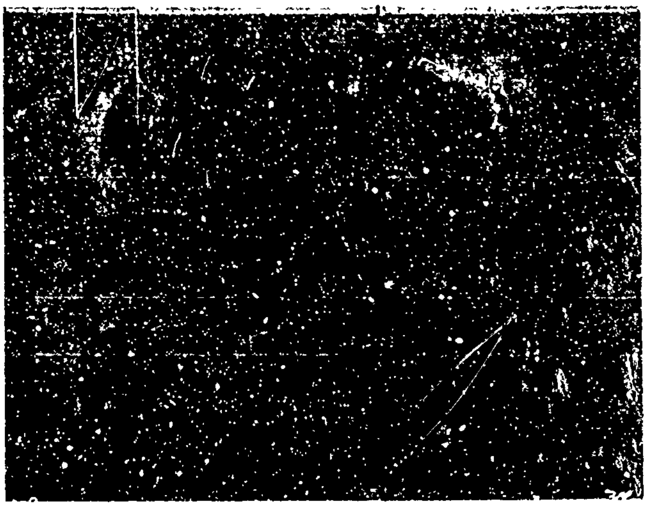
- Atmosphere quality
- Beryllium surface oxide
- Braze alloy surface oxide
- Gas in the beryllium (Ref. 2 and Appendix A)

For silver- and titanium-base alloys, these four conditions can be regulated so that wetting will occur. However, with aluminum-base alloys, only two of these conditions, atmosphere quality and beryllium surface oxide, can be controlled; the two remaining conditions, gas in the beryllium and braze alloy oxide, combine to restrict wetting.

Wetting and flow for silver- and titanium-base braze alloys will occur in spite of the gas evolution from the beryllium if the other three factors are controlled suitably. Under the same brazing conditions, failure to achieve wetting and flow with aluminum-base braze alloys must be the result of insufficient control of oxides on the braze alloy surface. None of the additions to the aluminum-base alloys were able to moderate the surface oxide condition sufficiently to reduce the flow temperature below 1610°F. In an attempt to modify the characteristic surface oxides, some work was done with braze alloy particles coated with copper. However, this technique did not appear to offer any advantage.

Further studies were made to compare the flow on beryllium for flux and flux-less brazements. This work was performed with two alloys that possessed relatively better flow properties than other aluminum-base alloys; these were Al-31.4Cu-5Ni and Al-31.4Cu-5Pd. Test specimens were of the T-configuration and were brazed in argon at 1450°F for one minute. The flux (No. S15-59) used is a Solar developed material that has a melting point of 985°F.

An examination of the brazed specimens with flux showed that excellent wetting and flow occurred and that fillets were smooth and full. A comparison of these results to the flow on flat plates where no flux was used (Fig. 27) shows that flux has improved wetting and flow considerably, in addition, maximum braze temperatures have been reduced by 400 degrees F by the use of flux.



FLUX
1450°F

NO FLUX
1850°F

Magnification: 2X

Al-31.4Cu-5.0Ni   Al-31.4Cu-5Pd

FIGURE 27. COMPARISON OF FLOW FOR FLUX AND NO-FLUX TYPE BRAZEMENT

Because the silver- and titanium-braze systems offered greater potential than the aluminum-base systems, the decision was made to discontinue work with the aluminum alloys at this point so that maximum effort could be applied to optimization of silver- and titanium-base alloys.

SECTION V

SELECTION OF ALLOYS FOR EVALUATION

Test data relating to silver- and titanium-base braze alloys were examined to aid in the selection of promising compositions for evaluation by a wider range of tests than those used in the preliminary screening work described in Section IV. Major considerations for this screening were melt-flow temperatures, wetting characteristics, and flow distance for isothermal conditions; however, some regard was placed on the sensitivity of the alloy to tolerance for adverse variations in brazing conditions (i. e., surface preparation and atmosphere quality).

Compositions from the six silver-base groups and the Ti-Zr base were included for screening. Because of poor results with aluminum-base alloys, none were considered for further study.

The decision was made to base selections on a 1400°F braze temperature because base metal properties are retained at this temperature (Table I). Alloys were rated according to the amount of flow shown for flat plate specimens. The choices, listed in order of decreasing flow values, are presented in Table XX. Although each silver-base alloy group contains from five to seven selections, the intent was to reduce this number further by continued evaluation. During these studies the less promising alloys were systematically eliminated by selecting only the most promising for further investigation.

TABLE XX

BRAZE ALLOY SELECTIONS FOR CONTINUED STUDY

Ag-Cu-Ge	**Ag-Cu-In (Cont)**
Ag-24.6Cu-9.1Ge-9Pd	Ag-23.6Cu-9.5In-0.6Li
Ag-63Cu-9.9Ge-0.5Ti	Ag-26.5Cu-9.9In-0.1Li
Ag-59.4Cu-9.5Ge-1.9Ti-5Pd	Ag-25.2Cu-9.5In-5Mn
Ag-59.4Cu-9.5Ge-1.9Ti-5Mn	
Ag-63Cu-10Ge	**Ag-Cu-Sn**
	Ag-24Cu-9.3Sn-1.9Li-5Mn
Ag-Cu-Li	Ag-33Cu-7Sn-3Mn
Ag-25.2Cu-0.5Li-9Pd	Ag-24Cu-9.3Sn-1.9Li-5Pd
Ag-25.6Cu-1Li-2Ti-5Mn	Ag-26.7Cu-9.9Sn-1Li
Ag-27.7Cu-0.5Li-0.1Ti	Ag-26Cu-10Sn-0.1Li
Ag-27.5Cu-0.5Li-1.5Sn	Ag-24.6Cu-9.5Sn-5Mn
Ag-26.4Cu-0.5Li-5Ni	
	Ag-Cu-Zn
Ag-Cu-P	Ag-50Cu-10Zn-0.1P
Ag-47Cu-0.3P-6Zn	Ag-47.2Cu-6Zn-0.1P
Ag-53Cu-0.2P-5Zn	Ag-26.5Cu-10Zn-0.1Ti
Ag-59.1Cu-1.9P-1.5Sn	Ag-22.8Cu-9Zn-4.7Ni-5Mn
Ag-47.5Cu-1.9P-5Mn	Ag-25.2Cu-9.6Zn-4Ti
	Ag-26Cu-6Zn-0.5Li
	Ag-50Cu-6Zn-1.9P
Ag-Cu-In	
Ag-23Cu-8.6In-8.5Pd-5Mn	**Ti-Zr**
Ag-23.6Cu-8.9In-8.8Pd-2Li	Ti-46.6Zr-5.3Ni-3.2Ag-4.5Be
Ag-23.6Cu-8.9In-8.8Pd-2Ti	

SECTION VI

EVALUATION OF SELECTED ALLOYS

The 33 silver-base and one titanium-base braze alloy selections in Section V were carried forward for further studies to obtain additional property data that would aid in selecting the most promising compositions for recommendation. Factors in the final evaluation included:

- Braze temperatures
- Capillary flow
- Tolerance for adverse conditions
- Structure of brazements
- Mechanical properties of joints to 1100°F

The objective was to develop alloys with maximum braze temperatures of 1400°F that could be used to braze wrought beryllium sheet without property loss resulting from recrystallization. Since many of the program alloys showed promise for this application, the work discussed in this section was performed to help rate the alloys for classification.

6.1 CAPILLARY FLOW

Evaluation was initiated by capillary flow tests on the 33 alloys from Table XX. Beryllium coupons for those tests and for the remainder of the program were prepared using the cleaning process discussed in Paragraph 2.2. Test specimens were the standard T-type; brazing was done at 1400°F for 10 minutes. After brazing, flow measurements were made. Results are presented in Table XXI.

The data in Table XXI show that maximum capillary flow was achieved by 19 of the 33 specimens tested. Although the Ag-63Cu-10Ge alloy showed excellent flat plate isothermal flow, capillary flow was comparatively less, as seen by the two test values - one being a verification check of the other. Only one Ag-Cu-Ge and Ag-Cu-P base alloy reached the one-inch maximum flow. All but one each of the Ag-Cu-In and Ag-Cu-Li base alloys tested attained maximum flow, however, Ag-Cu-In-0.1Li achieved 0.98 inch flow. Maximum flow was also reached by four Ag-Cu-Sn and two Ag-Cu-Zn base alloys.

TABLE XXI

ISOTHERMAL CAPILLARY FLOW AT 1400°F FOR SELECTED ALLOYS

Alloys	Capillary Flow (in.)
Ag-Cu-Ge	
Ag-24.6Cu-9.1Ge-9Pd	>1.00
Ag-63Cu-9.9Ge-0.5Ti	0.30
Ag-59.4Cu-9.5Ge-1.9Ti-5Pd	0.45
Ag-59.4Cu-9.5Ge-1.9Ti-5Mn	0.80
Ag-63Cu-10Ge	0.22, 0.28
Ag-Cu-In	
Ag-23Cu-8.6In-8.5Pd-5Mn	>1.00
Ag-23.6Cu-8.9In-8.8Pd-2Li	>1.00
Ag-23.6Cu-8.9In-8.8Pd-2Li	>1.00
Ag-26.3Cu-9.5In-0.6Li	>1.00
Ag-26.5Cu-9.9In-0.1Li	0.98
Ag-25.2Cu-9.5In-5Mn	>1.00
Ag-Cu-Li	
Ag-25.2Cu-0.5Li-9Pd	>1.00
Ag-25.6Cu-1Li-2Ti-5Mn	>1.00
Ag-27.6Cu-0.5Li-0.1Ti	0.875
Ag-27.5Cu-0.5Li-1.5Sn	>1.00
Ag-24.6Cu-0.5Li-5Ni	>1.00
Ag-Cu-P	
Ag-47Cu-0.3P-6Zn	0.90
Ag-53Cu-0.2P-5Zn	>1.00
Ag-59.1Cu-2P-1.5Sn	0.375
Ag-47.5Cu-1.9P-5Mn	0.325
Ag-Cu-Sn	
Ag-24Cu-9.3Sn-1.9Li-5Mn	>1.00
Ag-33Cu-7Sn-3Mn	>1.00
Ag-24Cu-9.3Sn-1.9Li-5Pd	>1.00
Ag-23.6Cu-9.9Sn-1Li	1.00
Ag-26Cu-10Sn-0.1Li	0.500
Ag-24.6Cu-9.5Sn-5Mn	>1.00
Ag-Cu-Zn	
Ag-50Cu-10Zn-0.1P	>1.00
Ag-47.2Cu-6Zn-0.1P	0.75
Ag-26.5Cu-10Zn-0.1Ti	>1.00
Ag-22.8Cu-9Zn-4.7Ni-5Mn	0.30
Ag-25.2Cu-9.6Zn-4Ti	0.15
Ag-26.1Cu-6Zn-0.5Li	>1.00
Ag-50Cu-6Zn-1.9P	0.40

Examination of isothermal capillary specimens disclosed that a small quantity of braze alloy residue (an unmelted portion of the alloy particle) remained on some specimens after brazing. The amount remaining varied from negligible quantities to moderate amounts. To aid in screening braze alloys, capillary flow samples were classified according to the degree of flow achieved and amount of residue remaining. This classification is presented in Table XXII.

To further narrow the number of alloys for continued evaluation and screening, test data for alloys shown in Table XXII were examined. Basis for rejections included poor reproducibility, corrosion potential associated with alloys containing high lithium and phosphorus, poor isothermal capillary flow, and residue. Of the 33 promising silver-base alloys used for isothermal capillary flow studies, 17 were selected for continued evaluation and screening.

TABLE XXII

CLASSIFICATION OF CAPILLARY FLOW SPECIMENS

Group A (1.0 inch maximum flow, no residue)	Group C (maximum flow of 0.75 inch or more, no residue)
Ag-26.5Cu-9.9In-0.1Li (0.98 inch)	Ag-59.4Cu-9.5Ge-1.9Ti-5Mn
Ag-25.2Cu-9.5In-5Mn	Ag-47Cu-0.1P-6Zn
Ag-23.6Cu-8.9In-8.8Pd-2Li	Ag-47Cu-0.3P-6Zn
Ag-27.5Cu-0.5Li-1.5Sn	Group D (maximum flow of 0.75 inch or more, slight residue)
Ag-23.6Cu-9.9Sn-1Li	Ag-27.6Cu-0.5Li-0.1Ti
Ag-33Cu-7Sn-3Mn	Group E (maximum flow of 0.45-0.75 inch, no residue)
Ag-24.6Cu-9.5Sn-5Mn	Ag-59.4Cu-9.5Ge-1.9Ti-5Pd
Ag-24Cu-9.3Sn-1.9Li-5Mn	Ag-26Cu-10Sn-0.1Li
Ag-24Cu-9.3Sn-1.9Li-5Pd	Ag-25.2Cu-9.6Zn-4Ti
Ag-26.1Cu-6Zn-0.5Li	Group F (maximum flow less than 0.50 inch, no residue)
Ag-50Cu-10Zn-0.1P	Ag-63Cu-10Ge
Group B (1.0 inch maximum flow, slight to some residue)	Ag-63Cu-9.9Ge-0.5Ti
Ag-24.6Cu-9.1Ge-9Pd	Ag-47.5Cu-1.9P-5Mn
Ag-26.3Cu-9.5In-0.6Li	Ag-59.1Cu-2P-1.5Sn
Ag-23Cu-8.6In-8.5Pd-5Mn	Ag-50Cu-6Zn-1.9P
Ag-23.6Cu-8.9In-8.8Pd-2Ti	Ag-22.8Cu-9.0Zn-4.7Ni-5Mn
Ag-24.6Cu-0.5Li-5Ni	
Ag-25.2Cu-0.5Li-9Pd	
Ag-25.6Cu-1Li-2Ti-5Mn	
Ag-53Cu-0.2P-5Zn	
Ag-26.5Cu-10Zn-0.1Ti	

6.2 STRUCTURE OF BRAZEMENTS

Braze joint structures were examined to further aid in screening promising alloys. This was another means used to assess the relative importance of the 17 silver-base alloys and one titanium-base alloy that had been carried ahead for final evaluation.

These studies, based on 1400°F and 10-minute capillary flow brazements, included joint gap measurements, beryllide formation, diffusion, and reaction. Electron microscopy was used to examine exceptionally narrow joints. Photomicrographs of typical structures were made for joint areas at two locations; at the base of the capillary and also near the point of maximum flow. These two locations were selected to compare structures for joints where a larger reservoir of alloy was available for longer times (base zone) to those where only a small quantity of alloy was available for a shorter portion of the braze cycle (point of maximum flow). These structures are presented in Figure 28. Comments regarding salient points for each structure follow. The term "interaction" in the comments refers to the interdiffusion between the braze alloy and beryllium.

Ag-59.4Cu-9.5Ge-1.9Ti-5Mn (Fig. 28A)

Base. Joint width = 0.003 inch. The overall reaction zone is quite narrow (0.0002 inch) in view of the wide joint gap width and, hence, the large amount of molten braze alloy available for reaction. On the other hand, the presence of dispersed beryllides of copper and other elements in the braze alloy indicates considerable solution of beryllium by the braze alloy. The beryllide at the braze alloy/beryllium interface is a very thin and incomplete band. Diffusion into the beryllium, indicated by a dark etching zone, is somewhat irregular but very limited. Limited reaction to form beryllides at the interface is characteristic of titanium- and manganese-containing alloys (Ref. 1).

Top. Joint width = 0.0006 inch. No diffusion into beryllium has occurred; reaction zones are less than 0.0001 inch.

Ag-26.3Cu-9.5In-0.6Li (Fig. 28B)

Base. Joint width = 0.0012 inch. Interdiffusion of braze alloy and beryllium (0.0002 inch), copper beryllide zones (0.0001 inch), and primary phase bands (0.00025 inch) parallel each side of the joint. The joint center appears to be largely eutectic. The band of primary phase is believed to result from selective removal of copper to form beryllide. The effect of indium found previously (Ref. 1) in causing greater beryllide reactions appears to be confirmed.

Top. Joint width = 0.0002 inch. No reaction or beryllide zones are shown for this narrow joint. The phases present appear to be primary plus eutectic.

Ag-26.5Cu-9.9In-0.1Li (Fig. 28C)

Base. Joint width = 0.0001 inch. Electron microscopy was used because the joint width was so narrow. Three phases are seen; an outer reaction zone, an intermediate area measuring 0.00003 inch, and a center portion that is probably eutectic based on the results for the 0.6Li alloy shown in Figure 28B.

Top. Joint width = 0.0004 inch. The joint appears dense and free of voids. Continuous beryllide bands, 0.0001 to 0.0002 inch, parallel the interface. No diffusion into the beryllium beyond the beryllide has occurred.

Ag-25.2Cu-9.5In-5Mn (Fig. 28D)

Base. Joint width = 0.001 inch. This unusual structure showing intermittent reaction can be explained on the basis of prior work (Ref. 1). It was suggested in Reference 1 that indium increases reaction for the Ag-Cu alloys thereby increasing the formation of copper beryllide, whereas manganese decreases reaction. The mechanism by which manganese decreases reaction was postulated to include:

- Depletion of braze alloy in manganese adjacent to beryllide
- Slower growth rate of the higher melting point manganese rich beryllide compared with copper beryllide

Where the manganese-rich beryllide remained intact (thin black band), interaction with beryllium was limited although diffusion into the beryllium beyond the beryllide has occurred. In other areas, the manganese beryllide has broken down and the more rapid formation of copper-rich beryllide (gray) has occurred. Evidence includes the presence of primary silver-rich areas in the braze alloy adjacent to the areas of copper beryllide.

Top. Joint width = 0.0002 inch. The combined effects of narrow joint width and shorter time for reaction have reduced interaction markedly. The beryllide appears to be predominantly copper beryllide, suggesting that the manganese content has been reduced by reaction at lower positions in the joint as the molten braze alloy flowed over the beryllium surface. There are some local areas where diffusion beyond the beryllide has occurred.

Ag-23.6Cu-8.9In-8.8Pd-2Ti (Fig. 28E)

Base. Joint width = 0.0008 to 0.0013 inch. At the wider section of the joint (0.0013 inch), the beryllide band is narrow (0.00015 inch); whereas, the beryllide thickness is approximately twice as great at the narrower section of the joint. The braze alloy shows two phases; primarily at the outer portion, and a eutectic core through the center section. As the joint narrows, the amount of primary phase decreases. The joint is dense. Some diffusion into the beryllium has occurred as indicated by irregular darkly etched regions.

Top. Joint width = 0.001 inch. Typical beryllide bands, dense and continuous, are bordered inwardly by narrow (0.0001 inch) bands of primary phase. The center portion is similar to the structure noted for the base area.

Ag-23Cu-8.6In-8.5Pd-5Mn (Fig. 28F)

Base. Joint width = 0.002 inch. Limited reaction and narrow, continuous beryllide zones, characteristic for alloys containing manganese, are located at each side of the joint. Small isolated beryllides are identified in the body of the alloy. No voids can be seen.

Top. Joint width = 0.0005 inch. Structures at the top appear identical to those at the base. Thicknesses of the beryllide bands are not consistent, possibly the effect of an irregular beryllium surface.

Ag-24.6Cu-0.5Li-5Ni (Fig. 28G)

Base. Joint width = 0.0008 to 0.001 inch. Irregular beryllide bands along the interface have average widths of 0.0003 inch. The darker bands at the outer edges indicate diffusion into the beryllium extends 0.0002 inch.

Top. Joint width = 0.0004 inch. Structure is very similar to the base, but penetration into beryllium is unexpectedly large for this narrow joint.

Ag-25.2Cu-0.5Li-9Pd (Fig. 28H)

Base. Joint width = 0.0025. Irregular beryllide zones (0.0003 to 0.0006 inch) parallel each interface. Partial reaction with beryllium substrate is evidenced by the darkly etched zones. The joints are dense. Growth of the beryllide has resulted in some breakaway from the beryllium substrate as shown by the white, silver-rich primary phase beneath the beryllide. This behavior is usually found with silver-base alloys only at high temperatures (Ref. 1).

Top. Joint width = 0.001 inch. This photomicrograph shows irregular and broken beryllide stratum at the interface. Although the joint is proportionately narrower than at the base, beryllide thickness is about equal. Lighter appearance of the residual braze alloy indicates the composition may be higher in primary phase. No voids are seen.

Ag-25.6Cu-1Li-2Ti-5Mn (Fig. 28I)

Base. Joint width = 0.0016 inch. Irregular, discontinuous reaction zones and beryllide bands appear along the interface. Braze alloy structure is basically fine-grain eutectic with large isolated islands of primary phase.

Top. Joint width = 0.0012 inch. The structure is similar to the base area structure.

Ag-27.5Cu-0.5Li-1.5Sn (Fig. 28J)

Base and Top. Joint width = 0.001 inch. Both base and top joint areas appear to exhibit the same structure and clearance. Continuous beryllide bands are 0.0001 to 0.0003 inch wide. The reaction zone (darker) appears continuous also.

Ag-26Cu-10Sn-1Li (Fig. 28K)

Base. Joint width = 0.0014 inch. Interaction appears to be extensive for certain areas. Beryllide bands (0.0004 inch) are irregular; beryllide is also seen bridging the joint. The joint center is fine eutectic structure with primary phase.

Top. Joint = 0.0003 inch. Because of the small amount of alloy available in the joint, interaction has been limited to less than 0.0002 inch. Beryllide structure is limited also to concentrated formations rather than bands along the interface. The joint center is similar to that for the base.

Ag-24.6Cu-9.5Sn-5Mn (Fig. 28L)

Base and Top. Joint width = 0.0007 inch. Top and bottom areas show similar structures; a reaction zone with beryllium (0.0002 inch), and a beryllide zone (0.0002 inch). The only difference is that the beryllide zones for the top area are not uniform in width, giving the appearance of nucleated growth along the interface.

Ag-33Cu-7Sn-3Mn (Fig. 28M)

Base. Joint width = 0.0025 inch. Beryllide bands measure 0.0001 inch. Primary phase zones (light bands) are 0.0005 inch while the center portion is largely eutectic. The residual braze alloy contains particles of a phase similar to the beryllide.

Top. Joint width = 0.0002 to 0.0005 inch. Reaction and beryllide bands are about equal.

Ag-26.1Cu-6Zn-0.5Li (Fig. 28N)

Base. Joint width = 0.0008 inch. Extensive beryllide formation in view of narrow joint width, with interaction between beryllium and beryllide extending 0.0002 to 0.0003 inch.

Top. Joint width = 0.0002 inch. The reaction zone is similar to the base area but no beryllides or other distinct structures are seen. The braze joint appears to be basically primary and eutectic.

Ag-53Cu-5Zn-0.2P (Fig. 28O)

Base and Top. Joint width = 0.0005 inch. From electron microscopy, three phases are indicated:

- Joint center - probably eutectic
- Joint edges - probably primary silver-rich area
- Diffusion zone - beryllide

Ag-26.5Cu-10Zn-0.1Ti (Fig. 28P)

Base. Joint width = 0.0012 inch. Distinct 0.0002 inch beryllide and reaction zones are seen.

Top. Joint width = 0.001 inch. Similar to the base area except that 0.0001 inch primary zones are seen along each side.

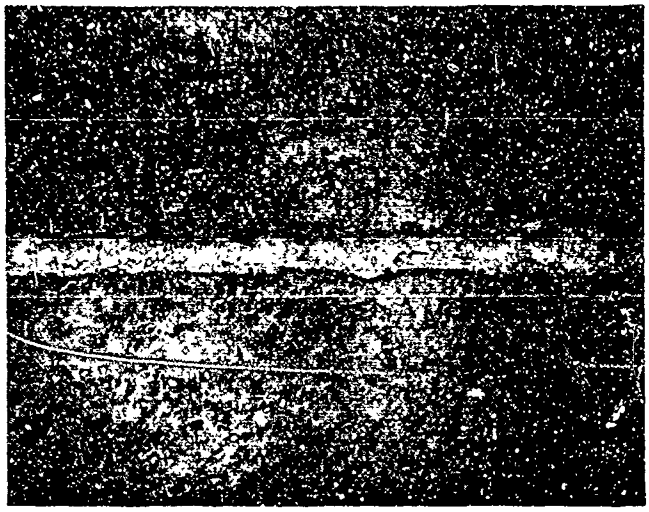
Ag-22.8Cu-9Zn-4.7Ni-5Mn (Fig. 28Q)

Base. Joint width = 0.0005 inch. Beryllide bands are irregular and narrow (approximately 0.0001 inch wide). Complex structures have formed in an irregular manner along the joint.

Top. Joint width = 0.0015 inch. Uniform beryllide bands are 0.0001 inch wide. The reaction zone with beryllium is very narrow also.

Ti-46.6Zr-5.3Ni-3.2Ag-4.5Be (Fig. 28R)

The section shown is typical for top and bottom areas. Joint width is 0.0002 to 0.0008 inch. No significant diffusion into or reaction with the beryllium has occurred; some beryllides are seen through the joint center. The joint is dense and free of voids.



A. Top

Ag-59.4Cu-9.5Ge-1.9Ti-5Mn

Etchant: Kroll's

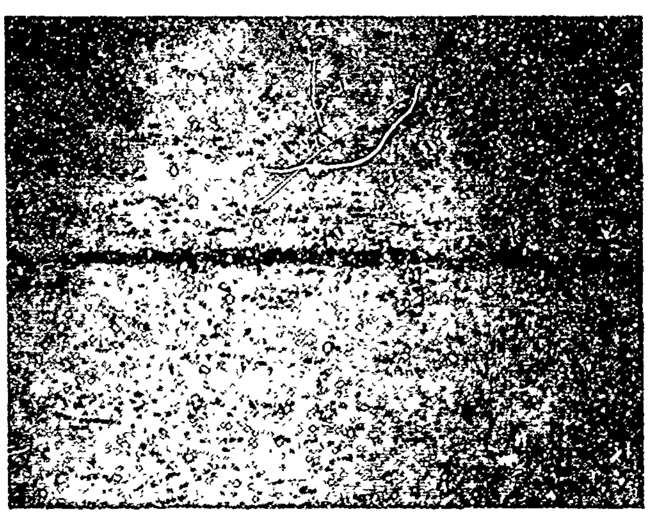
Magnification: 400X

A. Base

Ag-59.4Cu-9.5Ge-1.9Ti-5Mn

Etchant: Kroll's

Magnification: 400X



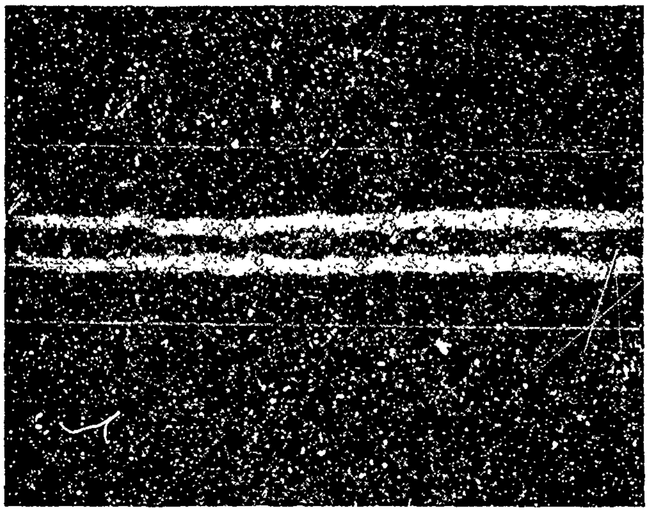
B. Top

Ag-26.3Cu-9.5In-0.6Li

Etchant: Kroll's

Magnification: 400X

FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 1 of 12)

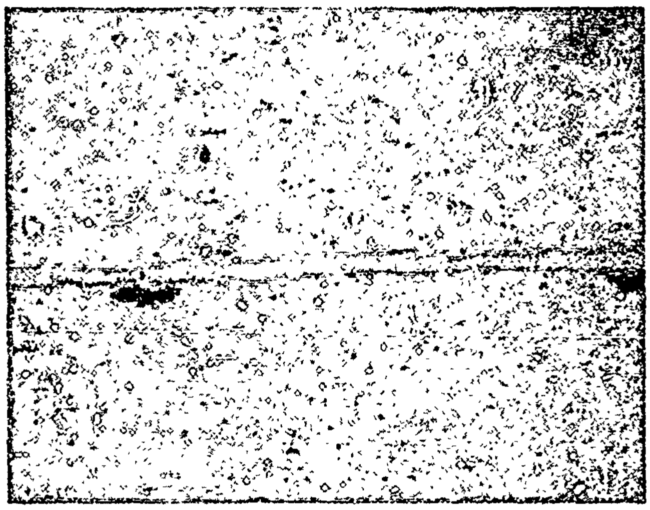


B. Base

Ag-26.3Cu-9.5In-0.6Li

Etchant: Kroll's

Magnification: 400X

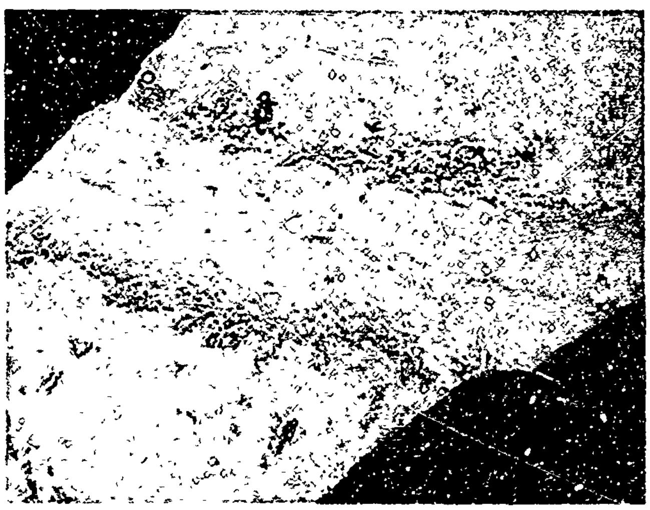


C. Top

Ag-26.5Cu-9.9In-0.1Li

Etchant. Ammonium Hydroxide

Magnification: 400X



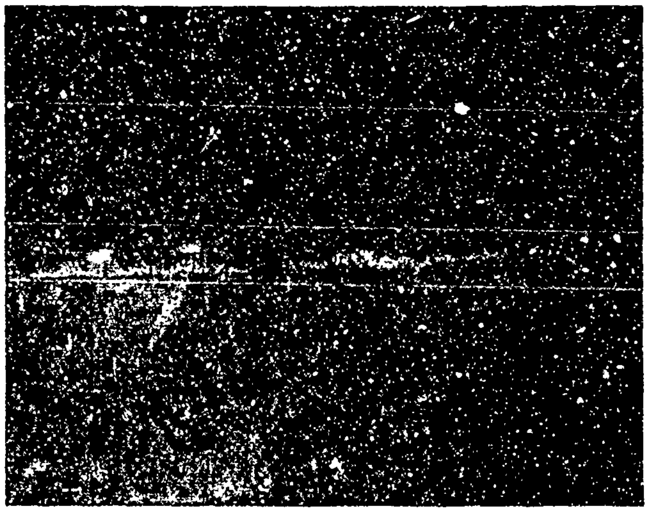
C. Base

Ag-26.5Cu-9.9In-0.1Li

Etchant. Chromic-Sulfuric-Phosphoric

Magnification: 2400X

FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 2 of 12)

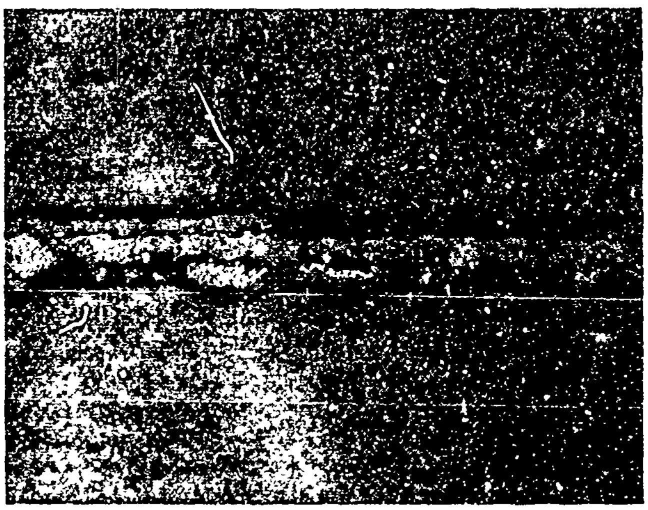


D. Top

Ag-25.2Cu-9.5In-5Mn

Etchant: Kroll's

Magnification: 400X

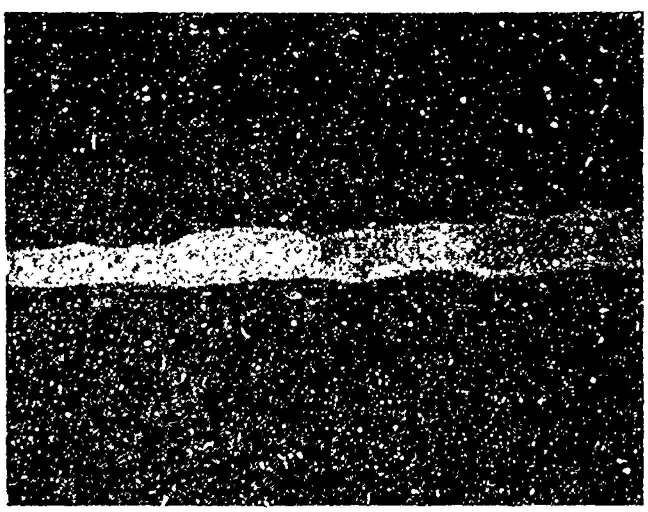


D. Base

Ag-25.2Cu-9.5In-5Mn

Etchant: Kroll's

Magnification: 400X



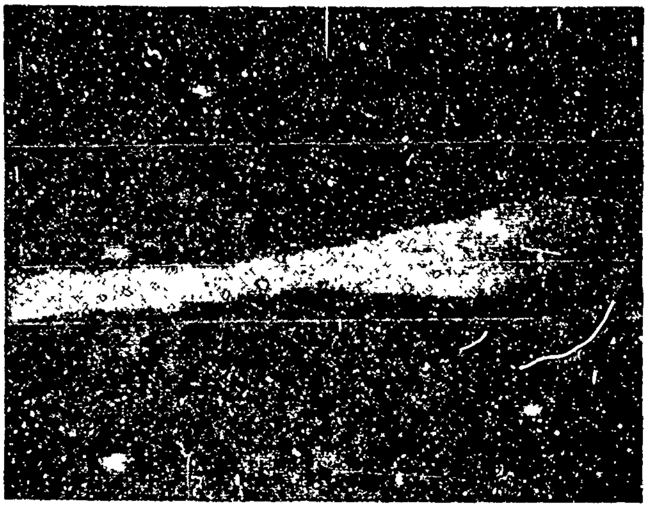
E. Top

Ag-23.6Cu-8.9In-8.8Pd-2Ti

Etchant: Chromic-Sulfuric-Phosphoric

Magnification: 400X

FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 3 of 12)

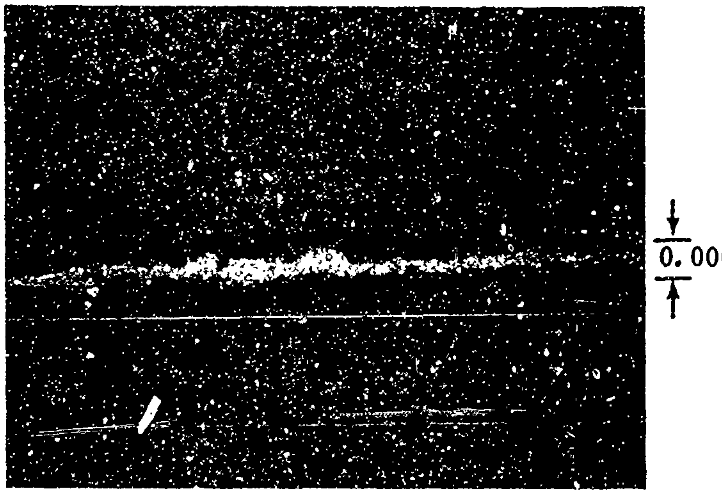


E. Base

Ag-23.6Cu-8.9In-8.8Pd-2Ti

Etchant: Chromic-Sulfuric-Phosphoric

Magnification: 400X

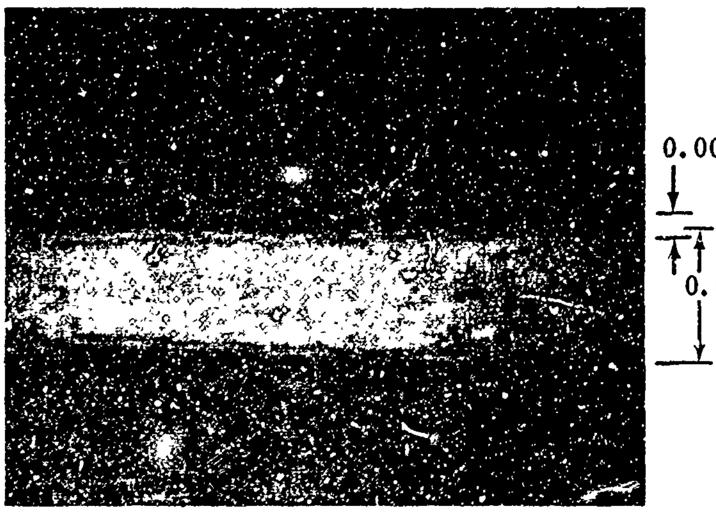


F. Top

Ag-23Cu-8.6In-8.5Pd-5Mn

Etchant: Chromic-Sulfuric-Phosphoric

Magnification: 400X



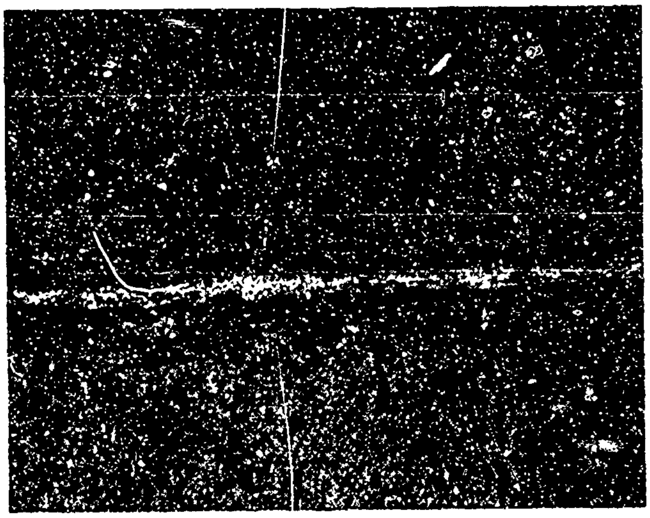
F. Base

Ag-23Cu-8.6In-8.5Pd-5Mn

Etchant: Chromic-Sulfuric-Phosphoric

Magnification: 400X

FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 4 of 12)

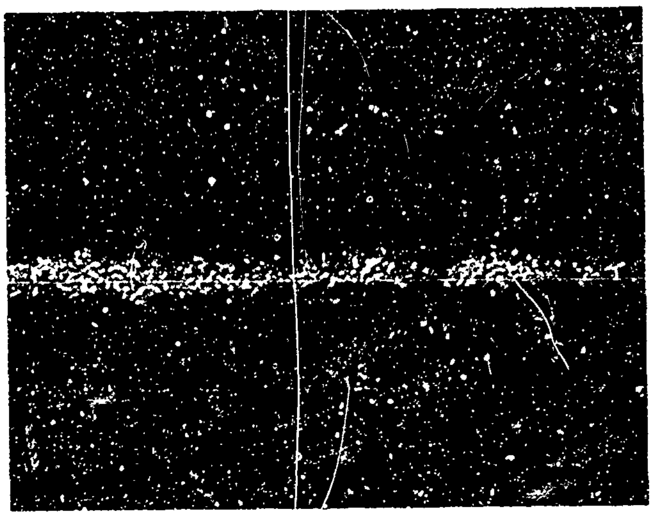


G. Top

Ag-24.6Cu-0.5Li-5Ni

Etchant: Kroll's

Magnification: 400X

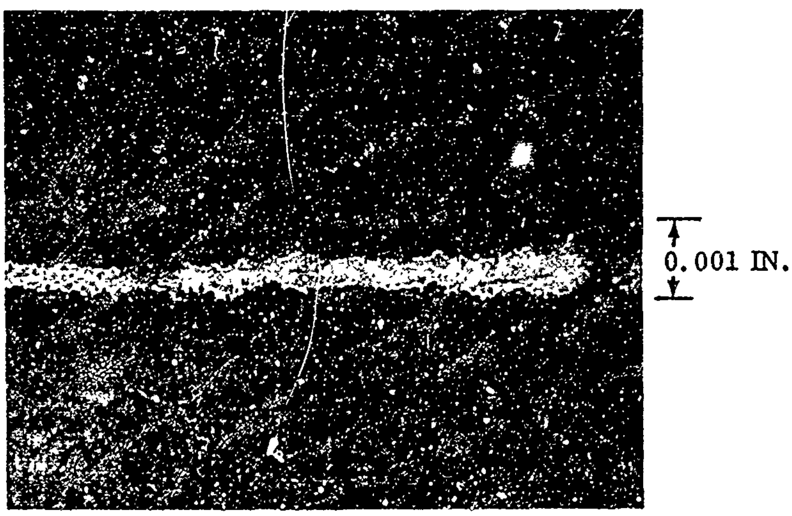


G. Base

Ag-24.6Cu-0.5Li-5Ni

Etchant: Kroll's

Magnification: 400X



H. Top

Ag-25.2Cu-0.5Li-9Pd

Etchant: Chromic-Sulfuric-Phosphoric

Magnification: 400X

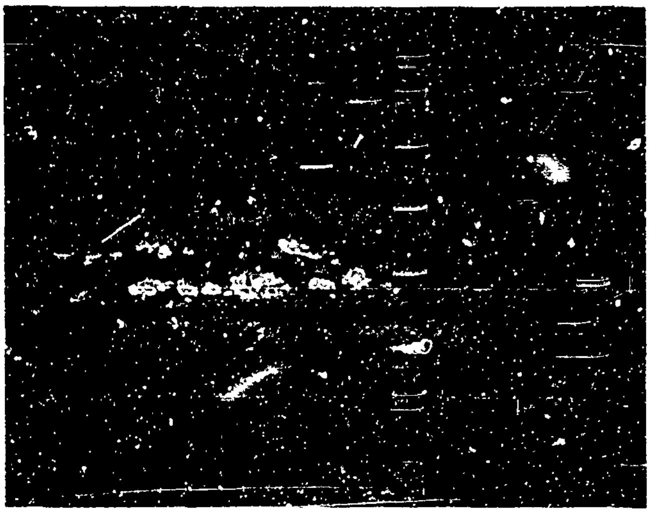
FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 5 of 12)

H. Base

Ag-25.2Cu-0.5Li-9Pd

Etchant: Chromic-Sulfuric-Phosphoric

Magnification: 400X

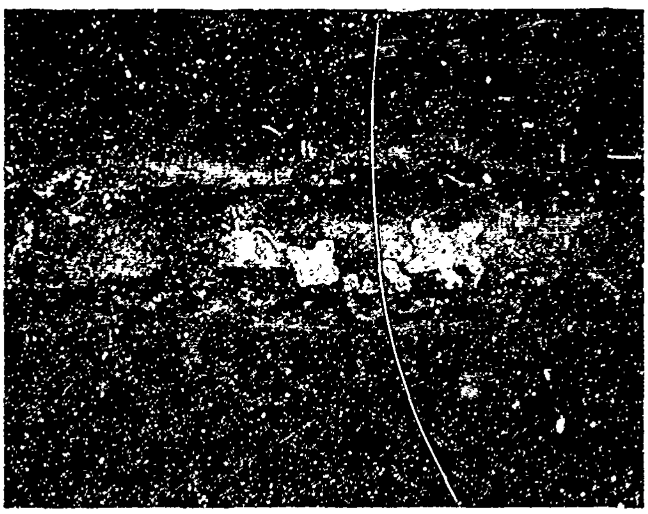


I. Top

Ag-25.6Cu-1Li-2Ti-5Mn

Etchant: Kroll's

Magnification: 400X



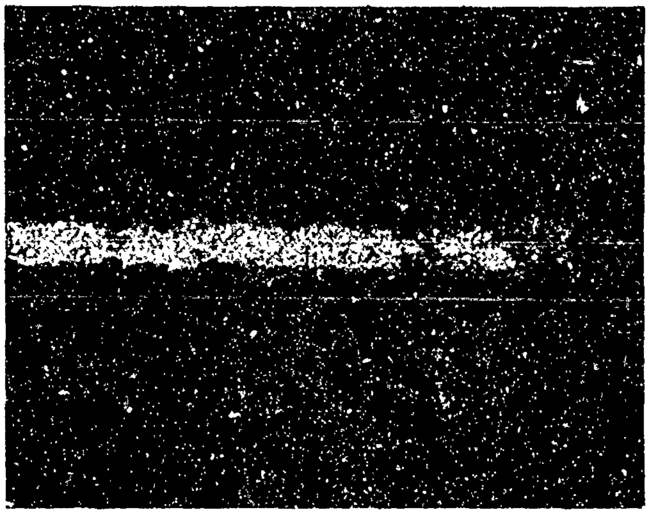
I. Base

Ag-25.6Cu-1Li-2Ti-5Mn

Etchant: Kroll's

Magnification: 400X

FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 6 of 12)

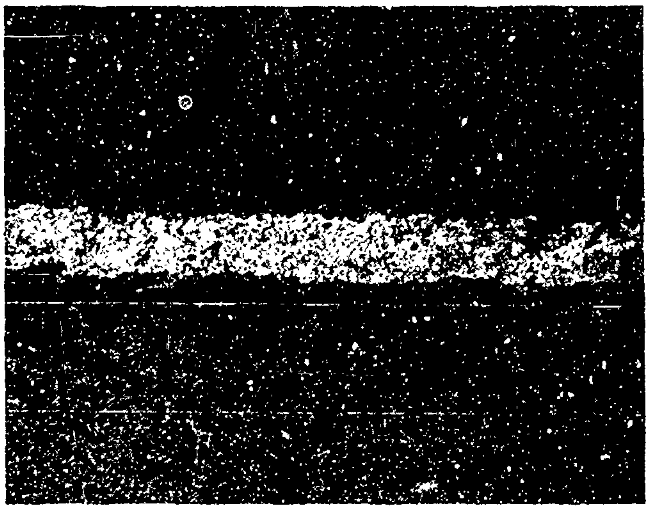


J. Top

Ag-27.5Cu-0.5Li-1.5Sn

Etchant: Kroll's

Magnification: 400X

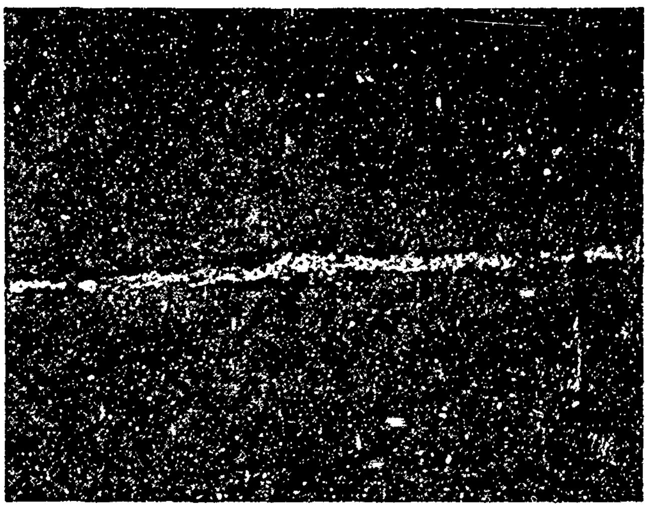


J. Base

Ag-27.5Cu-0.5Li-1.5Sn

Etchant: Kroll's

Magnification: 400X



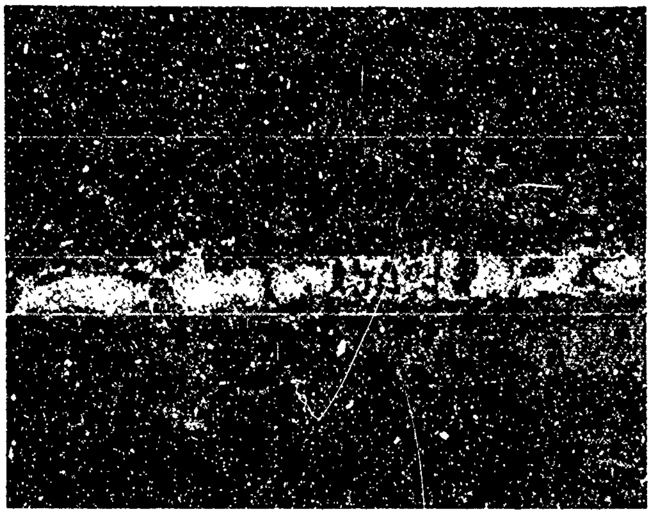
K. Top

Ag-26Cu-10Sn-1Li

Etchant: Kroll's

Magnification: 400X

FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 7 of 12)

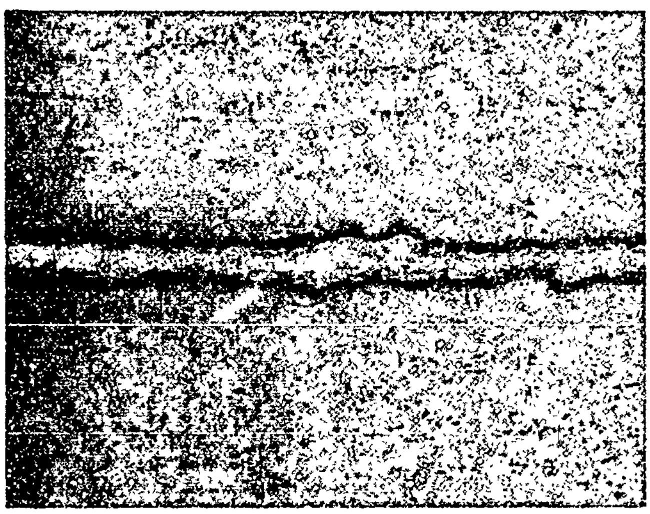


K. Base

Ag-26Cu-10Sn-1Li

Etchant: Kroll's

Magnification: 400X

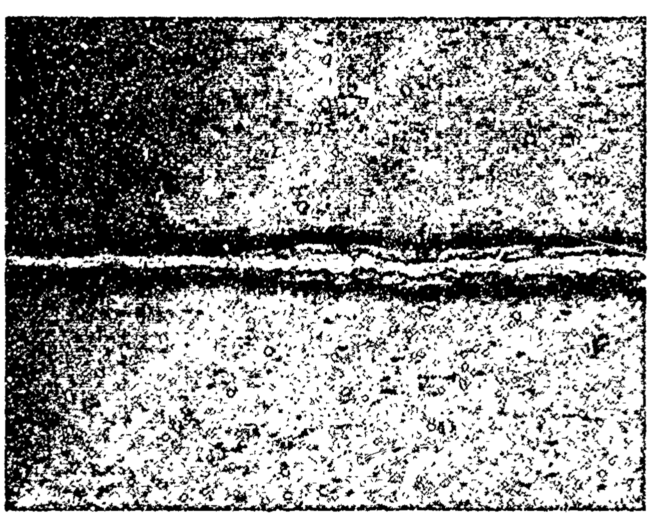


L. Top

Ag-24.6Cu-9.5Sn-5Mn

Etchant: Kroll's

Magnification: 400X



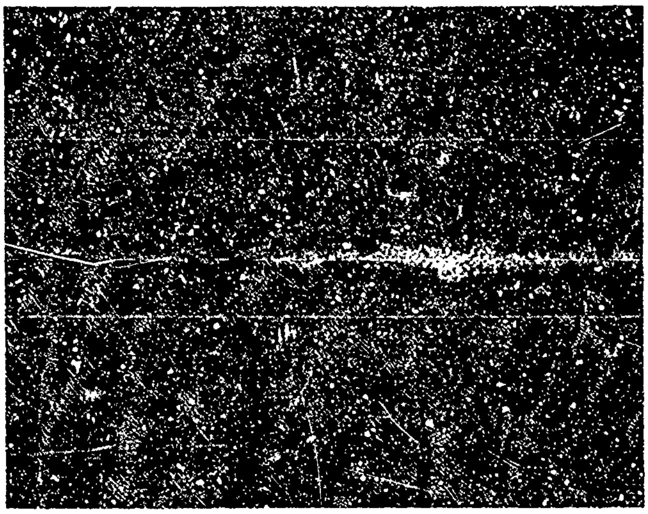
L. Base

Ag-24.6Cu-9.5Sn-5Mn

Etchant: Kroll's

Magnification: 400X

FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 8 of 12)

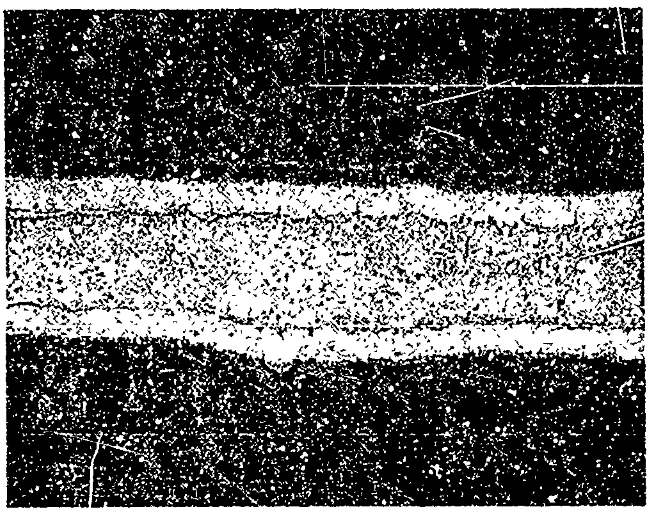


M. Top

Ag-33Cu-7Sn-3Mn

Etchant: Kroll's

Magnification: 400X



M. Base

Ag-33Cu-7Sn-3Mn

Etchant: Kroll's

Magnification: 400X

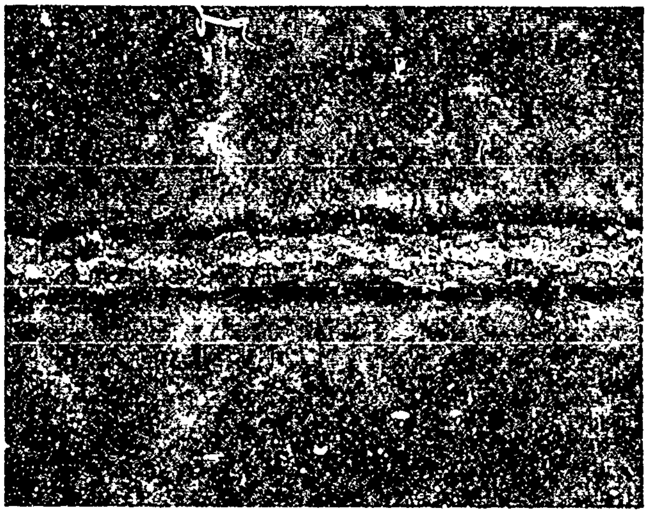
N. Top

Ag-26.1Cu-6Zn-0.5Li

Etchant: Kroll's

Magnification: 400X

FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 9 of 12)



N. Base

Ag-26.1Cu-6Zn-0.5Li

Etchant: Kroll's

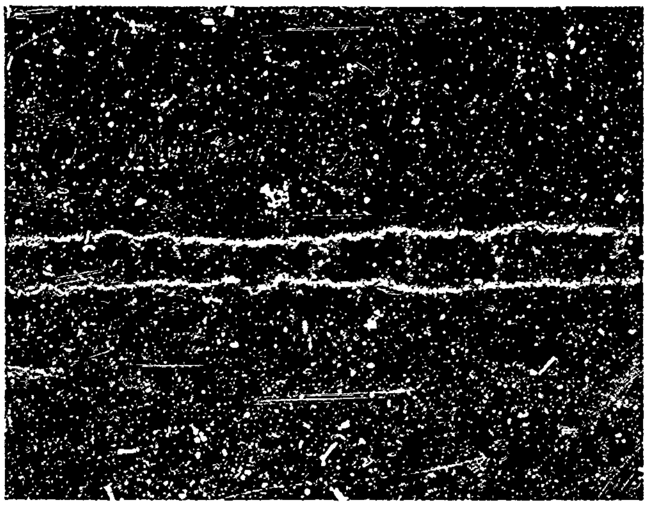
Magnification: 400X

O. Top and Base

Ag-53Cu-5Zn-0.2P

Etchant. Sulfuric-Chromic-Phosphoric

Magnification: 2400X



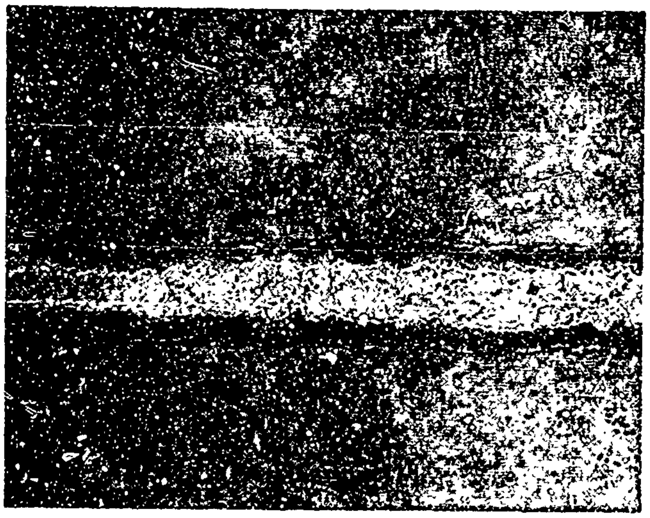
P. Top

Ag-26.5Cu-10Zn-0.1Ti

Etchant: 1. Kroll's
2. Ammonium-Hydroxide

Magnification: 400X

FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 10 of 12)



P. Base

Ag-26.5Cu-10Zn-0.1Ti

Etchant: 1. Kroll's
2. Ammonium Hydroxide

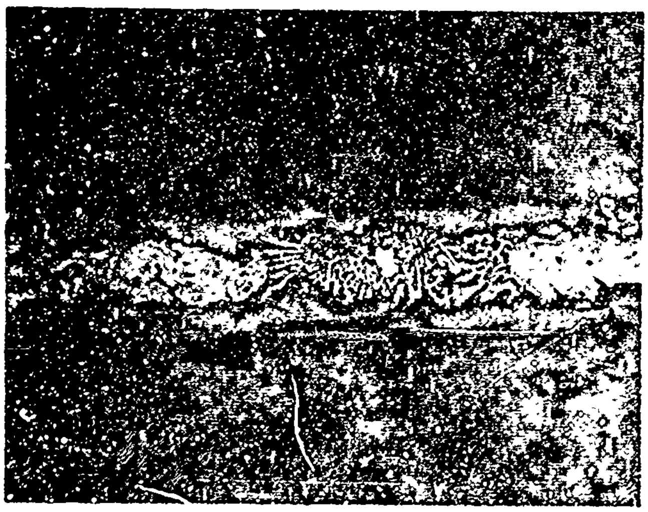
Magnification: 400X

Q. Top

Ag-22.8Cu-9Zn-4.7Ni-5Mn

Etchant: Ammonium Hydroxide

Magnification: 400X



Q. Base

Ag-22.8Cu-9Zn-4.7Ni-5Mn

Etchant: Ammonium-Hydroxide

Magnification: 1000X

FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 11 of 12)

R. Top and Base

Ti-46.6Zr-5.3Ni-3.2Ag-4.5Be

Etchant: Kroll's

Magnification: 400X

FIGURE 28. BRAZE JOINT STRUCTURES FOR PROGRAM ALLOYS (Sheet 12 of 12)

6.3 MECHANICAL PROPERTIES

In the next step, the 17 alloys carried through were evaluated for braze joint strength. Test joint configurations included the butt and double lap shear (Fig. 4). Although in practice the shear-type joint is generally used for braze joint evaluation, the butt joint was adopted to provide preliminary strength data since the values generated by this joint are more indicative of braze alloy strength than joint shear properties. This is especially true for beryllium where its high modulus causes stress concentrations in the shear-type joint.

Specimen coupons were cut from nominal 0.040-, 0.060-, and 0.080-inch thick cross-rolled beryllium sheet; these specimens were assembled to allow for a nominal gap clearance of 0.0005 to 0.0015 inch.

Brazing was performed in argon at 1400°F for 10 minutes. Joint strength tests were conducted at room temperature, 300, 600, 1000, and 1100°F. Prior to testing, both the lap and butt specimens were checked for alignment. Those specimens not within acceptable tolerances were either discarded or surface ground to obtain the correct alignment. Joint clearance measurements were made with an optical comparator and recorded to study the effect of gap on strength. Testing consisted basically of heating the specimens in an insulated electric heater sleeve and holding for five minutes to equalize temperature before pulling.

Results presented for both tensile and shear specimens are, in many cases, an average of multiple rather than single values. Repeat tests were conducted to verify questionable data or, in the case of shear tests at 300°F, to show the range of values for comparison to tensile results. Later, in selecting alloys for recommendation, strength values were rated according to the number of specimens tested for each temperature. For example, those alloys with results for three samples for a particular test temperature were rated slightly above those with only one value for the same set of conditions.

6.3.1 Butt-Joint Strengths

Butt-joint specimens were brazed with the 17 alloys carried through from the preceding section. Prior to testing, joint clearances were measured and recorded. Joints made with the selected alloys were tested at room temperature, 300, 600, 1000, and 1100°F; Table XXIII lists the alloys and includes strength data and gap measurements. Room temperature, 1000, and 1100°F tests were conducted first and data for these specimens are complete; however, because some alloys were dropped based on these results and prior capillary flow data, the 300 and 600°F columns have omissions. Strength-temperature curves were also plotted and are shown in Figure 29. Dotted lines in Figure 29 are used to indicate probable norm curves in areas where recorded points show an abrupt change in direction.

An examination of Figure 29 indicates that certain additions have greater influence on joint strength than others. An analysis was made of the data and a classification of the various additions is presented below.

	Number of Alloys Containing Addition Elements							
Strength Rating	Ge	In	Li	Mn	Pd	Sn	Zn	Ti
High (40 ksi)	1	1	0	5	0	2	0	1
Medium (30 ksi)	0	2	2	2	2	1	3	1
Low (20 ksi)	0	2	5	1	5	1	1	1

This comparison shows that manganese and tin influence braze alloy strength favorably; whereas lithium, palladium, and zinc are present in the lower strength alloys. Indium appears to weaken the alloy somewhat because the higher strength entries contain manganese. Similarly, the single entry containing germanium also contains manganese so the individual effect of germanium is not clear. The effect of titanium is not clear because:

- The three alloys contain only two percent of the addition
- All of the braze alloys are quinary composition so that the effect of the other alloying elements must be considered.

TABLE XXIII

STRENGTH OF BUTT JOINTS FROM ROOM TEMPERATURE TO 1100°F FOR 1400°F/10-MINUTE BRAZE

Letter Designation	Composition	Room Temperature		300°F		600°F		1000°F		1100°F	
		Strength (ksi)	Gap (mil)	Strength (ksi)	Gap (mil)	Strength (ksi)	Gap (mil)	Strength (ksi)	Gap (mil)	Strength (ksi)	Gap (mil)
A	Ag-59.4Cu-9.5Ge-1.9Ti-5Mn	36.4(3)(1)	0.9	42.0	1.2	34.0	0.5	28.8	9.0	15.7	0.6
B	Ag-26.3Cu-9.5In-0.6Li	13.3	1.0 to 1.5	-	-	17.0	0.5	27.4	1.1	16.0	1.0
C	Ag-26.5Cu-9.9In-0.1Li	5.4	1.0	-	-	24.1	0.5	30.0	0.7	17.7	1.0
D	Ag-25.2Cu-9.5In-5Mn	30.0	0.5 to 1.3	44.3	0.8	36.0(1)	0.5	28.0	0.6	21.6	1.0
E	Ag-23.6Cu-8.9In-8.8Pd-2Ti	18.4	9.7	26.3	1.1	23.2	0.5	22.6(3)	0.5	19.3	0.3
F	Ag-23Cu-8.6In-8.5Pd-5Mn	8.9	1.5	23.6(2)	0.7	27.4	0.5	32.3	0.75	28.8(1)	1.0
G	Ag-24.5Cu-0.5Li-5N	9.9	0.6	-	-	-	0.5	14.0	0.6	8.0	1.0
H	Ag-25.2Cu-0.5Li-9Pd	13.0	1.0 to 1.6	32.4	0.9	23.8	0.5	24.6	0.7	14.2	1.0
I	Ag-25.6Cu-1Li-2Ti-5Mn	8.9	0.8 to 1.3	-	-	-	0.5	19.0	0.8	12.7	1.0
J	Ag-27.5Cu-1.5Sn-0.5Li	7.5	1.4	-	-	16.0	0.5	27.2(2)	1.0	16.0	0.5
K	Ag-23.6Cu-9.9Sn-1Li	15.0	0.4 to 1.0	33.8	1.4	30.0	0.5	32.0(3)	0.9	11.3	1.0
L	Ag-24.6Cu-9.5Sn-5Mn	24.0(3)	2.0	35.0	1.2	41.5(1)	0.5	29.0	0.5	27.2	0.6
M	Ag-33Cu-7Sn-3Mn	24.0	0.5	36.0	0.6	39.4(1)	0.5	24.6	1.1	17.4	1.0
N	Ag-26.1Cu-6Zn-0.5Li	7.1(2)	1.0 to 1.3	-	-	-	0.5	19.5	1.0	12.5	1.3
O	Ag-53Cu-5Zn-0.2P	24.7(3)	0.7	27.0	0.7	27.4	0.5	27.8	0.6	26.3	1.0
P	Ag-26.5Cu-10Zn-0.1Ti	15.4	1.0	18.0(2)	1.3	34.5	0.5	30.0	1.3	32.0(1)	1.3
Q	Ag-22.8Cu-9Zn-4.7Ni-5Mn	9.1(2)	1.0 to 2.5	9.8	1.1	39.0(1)	0.5	32.2	1.25	29.0	1.5
-	Ag-27Cu-10Sn (std)	-	-	53.0	1.4	-	-	-	-	-	-
-	Ti-46.6Zr-5.3Ni-3.2Ag-4.5Be	-	-	15.0	0.7	-	-	-	-	-	-

1. Base metal failure. All other failures were in braze joint.

2., 3. Refer to number of tests if over one.

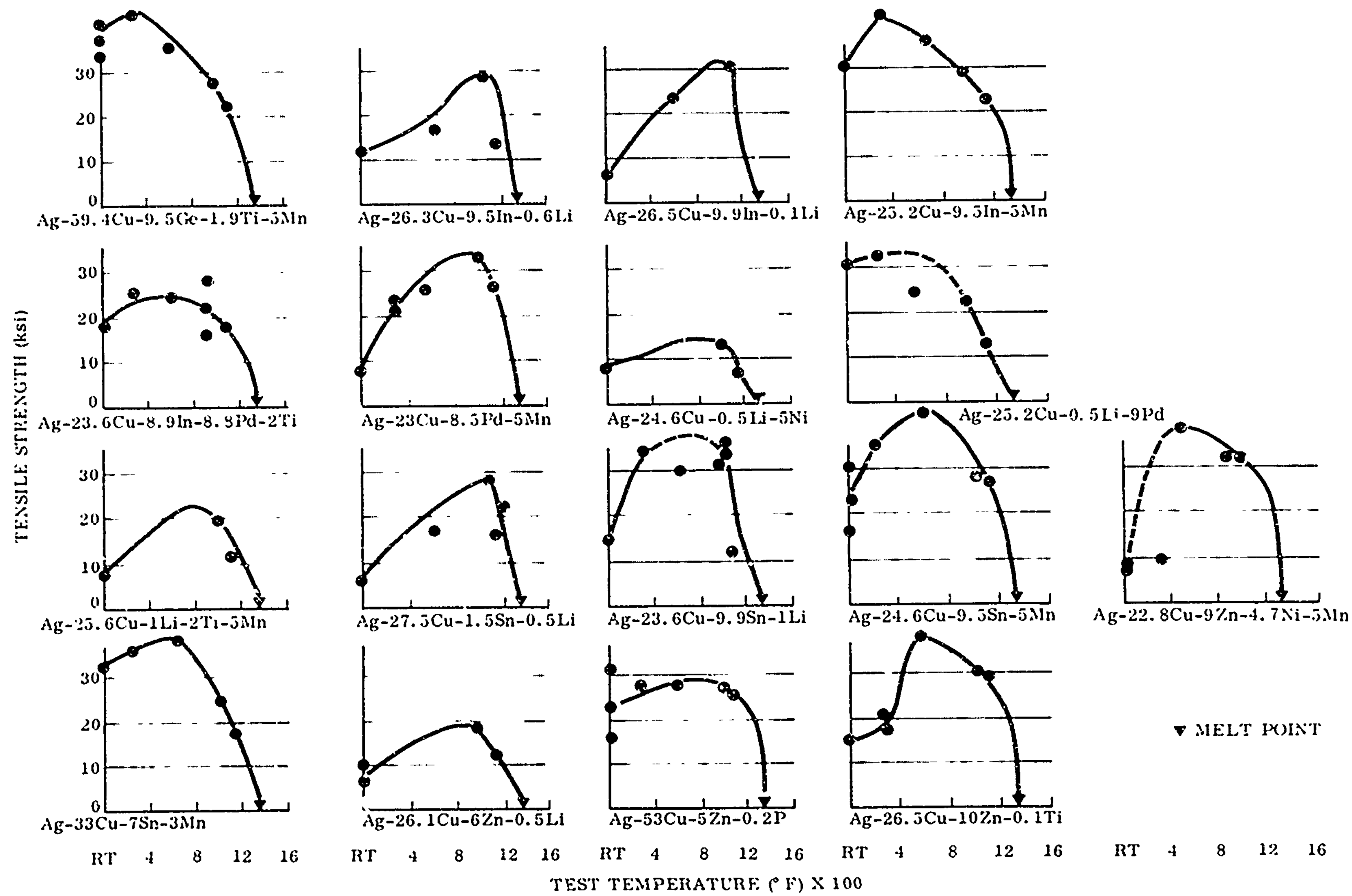


FIGURE 29. TENSILE STRENGTH OF CANDIDATE SILVER-BASE BRAZE ALLOYS

Because consistently low tensile strengths were found for candidate alloys G, I, and N (Ag-Cu-Li-Ni, Ag-Cu-Li-Ti-Mn, and Ag-Cu-Zn-Li) at room temperature, 1000, and 1100°F, these three compositions were excluded from further tests. The remaining 14 alloys were retained for further evaluation because they exhibited either promising strength characteristics or reproducibility of data.

Effect of Gap on Joint Strength

A comparison was made between joint-gap measurements and joint-strength values to study the effect of joint clearance for butt joints on specimen strength for all braze alloys. Strength versus gap values were plotted for four test temperatures, Figure 30 shows the relation. Clearance for the 600°F specimens was controlled by using 0.0005-inch spacers.

An examination of the data in Figure 30 shows that butt specimen joint clearance was generally between 0.0005 and 0.0015 inch. No definite trend with gap is indicated by the results; strength distributions are generally uniform within the 0.001-inch range of clearances shown. From this it appears that greater variation in gap would be required before changes or trends are established.

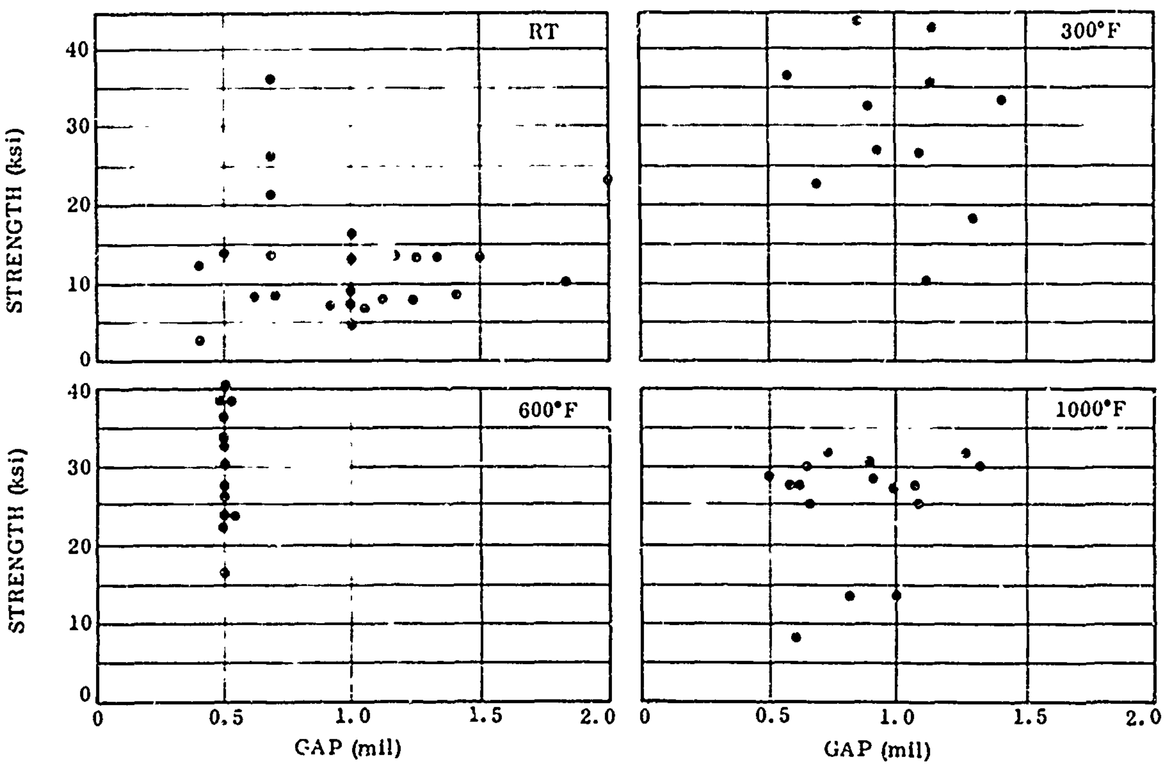


FIGURE 30. EFFECT OF GAP ON STRENGTH

6.3.2 Shear Strength Studies

Shear strength tests for candidate braze alloys were made with double-lap type specimens (Fig. 4). Alloy selections for these tests were based on a review of strength values for the 17 silver-base alloys used for butt-joint tests. For comparison, the promising titanium-base alloy (Ti-46.6Zr-5.3Ni-3.2Ag-4.5Be) and the standard alloy (Al-Cu-10Sn) were included.

Brazing parameters were the same as for butt-joint specimens - 1400°F for 10 minutes in argon using a heating rate of 50 degrees F/minute from 1000 to 1400°F. Testing was performed at room temperature, 300, 600, and 1000°F except for the standard titanium-base alloys which were evaluated at 300°F only. These two alloys were included so that tensile-to-shear ratios could be compared to other selected alloys. Alloy selections and shear stress results are presented in Table XXIV. In addition, a comparison of shear-to-tensile strength results for the 300°F specimens is presented in Figure 31 to show the relation between lap- and butt-joint brazements.

TABLE XXIV

SHEAR STRENGTH FOR DOUBLE LAP JOINTS

Specimen	Joint Shear Stress (ksi)				Tensile Stress in Base Metal (ksi)			
	Room Temperature	300°F	600°F	1000°F	Room Temperature	300°F	600°F	1000°F
A	10.5*	10.8*(3)	9.9	8.6*	67.0	58.4	56.0	43.0
D	11.2*	13.4(3)	9.8*	6.7	74.5	59.5	44.5	30.7
E	11.0*	12.0*(3)	8.8(2)	7.9(2)	59.0	56.0	41.4	39.3
H	10.8	14.0(3)	8.6	7.1	62.2	62.4	37.0	43.0
L	11.1	11.8*(3)	6.4	7.3*	72.5	53.0	43.0	41.5
M	10.5	8.5(3)	9.6*	7.7	70.0	57.7	44.5	35.0
O	11.5*	12.0(3)	10.0	8.4	69.0	42.0	32.0	30.2
Standard	-	11.6(3)	-	-	-	-	42.2	-
Ti-Zr	-	6.7(2)	-	-	-	-	25.2	-
Control+	-	-	-	-	71.6(2)	68.0(1)	57.0(1)	36.7(2)

* Base metal failure.
\+ Base metal specimens exposed at 1400°F for 10 minutes prior to test.
Note Numbers in parentheses denote number of tests if more than one. Lap length was 0.12 to 0.14 inch.

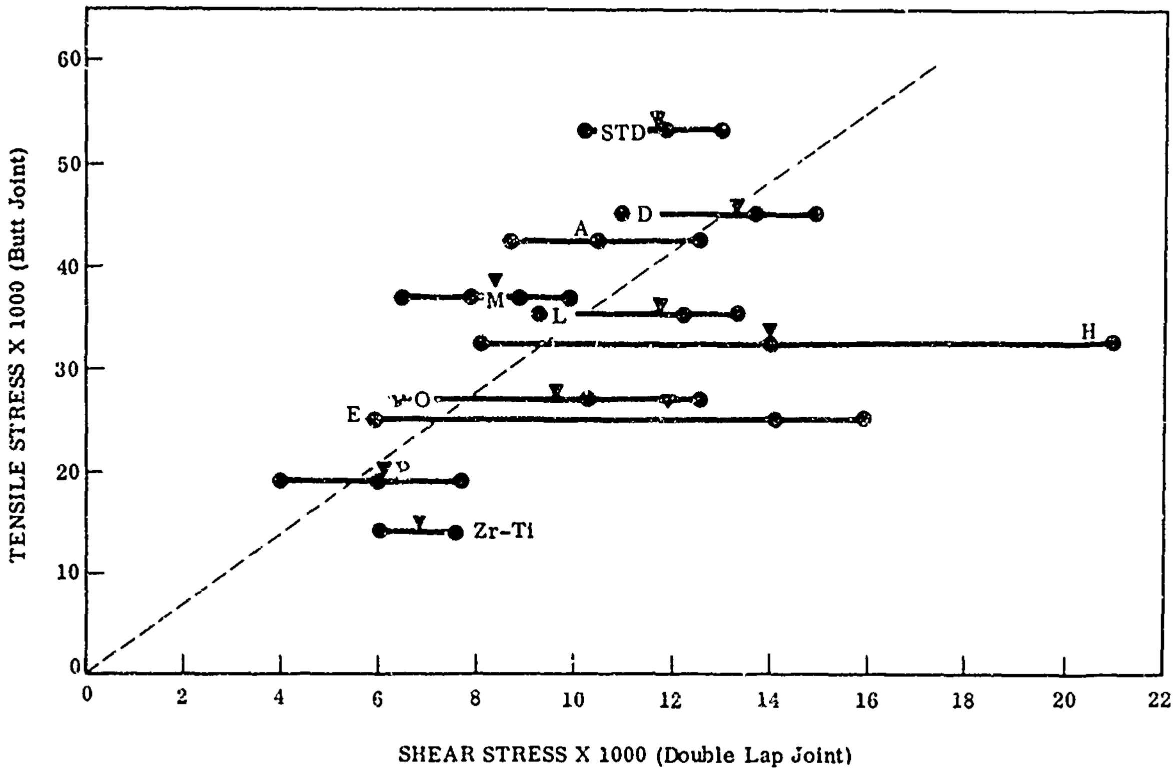


FIGURE 31. TENSILE VERSUS SHEAR STRENGTH AT 300°F

Both lap and butt joints show considerable scatter of strength data at room temperature and 300°F, but the data become more uniform as the test temperatures increase. This result is to be expected in view of the low ductility and high stiffness of beryllium at low temperatures, to which must be added the effects of stress concen trations caused by both types of joints.

The relation between joint shear and tensile stress at 300°F is shown for seven candidate silver-base alloys, the Ag-Cu-Sn standard alloy, and the promising zirconium-base alloy (Fig. 31). All data were plotted to show the scatter; average values are indicated by the delta mark.

From Figure 31, the butt- to shear-joint strength ratio appears to be 3.3 to 1; this value is shown by the broken line. Although the results presented show considerable scatter for alloy H and E, they do indicate that a close relationship exists between tensile and shear properties for beryllium brazements.

6.4 TOLERANCE OF ALLOYS FOR VARIATION IN CONDITIONS

The ability to wet and flow on beryllium under adverse braze conditions is a highly desirable feature of a braze alloy. Although an alloy may perform well for highly optimized braze parameters, its performance under less than optimum conditions may be grounds for its rejection. Therefore, the candidate alloys carried through were studied to determine their tolerance for variations in braze conditions.

The approach followed was to regulate two variables. The argon atmosphere quality and the degree of surface preparation. These variables were combined to effect three different braze conditions. A brief description of each is presented in succeeding paragraphs.

Condition A - Optimum Braze Condition

This included use of the most effective braze conditions that were selected or developed for the program. These conditions include optimum etching and rinsing procedures and gettered line argon plus additional argon scrubbing in the braze chamber by reaction with titanium fixturing and titanium wool plugs during the braze cycle.

Condition B - Optimum Cleaning and Gettered Line Argon Only

This arrangement was similar to Condition A, except that the additional scrubbing of braze chamber argon was deleted by removal of the titanium wool plugs and fixturing.

Condition C - Gettered Line Argon Only and Modified Cleaning

This condition was similar to Condition B, except that the beryllium coupons were cleaned only in the $HF-HNO_3$ etch and rinsed manually rather than using the optimized cleaning process. (The optimized cleaning procedure included etching in an ammonium bifluoride solution followed by a second etch in an $HF-HNO_3$ solution, and finally rinsing in an agitated deionized water bath. A complete description of the procedure is presented in Paragraph 2. 2. 3.)

The specimen selected for these tests was a T-type (Fig. 2). The base and vertical members are 0. 020-inch gage cross-rolled beryllium, 1. 0 inch long by 0. 25 inch wide. The alloy is placed on the base coupon at the end of the vertical member and capillary travel is monitored along the joint during flow tests.

Alloy selections for tolerance tests were based on a survey of joint strength data, metallographic analysis, and flow characteristics. From this survey, the seven most promising alloys were selected for study. In addition, the Ag-Cu-Sn standard and the most promising titanium-base alloy were included.

Brazing was performed at 1400°F for time periods up to 30 minutes. Test data were plotted to show the relation between time and flow distance; curves were drawn and results are shown in Figure 32.

The results in Figure 32 show that the flow of all alloys is reduced as less optimum conditions are applied. A discussion on the effect of the three sets of conditions on flow is contained in following paragraphs.

Condition A

For optimum conditions, all candidate alloys evaluated show that complete flow occurred within a period of from 7 to 11 minutes after reaching the 1400°F isotherm. Most alloys show a steady progress of flow; only alloy A (Ag-Cu-Ge-Ti-Mn) and Ag-Cu-Sn show cessation of flow under somewhat adverse conditions after 10 to 15 minutes. The standard alloy, included for comparison, requires the longest time to reach maximum flow.

Condition B

Maximum flow results for Condition B show alloys D, E, L, M, and the titanium-base alloy have a greater tolerance for less than optimum conditions than alloys A, O, H, and the standard alloy. Two alloys, L, and the titanium-base, achieved maximum flow in 23 and 21 minutes, respectively.

Condition C

For the poorest of test conditions used, alloy E shows the greatest flow. This is followed by alloys D, H, M, O, and the titanium-base alloy. Those showing the least tolerance are A and the standard alloy (Ag-Cu-Sn).

In summary, the tolerance of candidate alloys for changes in braze conditions can be described as follows:

- For optimum braze conditions, most candidate alloys reached maximum flow within 10 minutes.

- For fair braze conditions, alloys E, L, O, D, M, and the titanium-base are more tolerant than A, H, and the standard alloy.

- For poor braze conditions, alloys E and D appear best. The standard and A are least promising while the titanium-base and L, M, O, and H are rated as intermediates.

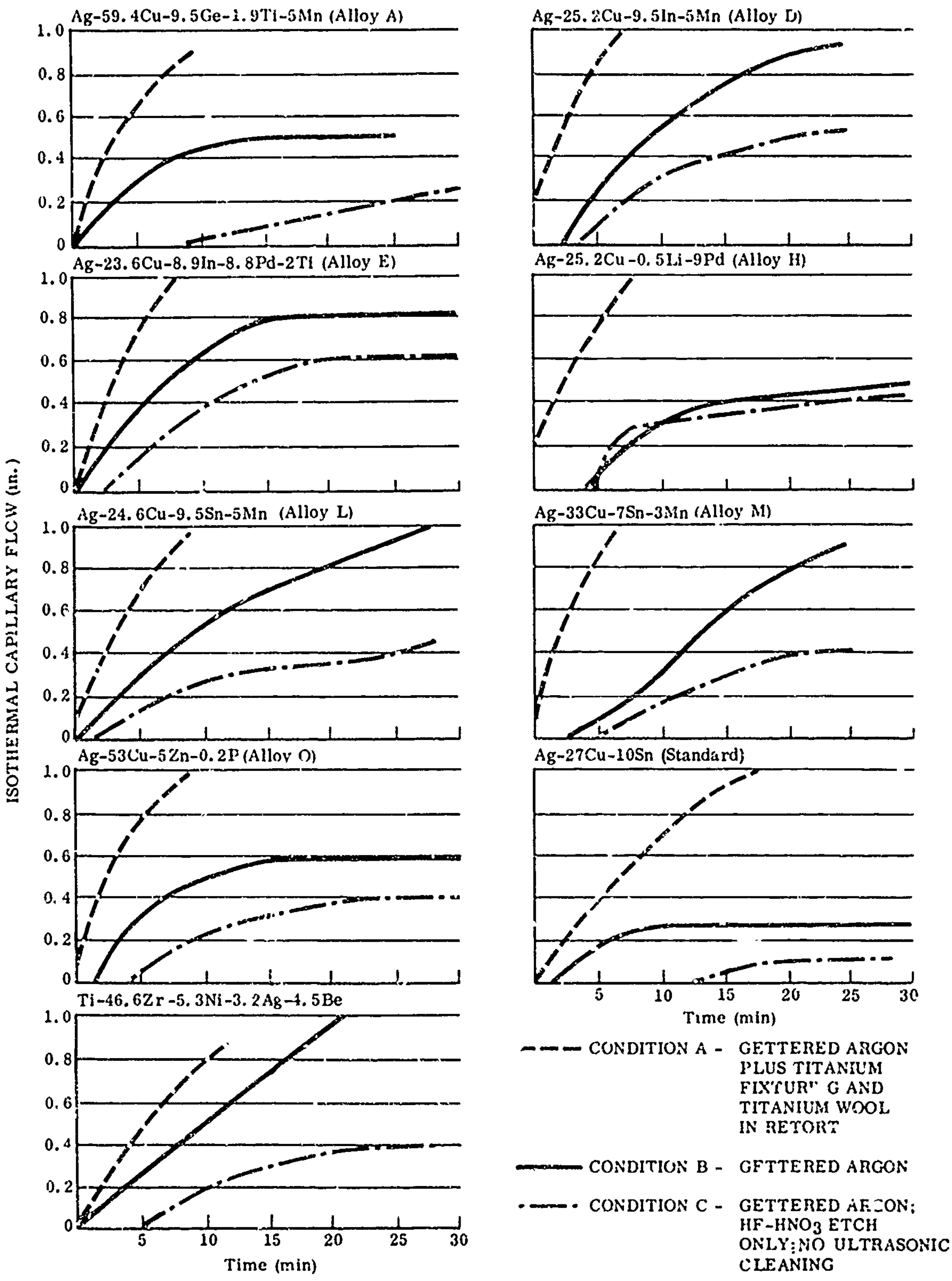


FIGURE 32. TOLERANCE OF ALLOYS FOR CHANGES IN CONDITIONS

6.5 HONEYCOMB SPECIMENS

All-beryllium simulated honeycomb specimens were brazed with eight of the most promising candidate silver-base braze alloys. The purpose in using a honeycomb type specimen was to evaluate the practical application of selected alloys. This type of specimen permitted further investigation of wetting, flow, filleting, and capillary travel on thin-gage beryllium for typical furnace braze procedures. Data generated from this study were used to further aid in the evaluation and screening of alloys for final selection.

Based on results for preceding evaluation tests, data were examined to select the most promising candidate alloys for brazing the honeycomb specimens. In addition, the Ag-Cu-Sn standard alloy was included for comparison. The alloys selected for this study are listed below.

Designation	Composition
A	Ag-59.4Cu-9.5Ge-1.9Ti-5Mn
D	Ag-25.2Cu-9.5In-5Mn
E	Ag-23.6Cu-8.9In-8.8Pd-2Ti
H	Ag-25.2Cu-0.5Li-9Pd
L	Ag-24.6Cu-9.5Sn-5Mn
M	Ag-33Cu-7Sn-3Mn
O	Ag-53Cu-5Zn-0.2P
Standard	Ag-27Cu-10Sn

Test specimens used for this study are described in Paragraph 2.2.2. Figure 2 shows the specimen components before braze and also a view of one as brazed. Assembly of parts for brazing is described in Paragraph 2.3.2. All eight samples were brazed together and assure equal conditions.

After cycle purging of the retort, brazing was performed as follows:

- Heat to 1200°F at a rate of 50 degrees F/minute and hold for 15 minutes. This operation controls thermal balance and permits outgassing to occur.

- In the next step, the temperature was increased to 1420°F at a rate of 25 degrees F/minute. Because of the large amount of beryllium surface area involved, a braze temperature of 1420°F was used to compensate for possible reduced flow from outgassing contamination. To ensure complete thermal equilibrium, the braze temperature was held for 15 minutes.

- The retort was removed from the furnace and cooled at a rate of 25 degrees F/minute to 600°F to prevent thermal shock.

An examination of the specimens after brazing indicated the braze atmosphere remained relatively good throughout the braze cycle; only a very small area showed discoloration due to contamination. Views showing the as-brazed specimens are presented in Figure 33. An analysis of the test results in terms of wetting, flow, filleting, and residue can be summarized as follows:

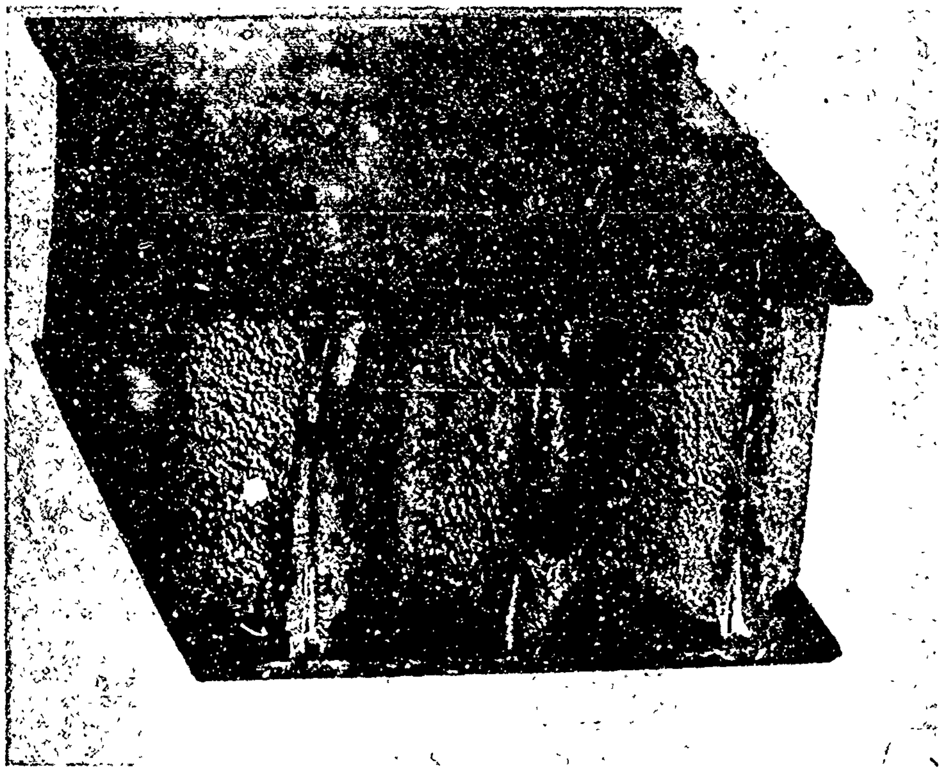
- Maximum properties (no residue, good wetting, flow, and filleting) for the D, L, M, and O alloys.
- Intermediate properties (slight residue, unbonded areas, good wetting and flow) for the A, E, H, and standard (Ag-Cu-Sn) alloys.

6.6 SUMMARY OF WORK DESCRIBED IN SECTION VI

Evaluation studies described in this section were conducted to analyze performance properties of the 33 silver-base alloys carried through from alloy development (Section IV). The optimized titanium-base alloy (Ti-46.6Zr-5.3Ni-3.2Ag-4.5Be) was tested to compare results to the silver-base alloys.

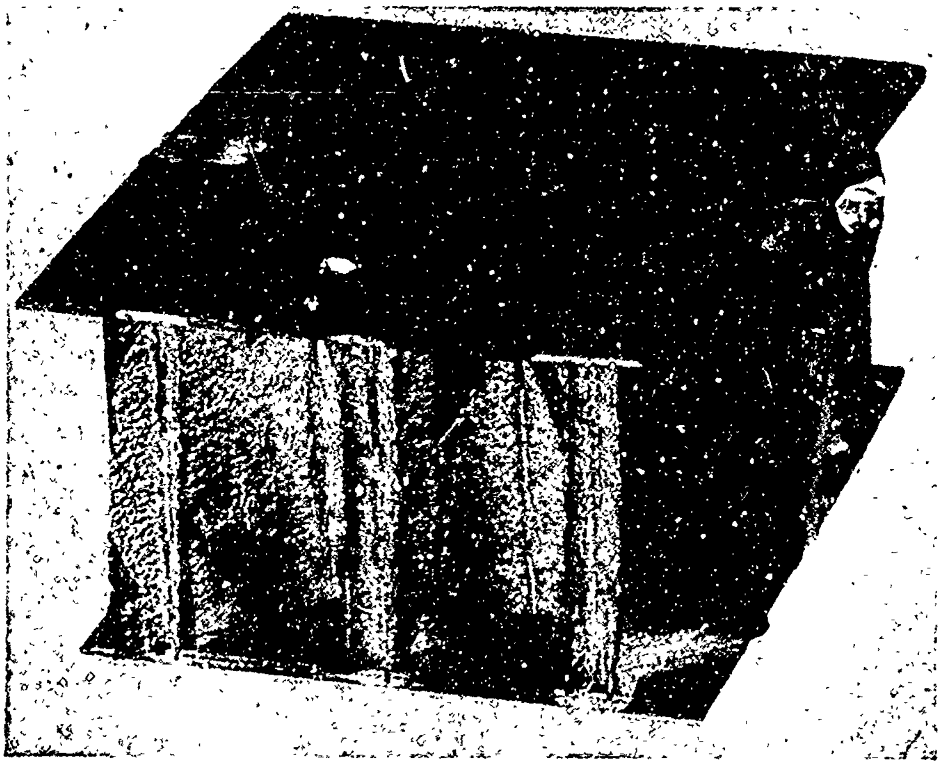
An investigation of capillary flow for the 33 silver-base alloys at 1400°F for a period of 10 minutes showed that 17 alloys reached the one-inch maximum flow. In the next step, joint structures for these 17 more promising alloys were examined. Special attention was paid to the degree of diffusion of braze alloy into beryllium and also to the formation of beryllide.

Mechanical strength of brazements was evaluated next. Butt and double-lap joints, brazed at 1400°F for 10 minutes, were tested at room temperature, 300, 600, 1000, and 1100°F. Butt specimens generally showed a greater scatter of results than the lap specimens. A comparison of joint strength to alloy composition indicates a relationship exists between the two; manganese and tin are present in the higher strength alloys whereas the lower strength alloys frequently contain lithium and zinc. Other elements exerted less well-defined effects on strength.



A.

Alloy A - Ag-Cu-Ge-Ti-Mn



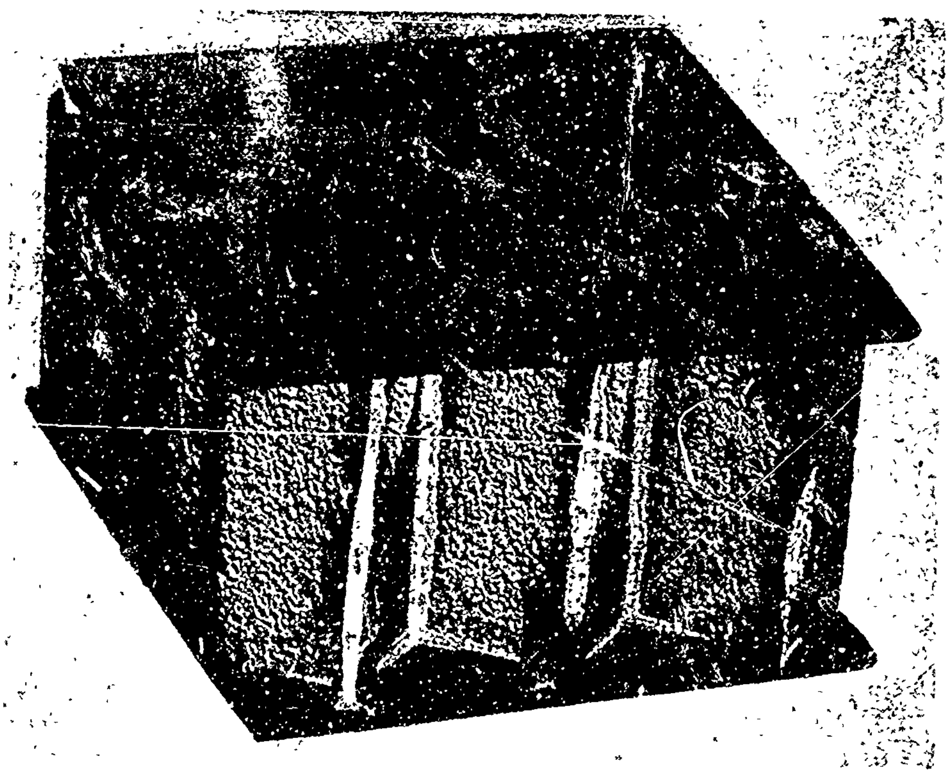
B.

Alloy D - Ag-Cu-In-Mn

FIGURE 33. SIMULATED HONEYCOMB SPECIMENS (Sheet 1 of 4)

C.

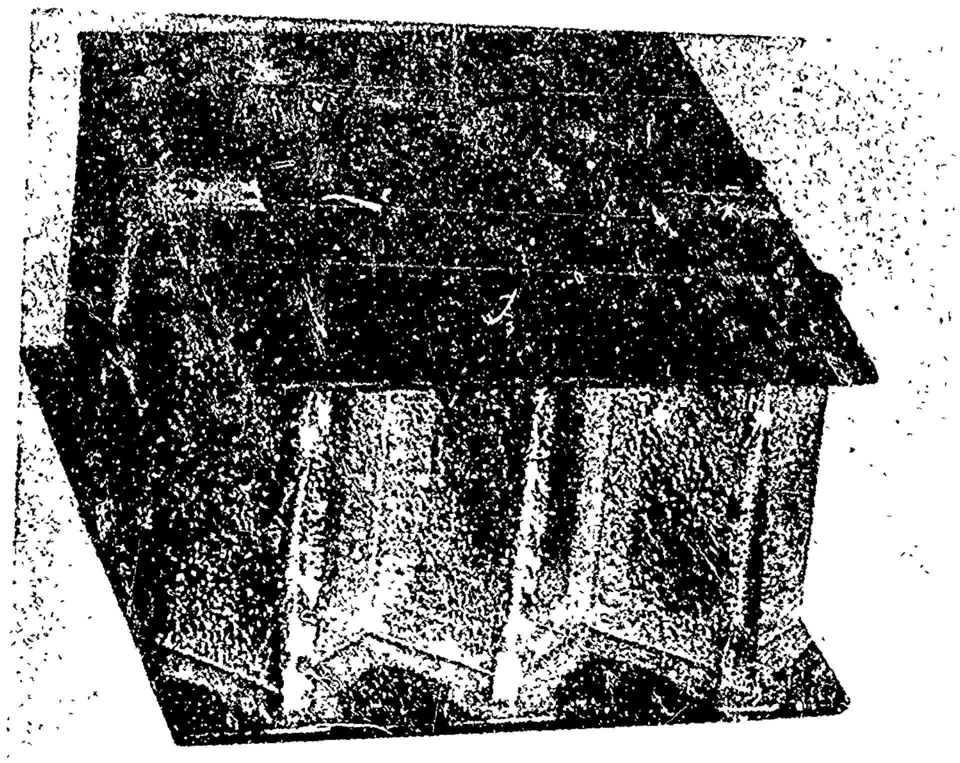
Alloy E - Ag-Cu-In-Pd-Mn



D.

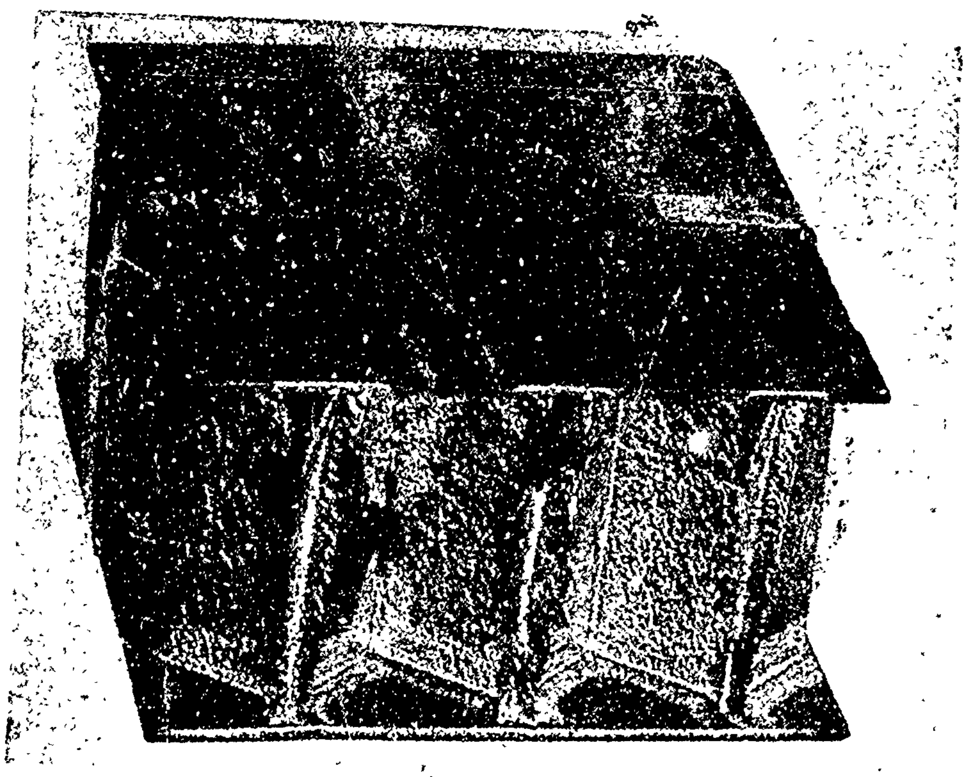
Alloy H - Ag-Cu-Li-Pd

FIGURE 33. SIMULATED HONEYCOMB SPECIMENS (Sheet 2 of 4)



E.

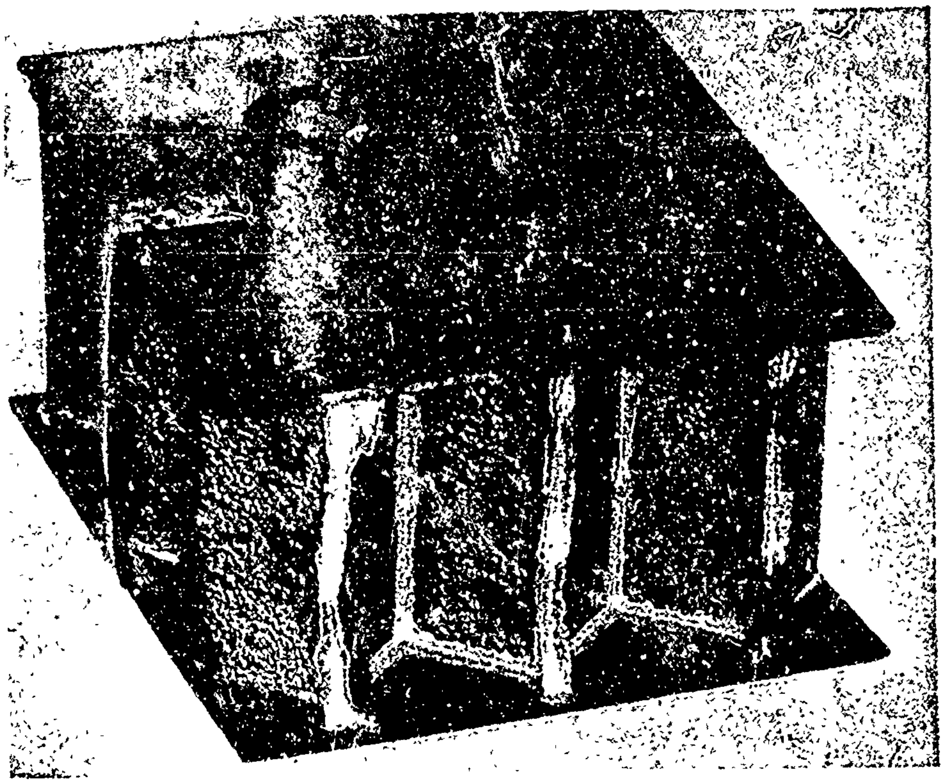
Alloy L - Ag-Cu-Sn-Mn



F.

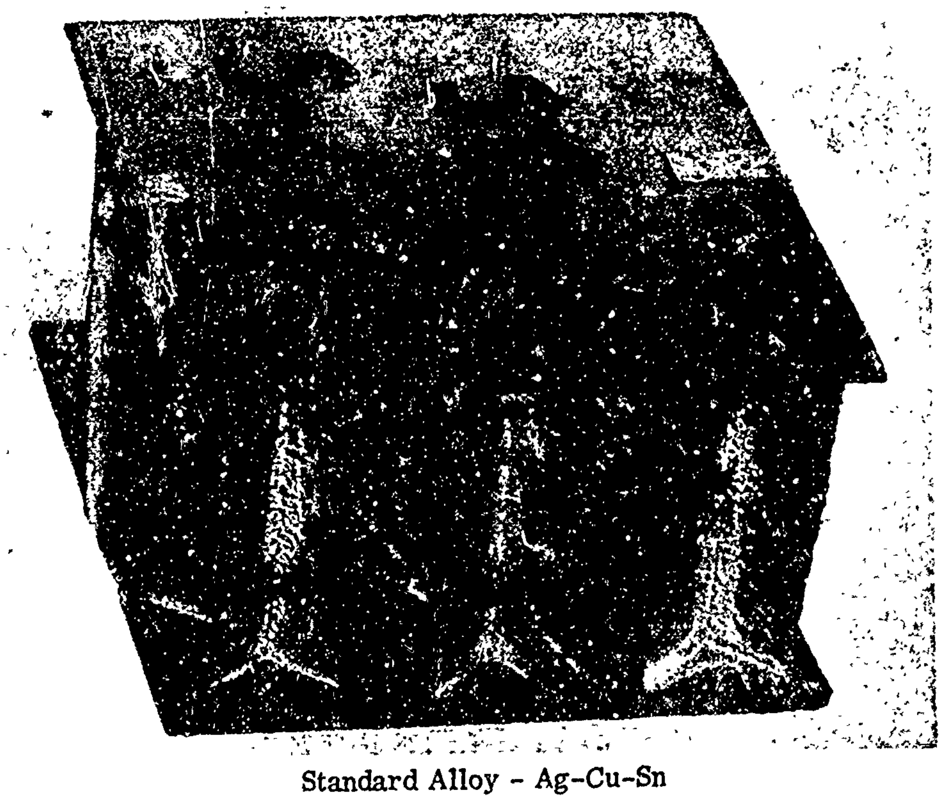
Alloy M - Ag-Cu-Sn-3Mn

FIGURE 33. SIMULATED HONEYCOMB SPECIMENS (Sheet 3 of 4)



G.

Alloy O - Ag-Cu-In-P



H.

Standard Alloy - Ag-Cu-Sn

FIGURE 33. SIMULATED HONEYCOMB SPECIMENS (Sheet 4 of 4)

Based on mechanical property tests, 7 of the 17 alloys evaluated were selected for tolerance studies and the brazing of typical honeycomb specimens. These studies were performed to develop data that would help in rating those alloys selected for recommendation.

The tolerance test results showed that alloy E (Ag-23.6Cu-8.9In-8.8Pd-2Ti) had excellent tolerance for adverse braze conditions while alloys H (Ag-25.2Cu-0.5Li-9Pd) and A (Ag-59.4Cu-9.5Ge-1.9Ti-5Mn) exhibited the least tolerance.

Honeycomb specimens were made to study the practical application of the seven finalist alloys. An analysis of the brazed specimens showed good correlation with the results of the tolerance tests.

SECTION VII

FINAL RATING OF BRAZE ALLOYS

During alloy evaluation where five different types of tests were performed (Section VI), those compositions showing the best results for any one test series were selected for the next set of tests. Of the 33 original silver-base alloys selected for qualification (Section V), the number for final rating had been reduced to seven; these are listed below.

Alloy Designation	Composition
A	Ag-59.4Cu-9.5Ge-1.9Ti-5Mn
D	Ag-25.2Cu-9.5In-5Mn
E	Ag-23.6Cu-8.9In-8.8Pd-2Ti
H	Ag-25.2Cu-0.5Li-9Pd
L	Ag-24.6Cu-9.5Sn-5Mn
M	Ag-33Cu-7Sn-3Mn
O	Ag-53Cu-5Zn-0.2P

In addition, the optimized titanium-base alloy (Ti-46.6Zr-5.3Ni-3.2Ag-4.5Be) is included in the final selection. This alloy was not compared directly with the silver-base alloys as it had been included based on merits of a titanium-zirconium base system.

In appraising the seven silver-base alloys, six factors were considered:

- Capillary flow distance
- Metallographic analysis of joint structures
- Tensile and shear braze joint strength
- Tolerance of alloys for adverse braze conditions
- Alloy residue
- Practical application of alloys to typical structures (honeycomb specimens)

These six factors were based on four major characteristics desired in a braze alloy.

- Brazing Properties. These properties include two conditions; capillary flow for capillary T-joints and completeness of alloy melting (residue). Capillary flow for the T-joint specimens was rated by measurement of flow distance. Whereas the amount of residue for candidate alloys was either slight or completely absent, this characteristic was rated qualitatively.

- Interaction with Beryllium. This factor was regarded as critical and rating was allocated in terms of interdiffusion between the braze alloy and beryllium.

- Joint Strength. Ratings for joint strength were based on tensile (butt joint) stress and shear (double-lap joint) stress for different temperature levels to 1100°F.

- Tolerance for Adverse Braze Conditions. This factor included two conditions; the flow achieved in capillary joints for different braze conditions and the wetting and flow exhibited by typical honeycomb specimens. For capillary flow specimens, those with the greatest flow distance were rated highest. For honeycomb specimens, braze flow was judged qualitatively; the highest rating was given those specimens exhibiting complete flow and preferred filleting characteristics.

Attempts to rank the seven silver-base braze alloys by using a series of points awarded for different attributes were unsuccessful. The basic reason for this lack of success was that the alloys were so close in performance that the ranking depended on the relative importance attached to each attribute. For example, if maximum tolerance for adverse conditions was desired to braze a complex part where atmosphere control was difficult, alloy E would be chosen. On the other hand, if interdiffusion and beryllide formation must be minimized (as in foil structures), alloy O would be favored. Again, alloy A with the highest indicated tensile shear strength has the lowest tolerance and also exhibits an intermediate amount of interaction with beryllium.

In analyzing data for the silver-base braze alloys, no specific advantage was uncovered to favor retention of alloy H in the final selection. Although it flowed the full one inch at 1400°F in 10 minutes to qualify for inclusion in the final selected alloys (Table XXV), excessive interdiffusion and beryllide formation, low shear strength at

TABLE XXV

COMPARATIVE REVIEW OF FINAL ALLOY SELECTIONS

Alloy Designation	Composition	Capillary Flow		Butt Joint Tensile Stress (ksi)				Double Lap Joint Shear Stress (ksi)				Metallography (in. x 10^{-4})		Tolerance	
		T-Joints (in.)	Residue	Room Temperature	300°F	600°F	1000°F	Room Temperature	300°F	600°F	1000°F	Inter-action	Beryl-lide	Capillary Flow (in.)(1)	Honeycomb
A	Ag-59.4Cu-9.5Ge-1.9Ti-5Mn	0.95	None	36.4	42.0	34.0	28.8	10.5	11.0	9.9	8.6	1.0	1.0	0.35	Good-fair
D	Ag-25.2Cu-9.5In-5Mn	1.0	Slight	30.0	44.3	36.0	28.0	11.2	13.4	9.8	6.7	2.0	2.0	0.65	Excellent
E	Ag-23.6Cu-8.9In-8.8Pd-2Ti	1.0	None	18.4	26.3	23.2	22.6	11.0	12.0	8.8	7.9	1.0	1.5	0.75	Very good
H	Ag-25.2Cu-0.5Li-9Pd	1.0	Slight	13.1	32.4	23.8	24.6	10.8	14.0	8.6	7.1	3.5	4.0	0.40	Fair-good
L	Ag-24.6Cu-9.5Sn-5Mn	1.0	Slight	24.0	35.0	41.0	29.0	10.5	11.0	9.6	7.7	2.0	2.0	0.55	Excellent
M	Ag-33Cu-7Sn-3Mn	1.0	None	24.0	36.0	39.4	24.6	11.5	8.2	10.0	8.4	2.0	1.0	0.60	Excellent
O	Ag-53Cu-5Zn-0.2P	1.0	None	24.7	27.0	27.4	27.8	11.1	10.0	6.4	7.3	1.0	1.0	0.60	Good

Note: All data are based on 1400°F/10-minute braze except tolerance at 1400°F/20 minutes and honeycomb at 1420°F/15 minutes.

1. Mean flow for two braze conditions at 1400°F.

1000°F, and poor tolerance for changes in brazing conditions are sufficient grounds for its exclusion. Each of the remaining six may have special application areas. The following discussion of their individual characteristics will attempt to bring out these special features. The selected titanium-base alloy is also included in this discussion.

- Alloy A (Ag-59.4Cu-9.5Ge-1.9Ti-5Mn). Although it has poor tolerance for flow under adverse brazing conditions, this alloy provides the highest consistent strengths found over the temperature range of room to 1000°F. Interaction with beryllium is intermediate. The poor tolerance and intermediate reaction are not desirable for honeycomb brazing, as confirmed by the rating in Table XXV.

- Alloy D (Ag-25.2Cu-9.5In-5Mn). Good tolerance but shows high reactivity with beryllium. Good performance on honeycomb substantiates these results, but long braze cycles should be avoided and use to 1000°F may not be desirable.

- Alloy E (Ag-23.6Cu-8.9In-8.8Pd-2Ti). Excellent tolerance supported by good performance on honeycomb. Reactivity is minor and strengths are moderate. Recommended as a good all-round alloy.

- Alloy L (Ag-24.6Cu-9.5Sn-5Mn). Intermediate tolerance, moderate reactivity, and somewhat above average strength. No special characteristics, but performance on honeycomb was very good.

- Alloy M (Ag-33Cu-7Sn-3Mn). Intermediate reactivity, good tolerance and intermediate strength combine to make this alloy a useful all-round alloy also. Its performance on honeycomb was excellent supporting its general rating.

- Alloy O (Ag-53Cu-5Zn-0.2P). Least reactivity with beryllium of any of the silver-base alloys. Has good tolerance but below average strength. Good performance on honeycomb.

- Ti-Zr Alloy (Ti-46.6Zr-5.3Ni-3.2Ag-4.5Be). This alloy is characterized by limited interreaction with the beryllium, lower than average tolerance, and below average strength. Its melt and flow points (1370 to 1390°F) make brazing in the temperature range of 1400°F extremely critical. Its flow performance on honeycomb was poor. This alloy would be desirable for thin gage sections where negligible interaction is essential.

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APPENDIX A

OUTGASSING STUDY ON BERYLLIUM

The vacuum outgassing of 0.020 inch thick beryllium sheet (Log 4802 Sheet HR363) was performed as requested at 1600°F. Two samples from the same sheet were analyzed to determine the effect of surface etching.

The tests were performed with the AeroVac AVA1 partial pressure analyzer using a baked chamber evacuated with an ion pump. Specimens 0.1 inch wide by 5 inches long were installed in the TSP cartridge and sealed into the chamber. The chamber was evacuated, without bakeout, to 10^{-8} Torr. The ion pump was then turned off and the chamber pressure was observed to equilibrate at about 1×10^{-6} Torr. A scan showed the background gases to be almost entirely CH_4 and CH_3 that is characteristic of ion pumped systems. There was no trace of either an air leak or water vapor.

The etched specimen was resistance heated and held at approximately 1600°F for about 3 minutes. The total pressure increased from 1.0×10^{-6} to 2.0×10^{-5} Torr. The ion pump was not restarted during the specimen outgassing period in order to maintain nearly constant conditions during the 2-1/2 minute interval required for scanning with the partial pressure analyzer.

The pump was then started and the chamber evacuated to 10^{-8} prior to repeating the same procedure with the unetched specimen. When the unetched specimen was heated, the pressure increased from 1.2×10^{-6} to 2.4×10^{-4} Torr.

The results of these measurements are shown in the following table:

M/E	Probable Gas	$\times 10^{-8}$ Torr Unetched	Etched*	Background
28	CO^+	650	200	3
44	CO_2^+	120	40	1
16	$CH_4^+ - O^+$	265	50	14
15	CH_3^+	200	35	12
14	$CH_2^+ - CO^{++}$	35	5	2
12	C^+	115	12	1
18	H_2O^+	1	1	1
17	OH^+	1	1	1

N_2^+ and N^+ are possible, but are thought to contribute only a small part of the pressure.

* Surface etching was done with a hot (200°F) Phosphoric-Chromic-Sulfuric acid solution. Approximately 0.002 inch was removed from each surface in 5 minutes.

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11 SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
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13 ABSTRACT Six silver-base braze alloys (including some high in copper), with a high tolerance for adverse braze conditions, were developed to give maximum capillary flow in unplated beryllium sheet without flux at 1400°F to avoid loss of base metal wrought properties. In addition, one titanium-base alloy showed promise for brazing beryllium as low as 1400°F.

Silver-base alloys were developed and optimized, by selected additions, for brazing in argon, starting from the silver-copper eutectic. The sequence used in the development and evaluation of braze alloys included determination of melt-flow temperatures and flow distance on flat plates of beryllium sheet, capillary flow over a vertical distance of one inch for isothermal conditions, analysis of braze joint structures, and strength of brazed joints.

The tolerance of alloys for changes in braze conditions was studied by varying the argon quality and methods of beryllium surface preparation, and by evaluating the practical application of alloys to beryllium honeycomb. Surface preparation techniques and additions that react unfavorably with beryllium or the atmosphere were found to influence flow considerably. Selected silver-base alloys and typical joint shear strengths at 1000°F are listed: Ag-59.4Cu-9.5Ge-1.9Ti-5Mn, 8.6 ksi; Ag-25.2Cu-9.5In-5Mn, 6.7 ksi; Ag-23.6Cu-8.9In-8.8Pd-2Ti, 7.9 ksi, Ag-24.6Cu-9.5Sn-5Mn, 7.7 ksi; Ag-33Cu-7Sn-3Mn, 8.4 ksi, Ag-53Cu-5Zn-0.2F, 7.3 ksi. Titanium alloys were studied. Compositions based on the titanium-zirconium base system were optimized to braze beryllium below its recrystallization temperature. The composition Ti-46.6Zr-5.3Ni-3.2Ag-4.5Be exhibited good wetting and capillary flow properties as low as 1400°F. Joint strength was slightly lower than for silver-base alloys. Aluminum-base braze alloys were also investigated, however, acceptable wetting and flow could not be achieved.

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14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Brazing						
Beryllium						
Silver-base alloys						
Titanium-base alloy						
Capillary flow						
Alloy optimization						
High tolerance for braze condition						
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