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ASD TR 61-313
PART II

DEVELOPMENT OF LOW TEMPERATURE BRAZING ALLOYS FOR TITANIUM HONEYCOMB SANDWICH MATERIALS

TECHNICAL REPORT NO. ASD TR 61-313, PART II

January 1963

Directorate of Materials and Processes
Aeronautical Systems Divisions
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 7351, Task No. 735102

(Prepared under Contract AF33(616)-7249
by Solar, A Subsidiary of International
Harvester Company, San Diego, California;
W. C. Troy, author.)

NOTICES

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FOREWORD

This report was prepared by the Research Division of Solar under USAF Contract No. AF33(616)-7249. The contract was initiated under Project No. 7351, "Metallic Materials," Task No. 735102, "Welding and Brazing of Metals." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Mr. P. L. Hendricks initially acting as project engineer and replaced by Mr. R. E. Bowman on 14 December 1961. This work was a continuation of work under the same title which was reported as ASD Technical Report 61-313 dated December 1961.

The present report covers work conducted from 1 December 1961 to 30 November 1962.

Personnel who contributed to the project include, A. G. Metcalfe, Associate Director; W. C. Troy, Supervisor of Advanced Research; C. W. Haynes, Research Engineer; R. Hutting and E. B. Mack, Research Technicians.

ABSTRACT

For brazing titanium under 1100° F, binary information formed the basis of selecting two promising ternary basis alloys for development, (1) Ag-Cu-Ge and (2) Ag-Cu-Sn. Melt and flow behavior was favorable with Ag-Cu-Sn base alloys, but work was discontinued because of excessive joint brittleness related to intermetallic films formed on the substrate. Alloys based on the Ag-Cu-Ge ternary also formed intermetallic films, but the joints had intermediate strength which justified evaluation. Average shear strength of lap joints varied from 10,750 psi for aged specimens to 11,900 psi for specimens after brazing at 1100° F. These marginal properties would justify only limited application of the Ag-Cu-Ge based alloys.

This technical report has been reviewed and is approved.

I. Perlmutter

I. PERLMUTTER
Chief, Physical Metallurgy Branch
Metals and Ceramics Laboratory
Directorate of Materials & Processes

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I. INTRODUCTION

Braze joining of titanium alloy lightweight structures usually is performed at temperatures corresponding with the solution heat treating temperature for the titanium alloy. Suitable silver-base alloys are available for braze joining within the range of 1300 to 1600° F, and the aging treatment can be applied subsequently to the brazed structure.

A preferred procedure would be one based upon braze joining the structure at a temperature corresponding with the aging temperature for the titanium alloy. In this case, the components of the structure would have been fabricated from forms which previously had received the solution heat treatment. This sequence would include metallurgical advantages such as quench delay time control during independent solution quenching of components. Further metallurgical advantages would include the opportunity for cold reduction between solution treatment and aging.

A process for brazing titanium at aging temperatures would offer numerous operating advantages. These include more precise dimensional control, less expensive tool equipment, and reduced retort costs.

This report describes the work performed during the second year (1 December 1961 to 30 November 1962) on development of a process that would realize the benefits of low temperature brazing of titanium. In the program for the first year (Ref. 1), gold-base filler alloys were determined to satisfy many of the requirements, but joint toughness was marginal because of the brittle interfacial films developed by the gold-base filler metal. The marginal properties persisted despite extensive variations in alloy composition and brazing procedure. Accordingly, work was discontinued on gold-base filler alloys, and the work in the second year concentrated on silver-base alloys because the Ti-Ag compound (69.25% Ag) was known to be ductile.

In development of the silver-base filler alloy, the first consideration was selection of solute elements to depress the melting temperature of silver so that braze alloy flow was a possibility within the 950 to 1100° F temperature range. Binary alloy information (Ref. 2) and previous experience directed attention to copper,

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germanium, and tin as solute elements. Aluminum and magnesium are potentially useful, but brazing experience at low temperatures has shown extreme difficulty in overcoming refractory surface films on the braze alloy. Even with alloys prepared under protective atmospheres and brazed in vacuum, sporadic behavior indicated that aluminum and magnesium would be impractical in any appreciable concentrations. Low-melting elements such as indium and gallium depress the melting temperature by a series of peritectic reactions with intermediate phase formation, and eutetic solidification does not occur until the indium or gallium content is in excess of about 60 percent. Silver-tin alloys are similar to the indium and gallium alloys, with the exception that eutectic melting occurs at much more dilute concentrations; namely, at approximately 30 percent tin. For this reason, tin was grouped with copper and germanium as potentially effective melting point depressants.

Copper and germanium both form eutectics with silver; the Ag-Cu eutectic lies at 28.1 percent copper and 1434°F, and the Ag-Ge eutectic occurs at 19 percent germanium and 1204°F. The copper-germanium system is characterized by a fairly extensive terminal solid solubility of germanium in copper, followed at higher germanium concentrations by a series of intermediate phases and a eutectic at 39.1 percent germanium and 1184°F between germanium and an unstable intermediate phase containing 30.2 percent germanium. According to the binary eutectic temperatures noted above, reasonable solute concentrations in the Ag-Cu-Ge ternary offered promise of a liquidus surface minimum that would be compatible with the requirements for low temperature brazing of titanium.

The reactivity of various solute metals with the titanium substrate is of vital importance. The reactivity factor determines the dominant or effective interfacial phase that will occur between the filler metal and the substrate. A ductile Ag-Ti intermediate phase would be ideal for joint toughness, but it was judged that only an experimental program could evaluate the interface situation in polycomponent systems.

II. EXPERIMENTAL PROGRAM

2.1 PROCEDURES

Uniform preparation and evaluation procedures were used throughout the work as described in the following sections.

2.1.1 Filler Alloy Preparation

The usual weight of filler alloy ingots was 15 grams. Early melts were prepared in high-density recrystallized alumina crucibles and were induction heated under pure argon. To obtain improved control of the melting temperature, the majority of the remaining ingots were prepared in the hot-wall vacuum retort shown in Figure 1. After initial outgassing of the charge at low temperatures, a pressure of one micron of mercury maximum was obtained in the retort. When the change contained volatile components, an appropriate pressure of argon was maintained in the retort.

The final series of alloys covering the Ag-Cu-Ge ternary eutectic composition was arc melted under argon in the apparatus in Figure 2. This unit had provision for evacuation and cycle purging with argon before the melt was started. Each button was flipped and remelted three times to assure homogeneity.

2.1.2 Thermal Analysis

Liquidus and solidus temperatures were determined on selected alloys using the cold-wall vacuum chamber illustrated in Figure 3. This apparatus contained provision for heating a recrystallized alumina crucible in a graphite container heated by electrical resistance. By external manipulation, the sheathed thermocouple probe was lowered into the melt, and the thermocouple output was recorded on a strip chart recorder during cooling.

Anomalies in the cooling curve occurred at low temperatures in the apparatus due to the ingot separating from the crucible. In certain alloys, eutectic solidification occurred in the same temperature region as the cooling curve anomalies.

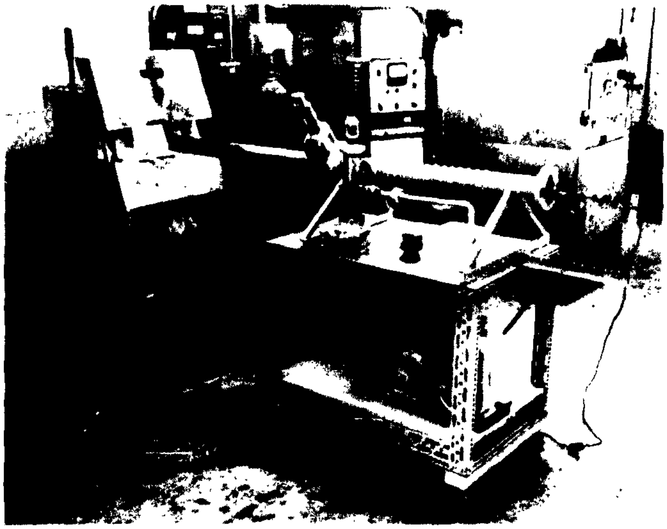


FIGURE 1.

HOT-WALL VACUUM RETORT USED FOR MELTING EXPERIMENTAL ALLOYS

FIGURE 2.

INERT ATMOSPHERE ARC MELTING APPARATUS

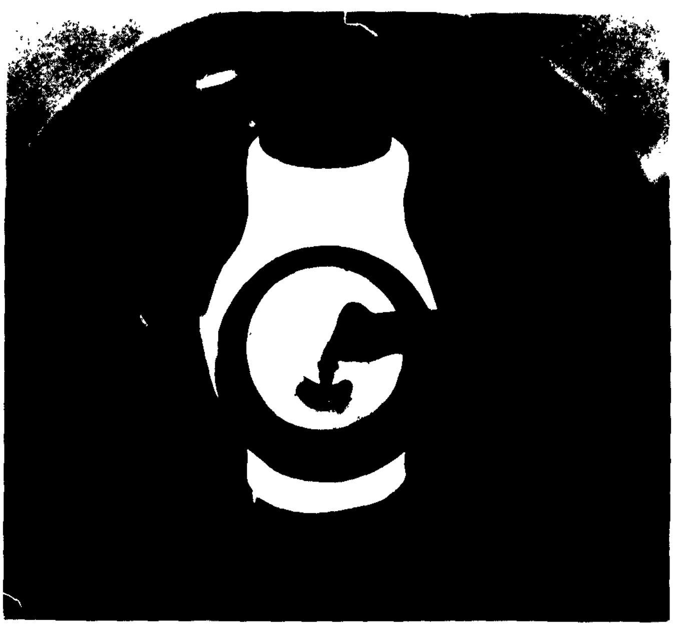


FIGURE 3.

THERMAL ANALYSIS APPARATUS
This view through the port of the cold-wall vacuum chamber shows a thermocouple immersed in a 1/2-inch diameter crucible containing the melt.

Accordingly, an alternate procedure was used wherein a small particle of filler alloy (approximately 3/16 inch) was suspended on the junction of a chromel-alumel thermocouple made from 0.008 inch wires. This combination was placed in a 1/2-inch diameter Vycor tube flushed with argon, heated above the liquidus temperature, and allowed to cool. Slight contamination in the system prevented metallurgical wetting between the thermocouple and the molten particle and retained the molten spheroid on the thermocouple junction. Figure 4 describes specimen preparation and assembly for this thermal analysis procedure.

2.1.3 Braze Alloy Performance Tests

Brazing at temperatures below 1100°F is unusually difficult because the normally helpful oxide decomposition reactions are virtually absent at these temperatures. At higher temperatures, brazing of titanium is aided by the self-cleaning characteristic of the substrate whereby minute surface films are dissolved while heating for brazing. Previous work (Ref. 1) indicated that the self-cleaning phenomenon occurs below 1100°F, but progress of the mechanism is so slow that filler metal flow must be preceded by a holding time varying from a few minutes to over one hour.

Because of the unpredictable holding time before initiation of flow, previous work was done in a Vycor retort so that alloy behavior could be observed. Many of the brazing tests in the present program were performed in a similar apparatus. Figure 5 illustrates adaptation of the 4-inch diameter Vycor tube to the vacuum system. Under this arrangement, braze alloy behavior was evaluated at pressures under one micron of mercury, measured in the diffusion pump inlet at a point about 15 inches from the specimen.

At a later stage in the program, the use of a Vycor retort was considered to be possibly inimical to filler alloy behavior in view of the stringent purity requirements. A leached and refined high silica ceramic contains a minor percentage of lower melting glasses, and such glasses are known to evolve chemisorbed and/or decomposition products during heating above 1000°F.

Since products evolved by the ceramic retort would interfere with filler alloy behavior, the occurrence of such contamination was evaluated by varying the holding time for a typical specimen in the Vycor retort. This test represented the view that a steady source of contamination such as a ceramic retort would lead to accumulative

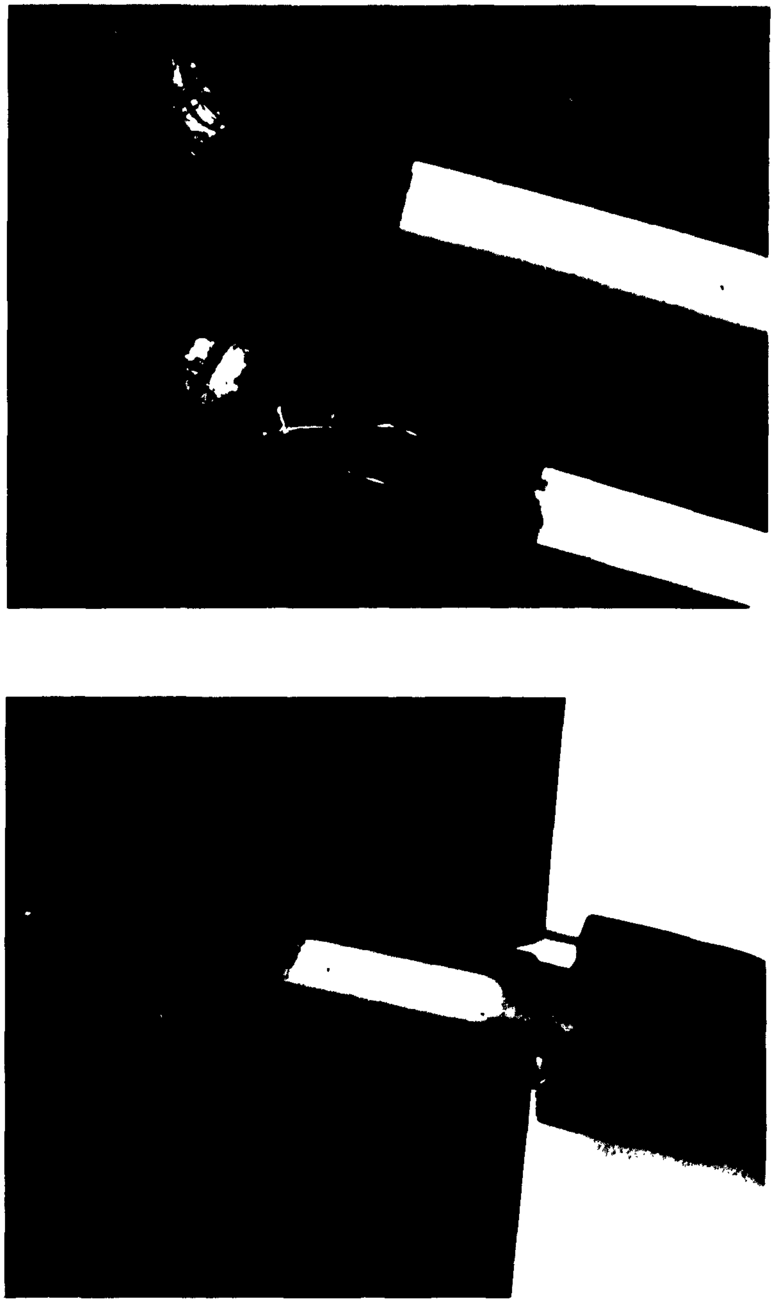
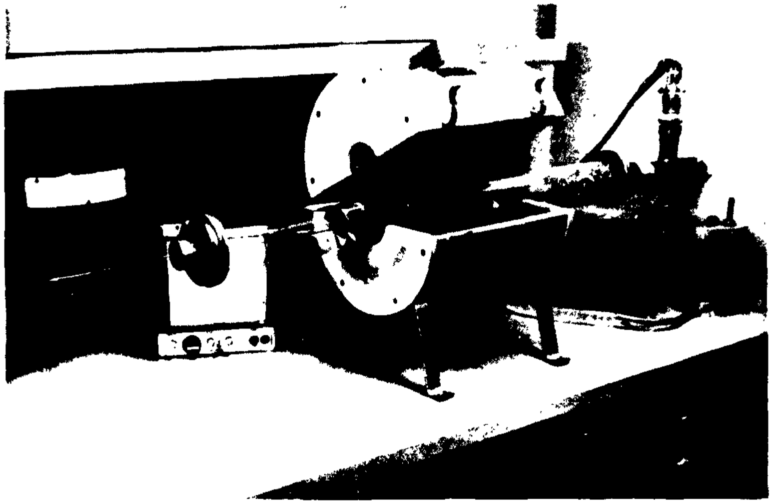


FIGURE 4. METHOD FOR THERMAL ANALYSIS
After assembly of the alloy particle and thermocouple (top photograph), they are placed in the Vycor tube (lower photograph) for torch heating under argon.



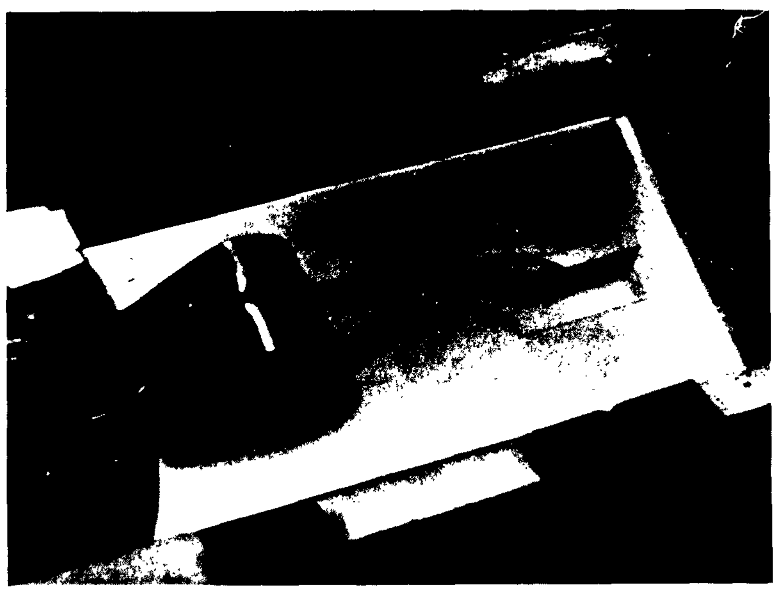


FIGURE 5. HOT-WALL VYCOR RETORT USED FOR BRAZING TESTS
The apparatus in the upper photograph was capable of operation under vacuum or inert atmosphere. The lower view through the Vycor tube represents typical assembly of the thermocouple probe with the specimen.

effects on specimens heated for several hours. Two tests were made with heating times of 30 minutes and 5 hours, respectively, using an Ag-Cu-Ge alloy on typical tee specimens heated under vacuum at 1200°F. The slowly heated specimen developed visible tarnish films which prevented alloy flow, but the rapidly heated specimen remained free from visible contamination and flow of the braze alloy was favorable.

Unfavorable behavior of the slowly heated specimen prompted an adverse evaluation of the ceramic retort from the viewpoint of contamination. In addition, the large volume and surface area of the retort in relation to the surface area of the active specimen were unfavorable for minimizing specimen contamination. A further unfavorable feature was the presence of ceramic thermocouple insulators in the hot portion of the retort.

To correct the above aspects of braze alloy evaluation in the ceramic retort, later evaluations were made in a 1/2-inch diameter retort consisting of a blind Type 302 stainless tube with thermocouples attached to the outside. This arrangement reduced the ratio of retort area to specimen area and permitted removal of all ceramics from inside the retort. Procedure included pickle cleaning of the inside of the retort after each usage. Figure 6 schematically illustrates this arrangement and typical specimens used in the 1/2-inch diameter retort.

Favorable alloy flow experience with the small diameter metal retort confirmed, at least to some extent, the assumptions pertaining to the ceramic retort. A corollary of this experience is that earlier evaluations in the ceramic retort may have been adversely affected to some extent by the procedure, despite the low pressure maintained during the tests.

2.1.4 Brazed Joint Evaluation

Tee Specimens

The initial survey of a large number of experimental specimens consisted simply in placing a particle of the alloy on a tee specimen prepared from two 1-1/4-inch by 3/4-inch pieces of 0.010 inch thick Ti-6Al-4V alloy sheet. The two members of the tee specimens were TIG welded at the ends, pickled in a mixture of nitric and hydrofluoric acids, distilled water rinsed, and dried. Before heating the specimen

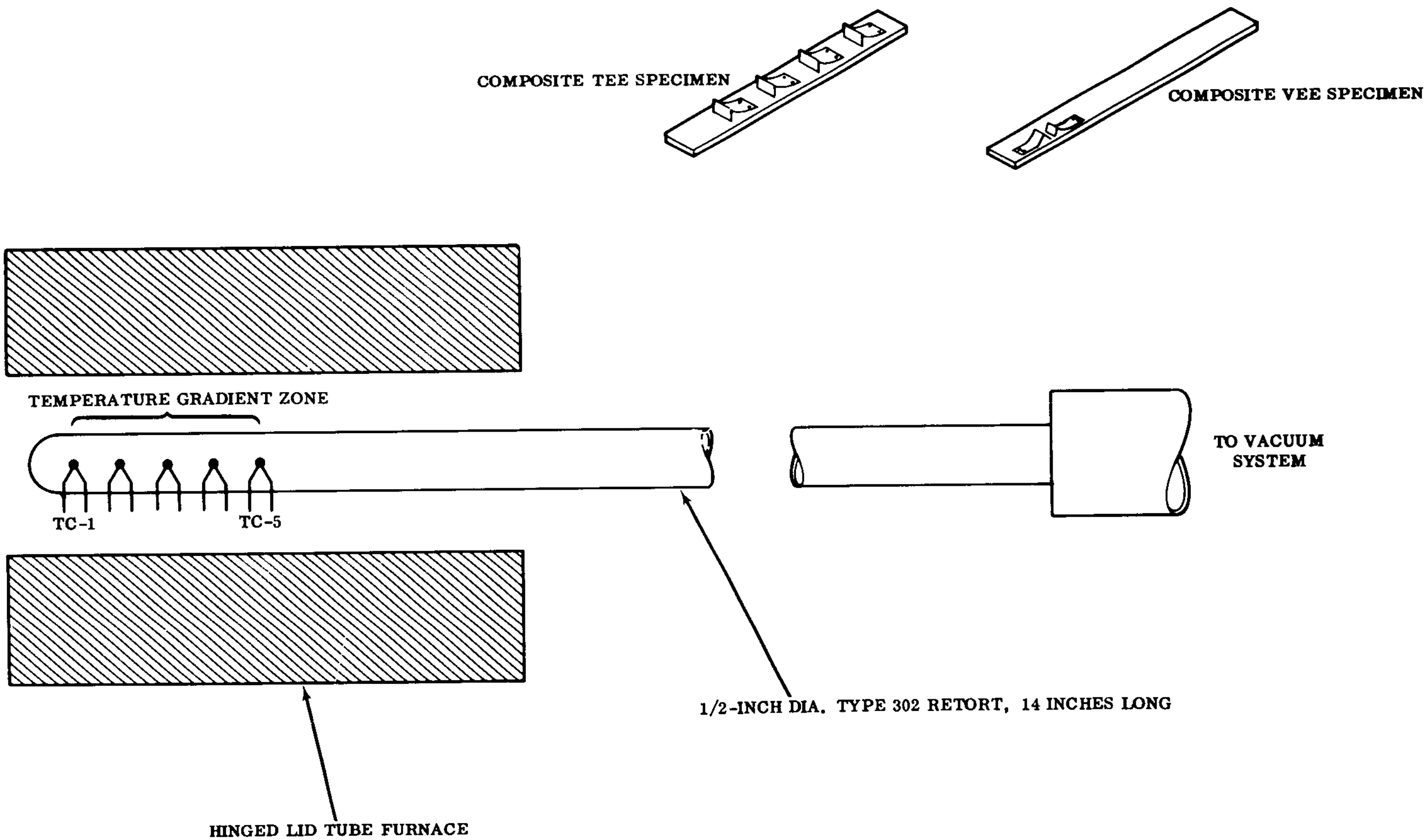


FIGURE 6. SCHEMATIC SKETCH OF METAL RETORT USED FOR BRAZING TESTS
The composite specimen was positioned within the temperature gradient portion of the retort, thus evaluating a series of temperatures in each furnace run.

for brazing, the retort was heated to 600°F under vacuum and cycle purged with gettered argon. Response of the individual alloys was varied but not consistently characteristic of the individual alloys. In some cases, the particle appeared completely refractory and gave no evidence of melting even at temperatures 200°F above the liquidus. In other cases, the alloys melted into a ball, wetted the substrate beneath the ball, but did not flow or form fillets. Other forms of alloy behavior included ideal fillet formation, or the formation of thin films which wetted the entire specimen with virtually no fillet formation. Examples of these types of filler alloy behavior appear in later photographs describing typical alloys.

Tee specimens were used also to evaluate the effect of filler alloy particle size, influence of binders, and effectiveness of brazing under inert atmosphere.

Tension tests were performed on 1-4-inch long tee specimens prepared from the 1-1/4-inch long specimens. The leg of the tee was held in a mechanical clamp and a clevis type fixture engaged the cross of the tee to apply the tension load. Stress was computed empirically from the load divided by the cross sectional area of the leg of the tee. Figure 7 illustrates a typical room temperature test in progress using a Type W Hounsfield tensiometer at a constant strain rate of 0.070 inch per minute. Elevated temperature tensile tests of the specimens were performed by the dead weight loading method illustrated in Figures 8 and 9.

Tensile Lap Shear Tests

Miniature single-shear lap joints (1/4 inch wide by 0.080 inch lap) were fabricated from 0.010-inch thick Ti-6Al-4V alloy, brazed and tested at room temperature and elevated temperature.

2.2 EXPERIMENTAL ALLOYS

2.2.1 Ag-Cu-Ge Base Alloys

To determine the optimum ternary composition from the viewpoint of minimum melting temperature and minimum liquidus-solidus spread, the alloys listed in Table I were prepared. The compositions studied indicate an effort to approach the optimum composition from well established binary eutectics; namely, Ag-Cu at 28.1 percent copper and Ag-Ge at 19.0 percent germanium.

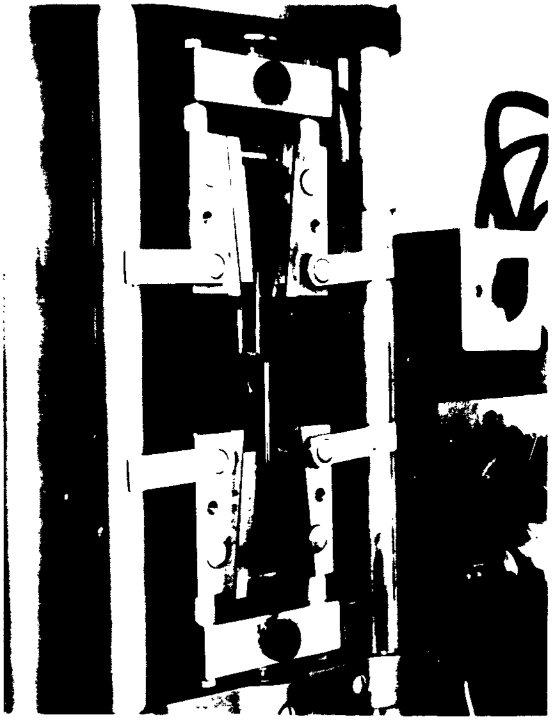


FIGURE 7.

ROOM-TEMPERATURE TENSION TEST OF TEE SPECIMEN The specimen is contained in the loading fixtures between the testing machine chucks.

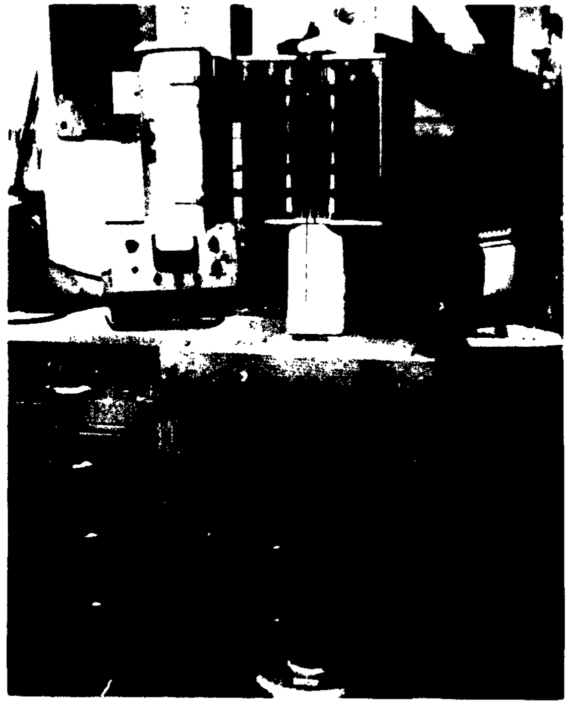


FIGURE 8.

ELEVATED-TEMPERATURE TENSION TEST OF TEE SPECIMENS

FIGURE 9.

LOADING FIXTURE FOR TEST ILLUSTRATED IN FIGURE 8.

TABLE I

Ag-Cu-Ge ALLOYS RELATED TO TERNARY EUTECTIC

Alloy No.	Composition	Remarks
106	Ag-10.5Cu-12Ge	Metallographic examination
107	Ag-25Cu-12Ge	Metallographic examination
108	Ag-10.5Cu-19Ge	Metallographic examination
109	Ag-28Cu-19Ge	Metallographic examination
110	Ag-30Cu-12Ge	Metallographic examination. Solidification range: 1340° to 1050°F
123	Ag-20Cu-20Ge	Metallographic examination. Solidification range: 1130° to 9[illegible]°F.
126	Ag-20Cu-15Ge	Metallographic examination. Solidification range: 1240° to 980°F.
127	Ag-20Cu-25Ge	Metallographic examination. Solidification range: 1170° to 980°F.
128	Ag-15Cu-20Ge	Metallographic examination. Solidification range: 1180° to 980°F.

For the alloys listed in Table I, constitution is reported in Figures 10 through 12 to illustrate, respectively, a nearly eutectic alloy (No. 123), a silver-rich alloy (No. 128), and a copper-rich alloy (No. 110). Alloy 128 (Ag-15Cu-20Ge) contained considerable light-colored phase believed to be the fairly extensive silver-rich terminal solid solution. In Figure 12 (Ag-30Cu-12Ge), the dark-etching Cu-Ge compound phase occupied a dominant portion of the structure. Finally, the minimum liquidus alloy of those studied (Fig. 10, Ag-20Cu-20Ge) showed evidence of extensive eutectic solidification both structurally and by thermal analysis, and this composition was viewed as an interim approach to the eutectic composition.

Alloy Additions to Ag-20Cu-20Ge Alloy

Modifications of the Ag-20Cu-20Ge base alloy included the following additions: titanium, magnesium, lithium, columbium, zirconium, and vanadium. The purpose

FIGURE 10.

ALLOY 123: Ag-20Cu-20Ge

Unetched

Mag. 250 X

Melting Range: 1130° to 980°F

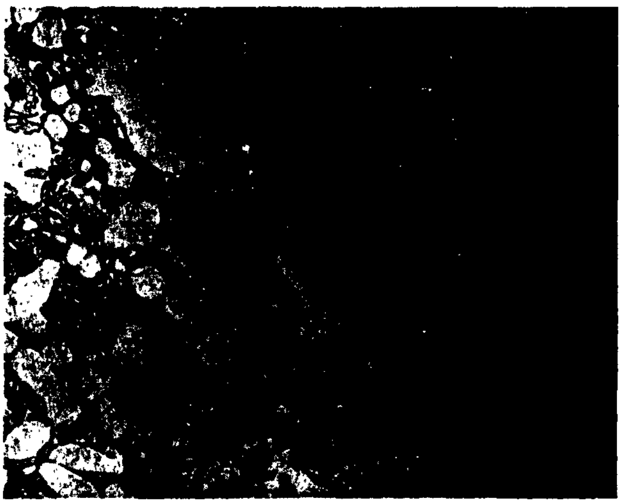


FIGURE 11.

ALLOY 128: Ag-15Cu-20Ge

Nital etched

Mag. 250 X

Melting Range: 1180°F to 980°F

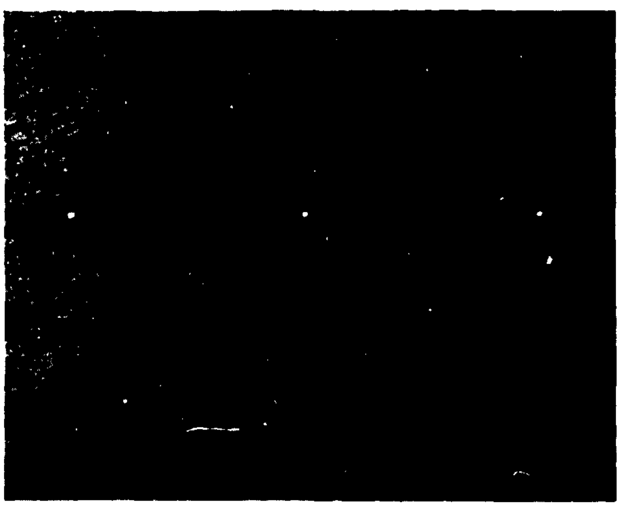


FIGURE 12.

ALLOY 110: Ag-30Cu-12Ge

Nital etched

Mag. 250 X

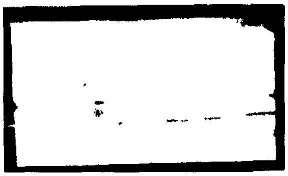
Melting Range: 1340° to 1050°F

of studying these additions was to assess their effectiveness in improving the wetting and flow and fillet forming characteristics of the alloy. Melting was done in recrystallized alumina crucibles under vacuum, with the exception of the magnesium and lithium alloys which were prepared under gettered argon. Identification is contained in Table II, and filler alloy behavior is illustrated in Figure 13, Alloys 137 to 162.

TABLE II

MODIFIED Ag-Cu-Ge ALLOYS

Alloy No.	Cu	Ge	Composition	Ag
137	20	20	2.0Mg	Balance
142	20	20	10Av-0.2Li	↑
145	20	20	1.8Li	
147	20	20	1.0Ti	
152	20	20	0.1Ti	
159	19	19	4.0Mn	
160	20	20	0.2V	
161	20	20	0.2Cb	
162	20	20	0.2Zr	
163[1]	20	20	--	
164	18	18	9.7Pt-0.3B	↓
165	20	20	10Au-0.1Ti	Balance



ALLOY 137

Ag-20Cu-20Ge-2Mg

ALLOY 160

Ag-20Cu-20Ge-0.2V

ALLOY 142

Ag-20Cu-20Ge 10 Au-0.2Li

ALLOY 161

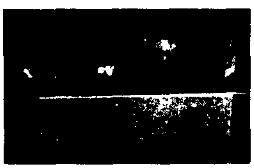
Ag-20Cu-20Ge-0.2Cb

ALLOY 145

Ag-20Cu-20Ge-1.8Li

ALLOY 162

Ag-20Cu-20Ge-0.2Zr



ALLOY 147

Ag-20Cu-20Ge-1.0Ti

ALLOY 163

Ag-20Cu-20Ge MELTED IN Ta CRUCIBLE

ALLOY 152

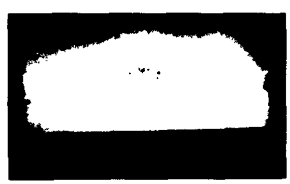
Ag-20Cu-20Ge-0.1Ti

ALLOY 164

Ag-18Cu-18Ge 9.7Pt-0.3B

ALLOY 159

Ag-19Cu-19Ge-4Mn



ALLOY 165

Ag-20Cu-20Ge 10Au-0.1Ti

FIGURE 13. MELT AND FLOW CHARACTERISTICS OF MODIFIED Ag-Cu-Ge ALLOYS

Due to the adverse effect of certain contamination believed to reside in the filler alloy particle itself, an unmodified melt of Ag-20Cu-20Ge alloy was prepared in a tantalum-lined crucible to isolate the effect of the refractory crucible. The melt wet the tantalum liner and may have picked up an undetermined amount of tantalum. The alloy did not show improved behavior in the tee-specimen wetting test (Alloy 163 in Fig. 13).

The low melting Au-Ge eutectic (673 F) prompted the addition of a minor percentage of gold to the Ag-Cu-Ge alloy despite the known brittleness of Au-Ti intermediate phases. Alloy 142 (Ag-20Cu-20Ge-10Au-0.2Li) and Alloy 165 (Ag-20Cu-20Ge-10Au-0.1Ti) were prepared, and their performance is represented by specimens in Figure 13. A significant difference between the two alloys is the titanium addition in Alloy 165. This addition has benefited alloy behavior in a number of cases, and it is believed responsible for the favorable performance of Alloy 165.

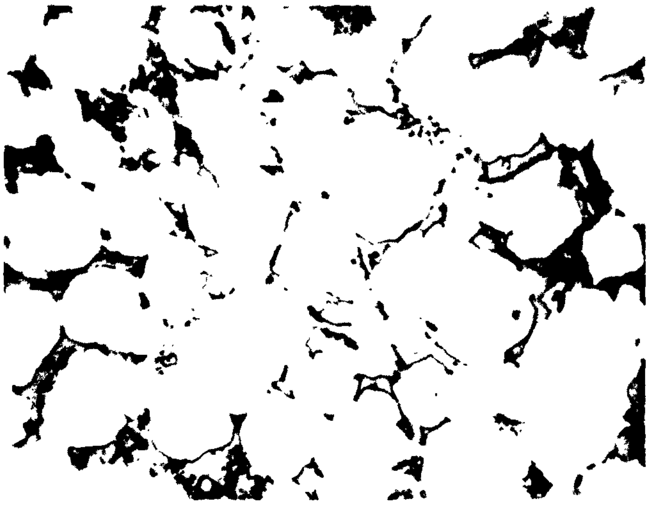
Although boron is not a melting point depressant for silver, it is an effective depressant for other metals such as platinum. Accordingly, a boron addition was made in the form of the Pt-B eutectic to assess a possible reduction in melting range. The resulting alloy (No. 164) has the composition Ag-18Cu-18Ge-9.7Pt-0.3B, and its behavior is illustrated in Figure 13. This modification of the Ag-Cu-Ge alloy was not evaluated as affording improved flow or fillet characteristics.

Melting Behavior of Ag-Cu-Ge Alloys

In most of the tee specimen tests described in Figure 13, a substantial portion of the filler alloy particle apparently remained unmelted as a refractory residue. This situation occurred even when the brazing temperature exceeded the liquidus by approximately 300°F. To describe this refractory residue more adequately, the section illustrated in Figure 14 was prepared through a residual particle of Alloy 168. The microstructure of the particle residue at 50X (Fig. 14) and 750X (Fig. 15) can be contrasted with the nearly eutectic structure of the original alloy at the same magnifications in Figures 16 and 17. The preponderance of the light-etching silver-rich solid solution phase indicates probable liquation of the Cu-Ge low-melting phase, leading to a stable residue too refractory to melt at the brazing temperature. Preferential reactivity of copper and germanium with the titanium substrate may be a further factor contributing to silver-rich residue. The observed performance of the alloy emphasized the desirability for conformity with the eutectic composition to minimize the melting range.

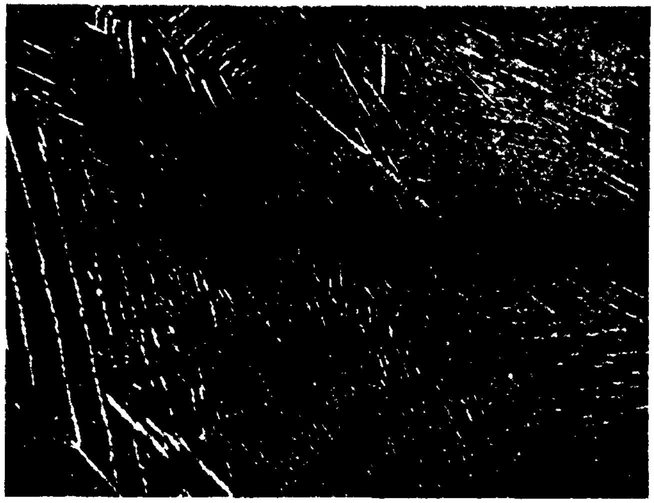
Mag. 50 X Etchant: $(NH_4)_2S_2O_8$

FIGURE 14. UNMELTED RESIDUE OF ALLOY 168



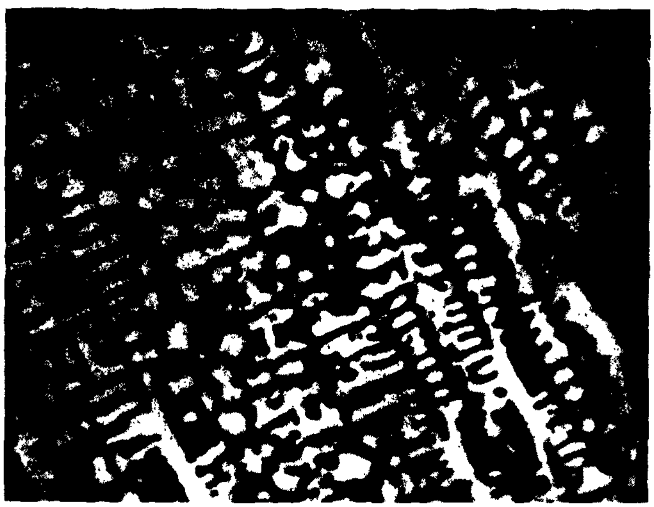
Mag. 750 X Etchant: $(NH_4)_2S_2O_8$

FIGURE 15. STRUCTURE OF PARTICLE SHOWN IN FIGURE 14



Mag. 50 X   Etchant: $(NH_4)_2S_2O_8$

FIGURE 16. MACRO STRUCTURE OF ALLOY 168 INGOT



Mag. 750 X   Etchant: $(NH_4)_2S_2O_8$

FIGURE 17. STRUCTURE OF ALLOY 168 INGOT
The contrast between the constitution shown here and that in Figure 15 is due to liquation leading to the residual particle.

Effect of Particle Size in Ag-Cu-Ge Alloy

The melting behavior of coarse particles at various temperatures was evaluated by gradient heating the composite tee specimen illustrated in Figure 6. Filler alloy particles (1/16 to 3/32 inch) were placed adjacent to tee specimens on the composite shown in Figure 18, and the composite was gradient heated in the metal tube retort to furnish temperatures from 905° to 1105°F under the time conditions noted. Subsequent similar tests are described in Figures 19 and 20, which cover a wider range of temperatures and various time relationships.

The tests described in Figures 18 through 20 established that coarse particles were capable of forming suitable fillets at temperatures in the region of 1080°F. Some refractory residue remained on the specimens, independently of the brazing temperature. A further indication from the tests is that fillet formation is favored by rapid heating and by the use of relatively low holding temperatures.

A light tack weld held the alloy particles to the tee specimens in Figures 18 through 20, and visible contamination at the weld prevented alloy flow on the 1105°F specimen in Figure 18. In subsequent tests, a clip held the alloy particle in place to avoid possible weld contamination. Figure 21 illustrates favorable filler alloy performance under these conditions at 1115°F. In the specimen at the center of the figure, the alloy flowed to form a satisfactory fillet; on the specimen at the right of the figure, the alloy flowed exclusively into the capillary under the clip. A photomicrograph of favorable fillet flow on the center specimen is shown in Figure 22.

At a slightly lower temperature (1085°F) a repetition of the above test resulted in virtually no alloy flow, as shown in Figure 23. The filler alloy particle coalesced and slightly wetted the substrate. Although the temperature was within the flow range for the alloy, fillet flow did not occur, probably due to a transient contamination. These observations lead to the view that 1/16 to 3/32-inch particles show favorable flow characteristics, and anomalous behavior usually is related to contamination.

The effect of finer particle size variations was assessed by preparing a composite specimen with particle sizes in the range from 1/8 inch to -50 + 100 mesh. Composite vee specimens shown in Figure 6 were used for these tests, but furnace equipment was operated to furnish a uniform temperature rather than a gradient. Behavior of the various particle sizes is shown in Figure 24.

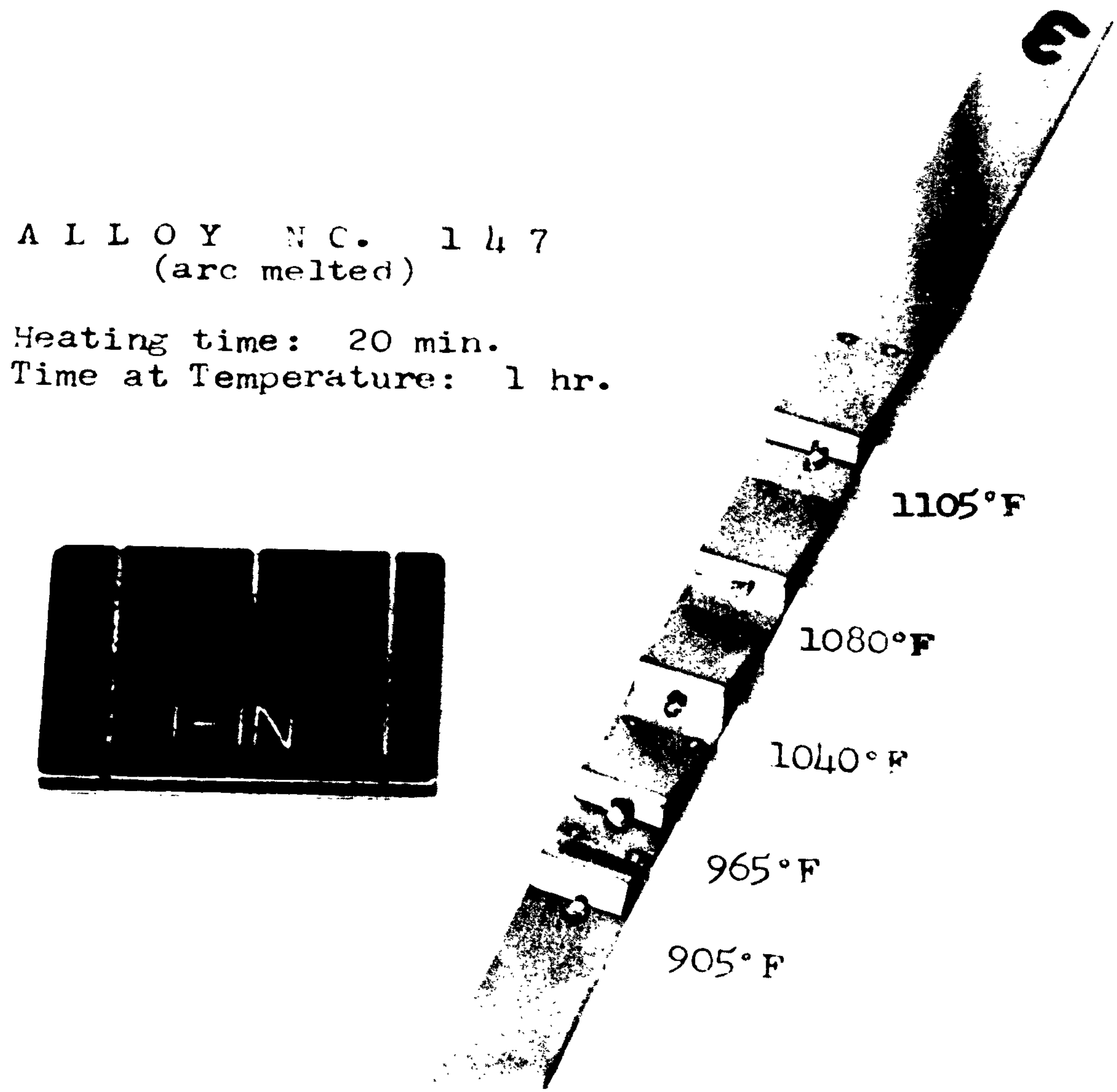


FIGURE 18. FLOW BEHAVIOR AT VARIOUS TEMPERATURES (Ag-20Cu-20Ge-1.0Ti)
Flow at 1105°F was arrested by weld contamination at the braze alloy particle.

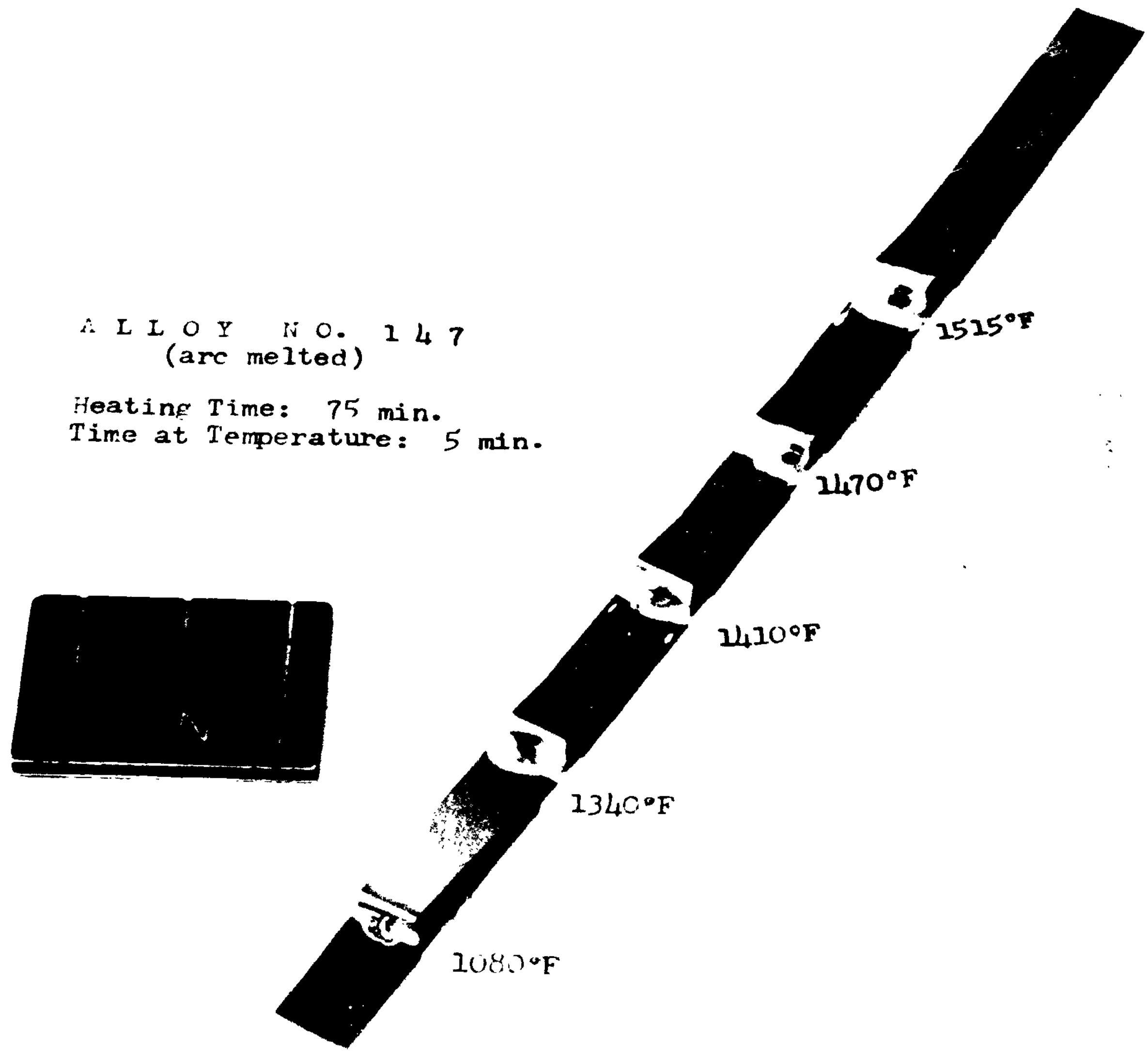


FIGURE 19. FLOW BEHAVIOR AT VARIOUS TEMPERATURES (Ag-20Cu-20Ge-1.0Ti) A favorable fillet occurred at 1080°F, but higher temperatures caused extensive flow-out.

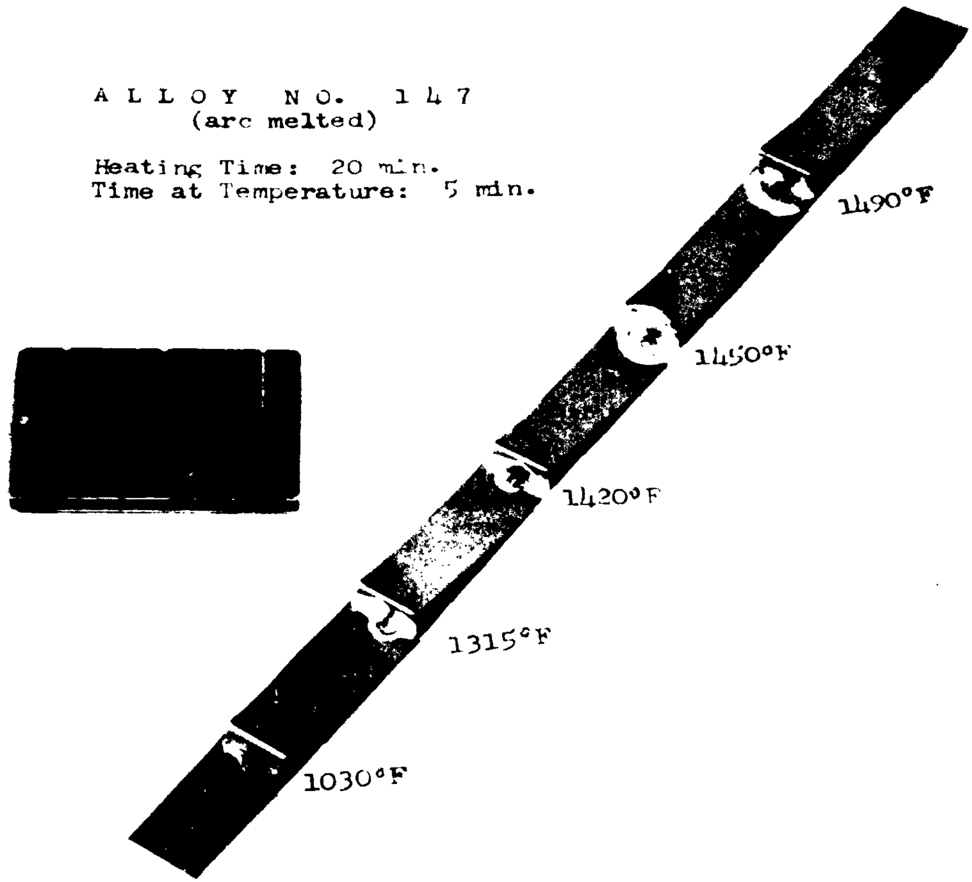


FIGURE 20. FLOW BEHAVIOR AT VARIOUS TEMPERATURES (Ag-20Cu-20Ge-1.0Ti) Partial melting occurred at 1030°F. Other temperatures were too high for fillet retention.

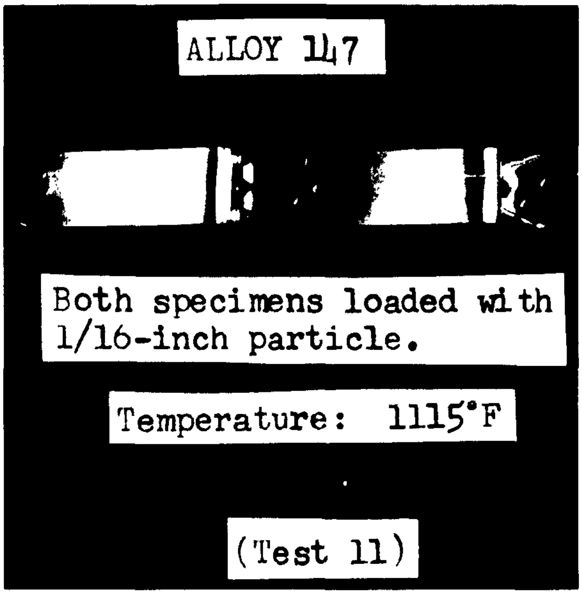
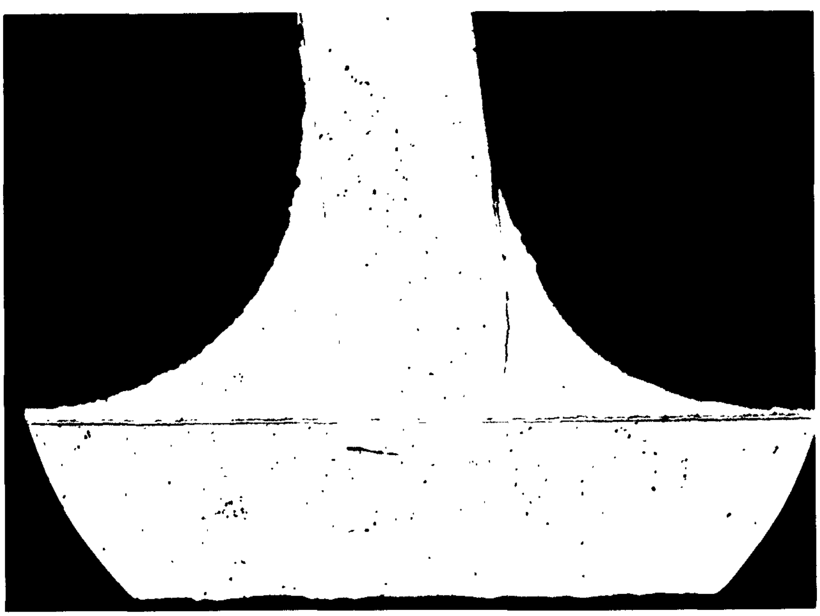


FIGURE 21. FLOW BEHAVIOR OF Ag-20Cu-20Ge-1.0Ti. Alloy particles were held in place with titanium clips. In the left specimen, the alloy flowed in the tee joint. At the right, the alloy flowed into the capillary under the clip.

FIGURE 22. MICROSECTION OF TEE JOINT IN FIGURE 21.



Unetched

Mag. 100X

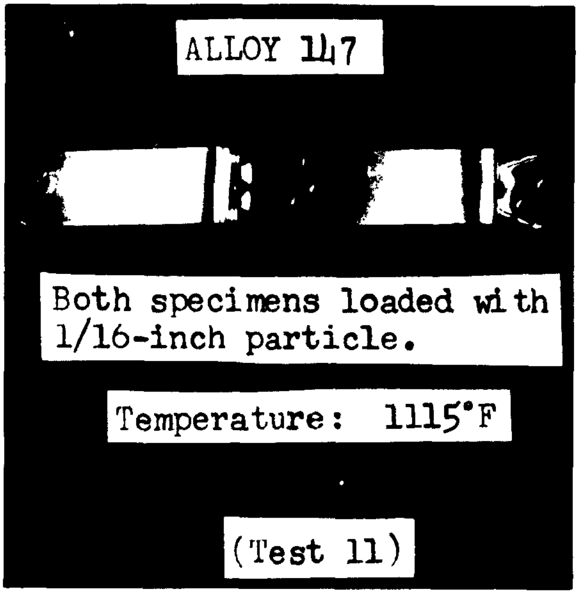
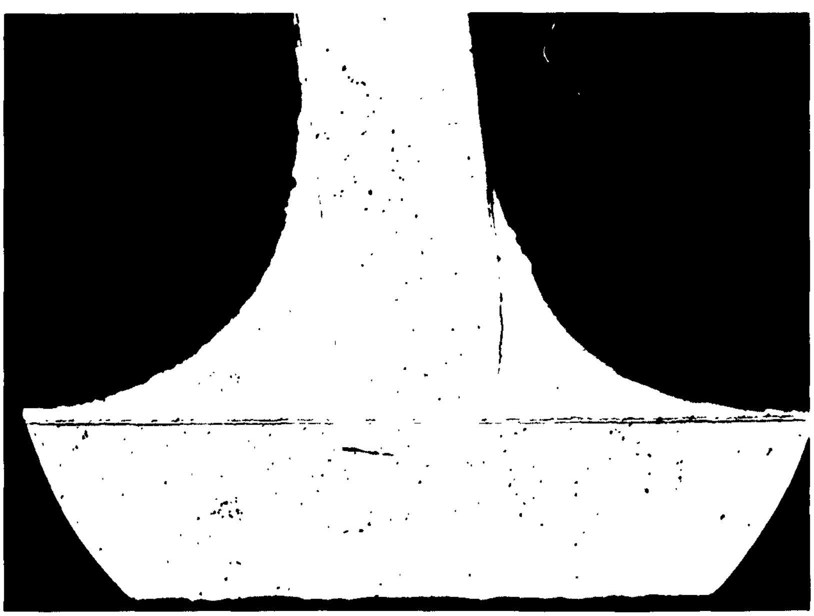


FIGURE 21. FLOW BEHAVIOR OF Ag-20Cu-20Ge-1.0Ti. Alloy particles were held in place with titanium clips. In the left specimen, the alloy flowed in the tee joint. At the right, the alloy flowed into the capillary under the clip.

FIGURE 22. MICROSECTION OF TEE JOINT IN FIGURE 21.



Unetched

Mag. 100 X

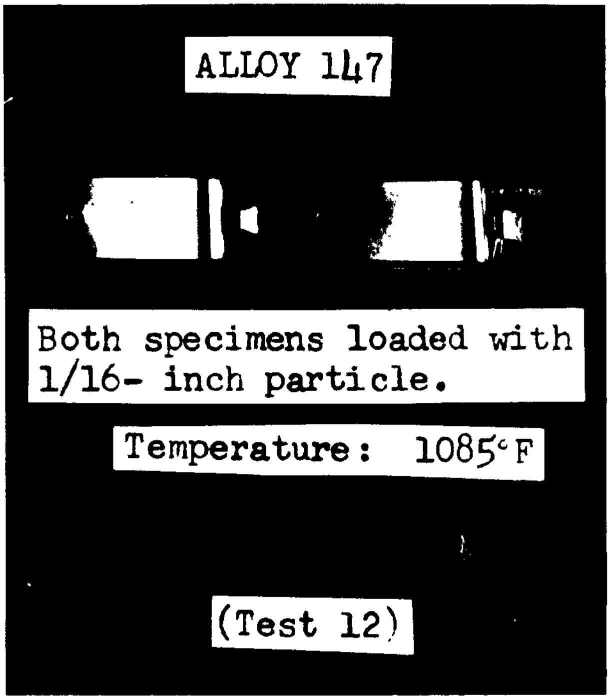


FIGURE 23.

UNFAVORABLE BEHAVIOR OF Ag-20Cu-20Ge-1.0Ti ALLOY
Lack of flow at this temperature was attributed to a transient contamination during the cycle, not accompanied by visible evidence of contamination of the specimen.

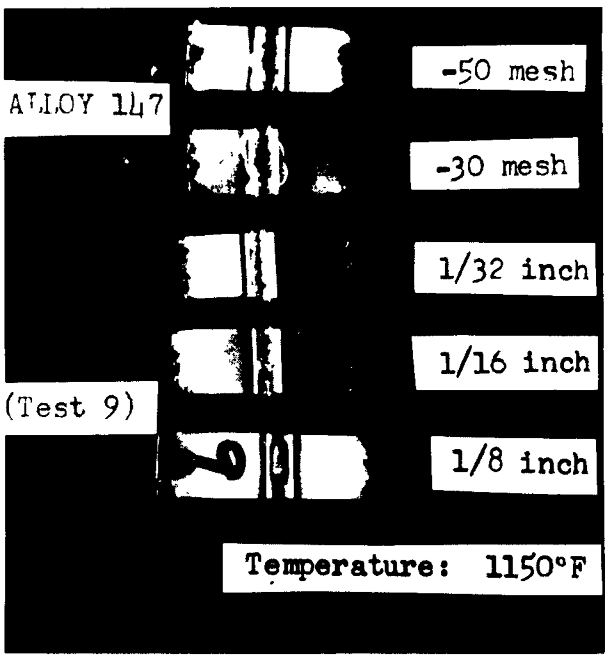


FIGURE 24.

EFFECT OF PARTICLE SIZE ON ALLOY BEHAVIOR At 1150°F particles finer than 1/32-inch exhibited exaggerated liquidation and flow-out. The 1/8-inch particle probably did not flow because of specimen contamination.

Lack of flow on the 1/8-inch particle is not representative of usual behavior, but the other specimens show typical performance for the particular particle sizes involved. When the size is under 1/32 inch, the filler alloy usually forms an extended thin film on the substrate, yields only a marginal fillet, and leaves appreciable residual alloy apparently unmelted.

Eutectic Composition Study

Tests on the Ag-20Cu-20Ge base alloy indicated a slight deviation from the ternary eutectic composition because of liquation effects and a spread in the liquidus-solidus temperatures. The composition Ag-24.6Cu-19.6Ge was reported (Ref. 3) to be the eutectic point at 968°F between Cu_3Ge, silver-solid solution, and germanium. Accordingly, this composition was included in a group of alloys centered around the ternary eutectic.

Minor additions of titanium repeatedly were associated with favorable wetting and flowing characteristics. This behavior was related to a reported Ag-Ti eutectic at 96 percent and 1650°F. Accordingly, the series of alloys in Table III included titanium variations up to 5 percent. The alloys were multiple arc melted under gettered argon. Microstructure of a Ag-4Ti alloy separately melted (Fig. 25) indicated a eutectic in silver-rich alloys.

TABLE III

Ag-Cu-Ge MODIFIED ALLOYS

Alloy No.	Composition (percent) Cu	Ge	Ti	Ag	Melting Range (°F)
166	20.0	20.0	1.0	Balance	980 - 1170
167	24.6	19.6	-	Balance	985 - 1030
168	24.4	19.3	1.0	Balance	975 - 1150
169	23.6	18.8	4.0	Balance	975 - 1250
170	23.6	18.6	5.0	Balance	950 - 1410

Nital Etched Mag. 250 X

FIGURE 25. STRUCTURE OF Ag-4 Ti ALLOY

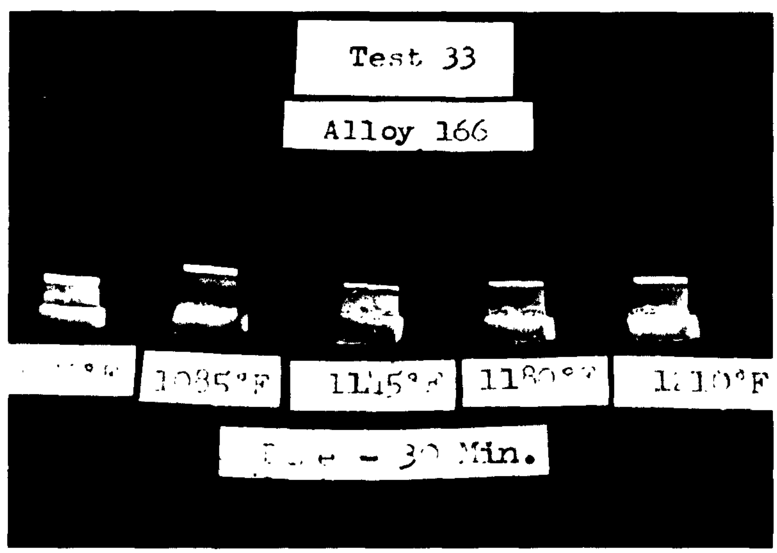


FIGURE 26. TYPICAL BEHAVIOR OF FINE PARTICLES (Ag-20Cu-20Ge-1.0Ti) Particle liquation effects interfered with complete melting and coalescence necessary for flow and fillet formation.

Melting temperatures in Table III showed nearly eutectic composition for Alloy 167. Alloys 166, 167, and 168 were evaluated as -100 mesh powders placed on tee specimens with polybutene binder and vacuum brazed under the temperature gradient composite specimen procedure. Typical behavior of fine powders wherein liquation effects interfered with the normal melting reaction is represented in Figures 26 and 27. It was further noted that contamination was apparent in all tests with Alloy 167 which did not contain titanium. Alloys 169 and 170 showed adverse flow behavior, possibly due to refractory residues and chemical effects related to the high titanium content. In consequence of these tests, Alloy 168 was selected for subsequent mechanical property evaluation; approximately 30 specimens were processed with consistently favorable filler alloy performance. Two typical tee specimens which were brazed in gettered argon, using approximately 1/16 inch particles of filler alloy, are illustrated in Figure 28. The slight unmelted residue in this case may be related to an undetermined high melting constituent responsible for the very weak jog in the cooling curve at 1150°F (Table III).

2.2.2 Ag-Cu-Sn Base Alloys

Alloys in Table IV list the first compositions tested in the Ag-Cu-Sn base series. They represent tin additions to the Ag-28.1Cu eutectic melting at 1434°F. Tin depresses the melting temperature of silver by a series of peritectics, leading to a eutectic between Ag_3Sn and Sn at 96.5 percent Sn and 430°F.

TABLE IV

Ag-Cu-Sn ALLOYS

Alloy No.	Composition (percent) Cu	Sn	Ag	Melting Range (°F)
103	27.0	27	Balance	-
104	25.0	25	Balance	-
105	22.5	23	Balance	-
116	10.0	10	Balance	1030 - 1470
117	20.0	20	Balance	1120 - 1420
122	10.0	10	Balance	1000 - 1260

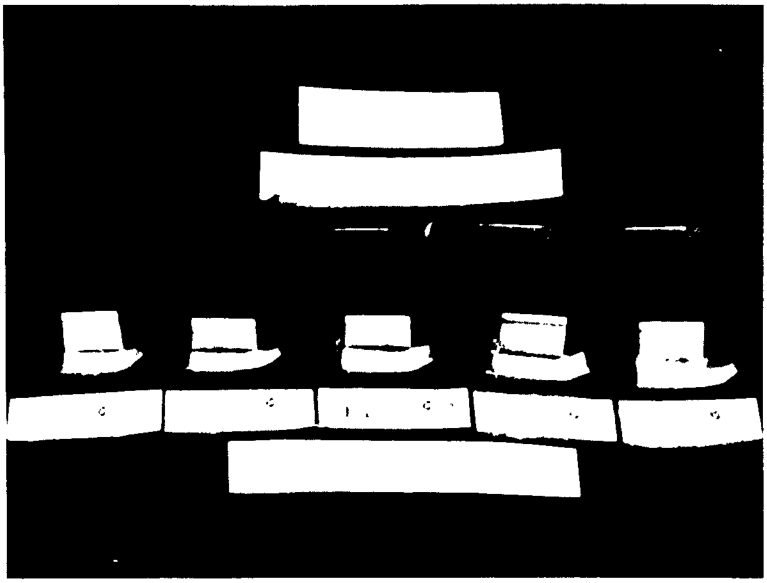


FIGURE 27. TYPICAL BEHAVIOR OF FINE PARTICLES (Ag-24.6Cu-19.6Ge) Performance of this eutectic composition was essentially similar to Figure 26.

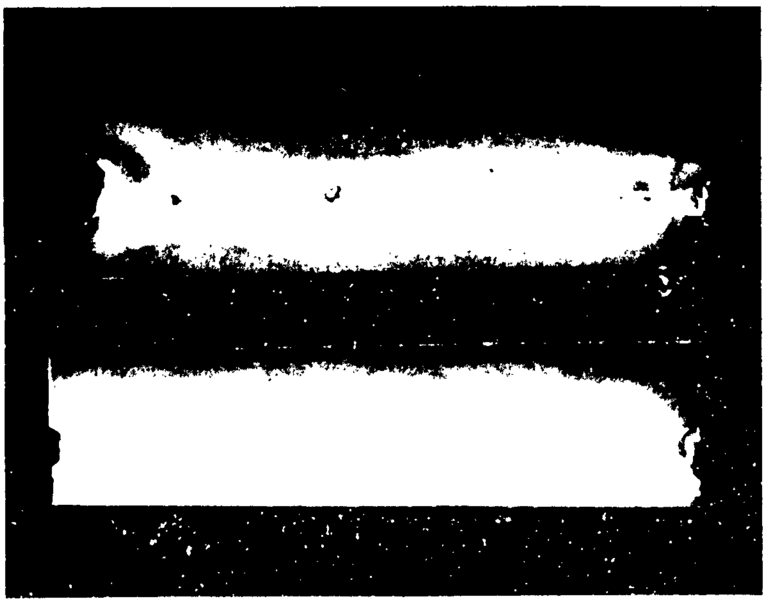


FIGURE 28. TYPICAL TEE SPECIMENS SHOWING FLOW BEHAVIOR OF ALLOY 168

Since the ternary alloys in Table IV showed promise by approaching the low melting requirement, a further series of alloys was prepared to observe the effects of adding titanium, magnesium, and lithium (Table V). These alloys also embody a progressive increase in tin content up to 50 percent, where appreciable amounts of the Ag-Sn eutectic were present. An illustration of melt and flow characteristics of typical alloys from this group when brazed under vacuum in the Vycor retort apparatus is shown in Figure 29.

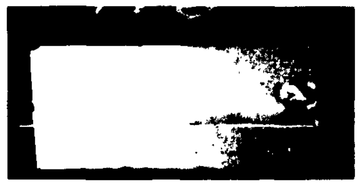
TABLE V

MODIFIED Ag-Cu-Sn ALLOYS

Alloy No.	Composition (percent) Cu	Sn	Other	Ag
130	20	20	1.0 Ti	Balance
132	20	20	2.0 Ti	Balance
136	19	25	1.0 Ti	Balance
138	18	25	2.0 Mg	Balance
143	15	30	0.2 Li	Balance
146	17	30	1.6 Li	Balance
148	15	30	1.0 Ti	Balance
149	15	35	1.0 Ti	Balance
150	16	35	1.7 Mg	Balance
153	15	30	0.1 Ti	Balance
154	15	35	0.1 Ti	Balance
155	1	50	0.2 Ti	Balance

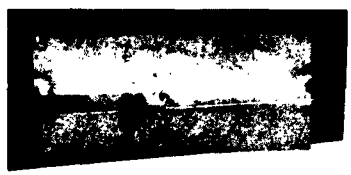
ALLOY 136

Ag-19Cu-25Sn-1.0Ti



ALLOY 148

Ag-15Cu-30Sn-1.0Ti



ALLOY 149

Ag-15Cu-35Sn-1.0Ti

ALLOY 154

Ag-15Cu-35Sn-0.1Ti

ALLOY 155

Ag-50Sn-1Cu-0.2Ti

FIGURE 29. MELT AND FLOW CHARACTERISTICS OF MODIFIED Ag-Cu-Sn ALLOYS

Tin-Rich Alloy (Ag-50Sn-1Cu-0.2Ti)

This alloy departed somewhat from the project plan of concentrating on silver-rich alloys which promise tough interfacial films because of the ductility of the Ti-Ag compound. However, the alloy was included to evaluate the possible benefit of extensive eutectic melting which occurs at 415°F. One possible benefit was considered to be formation at a low temperature of an appreciable fraction of melt which would remain in place and furnish opportunity for the melt-solid reaction necessary for complete melting as the nominal liquidus temperature is approached.

Large particles of Alloy 155 (Ag-50Sn-1Cu-0.2Ti) were compared with Alloy 152 (Ag-20Ge-20Cu-0.1Ti) by placing on a composite vee-groove specimen. Figure 30 illustrates relative behavior at 1040°F and 1115°F. The Ag-Ge-Cu alloy showed virtually no evidence of melting at 1040°F and only marginal flow at 1115°F. Alloy 155 (high tin) formed an adequate fillet at 1040°F and flowed extensively at 1115°F. Two additional duplicates of the above test are represented in Figure 31, demonstrating consistently favorable fillet performance for Alloy 155 when used as a coarse particle.

Fine particles of Alloy 155 were evaluated as -50 mesh filings and -200 mesh carbide milled powder. Filings were prepared with a carbide file submerged in carbon tetrachloride. After collection and drying, the -50 mesh fraction was selected for brazing tests. Milled powder was prepared from filings by use of a carbide mill with carbide balls. In the initial tests, the mill contained normal air atmosphere, and considerable contamination was evident. Subsequently, the mill was purged with purified argon, and the specular bright powder indicated freedom from contamination.

The above powders repeatedly demonstrated unfavorable performance in that the tin-rich eutectic separated from the powders by a liquation process while heating above 415°F. The resulting residual ϵ-phase (Ag_3Sn) undergoes peritectic decomposition to ζ-phase at 896°F, yielding a product too refractory to melt at temperatures within the scope of this investigation.

A typical operation of the above events is illustrated in Figure 32, showing two samples of Alloy 155 powder heated on a flat titanium surface. Balls of liquated eutectic formed on both the filled and milled powders, and these formations are illustrated at higher magnification in Figures 33 and 34. Low melting, tin-rich eutectic

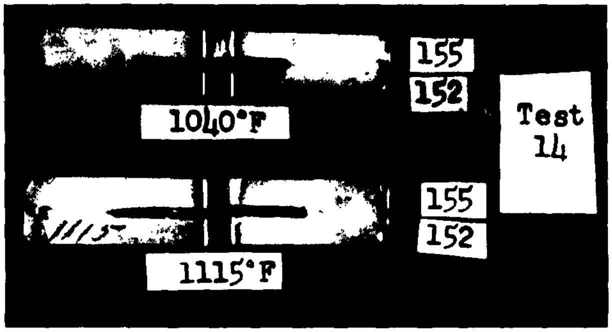


FIGURE 30.

RELATIVE BEHAVIOR OF Ag-50Sn-1Cu-0.2Ti ALLOY AND Ag-20Cu-20Ge-0.1Ti COARSE PARTICLES

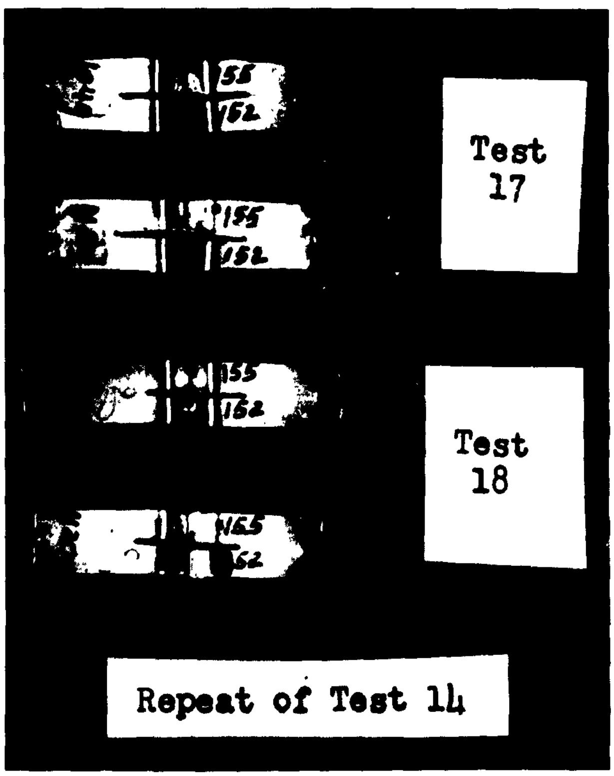


FIGURE 31.

REPRODUCIBILITY OF BEHAVIOR SHOWN IN FIGURE 30.

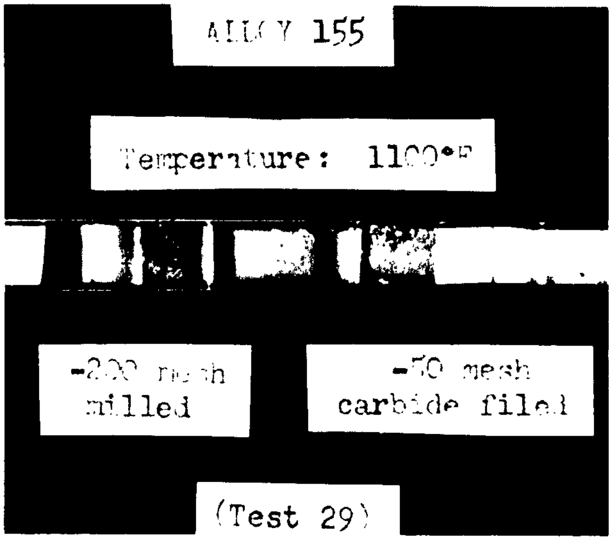


FIGURE 32.

TYPICAL BEHAVIOR OF FINE POWDERS (Ag-50Sn-1Cu-0.2Ti)
In massive form the liquidus is approximately 900°F, but liquation effects apparently prevent complete melting up to 1100°F

FIGURE 33.

VIEW OF MILLED POWDER SPECIMEN IN FIGURE 32

Mag. 8X

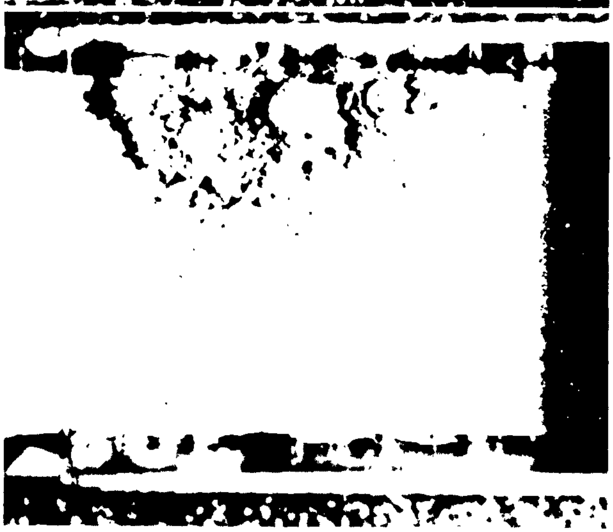


FIGURE 34.

VIEW OF FILED POWDER SPECIMEN IN FIGURE 32

Mag. 8X

apparently migrated over both powders, leaving the relatively refractory powder without the presence of melt necessary for normal melting reaction. Figures 35 and 36 illustrate, respectively, microstructures of the liquated balls and residual particles. The bright, central portion of the ball is rich in Ag-Sn eutectic, and the voids in the residual particles are a product of peritectic decomposition of ϵ -phase on heating above 896°F.

Adverse behavior of the powders is believed to derive from intrinsic characteristics of the titanium substrate. Liquid phase formed during initial heating does not readily wet the titanium, thus becoming available for migration into the minimum surface energy ball form. Subsequent partial wetting that does occur on the titanium does not benefit the complete melting reaction because of the high reactivity with titanium.

Products of this reaction are refractory, thereby essentially circumventing the liquid-solid physical contact necessary for the melting reaction to ensue. With powder filler alloy, these events occur largely with individual particles rather than as a bulk reaction in the alloy.

A summary evaluation of braze alloy behavior described above led to re-emphasis on an alloy of eutectic composition to avoid any intentional liquidus-solidus temperature separation.

Following optimization of brazing procedure for Ag-Cu-Sn filler alloys, a number of tee specimens and several lap specimens were observed for strength characteristics. Extreme brittleness of joints occurred consistently and in many cases caused fracture of the specimen during careful preparation for testing. This experience was interpreted to demonstrate intrinsic brittleness associated with intermetallic films formed on the titanium substrate, and further work on Ag-Cu-Sn base alloys was discontinued.

2.2.3 Mechanical Properties Evaluation

Selection of a filler alloy for mechanical evaluation was based chiefly on the ability of the alloy to flow and form suitable fillets below the 1100°F temperature limitation. This criterion indicated Alloy 168 (Ag-24.4Cu-19.3Ge-1.0Ti) for evaluation. Unfavorable factors applied to other alloys included the following: inadequate melting below 1100°F, objectionable liquation effects, and apparent deficiencies in flow and fillet behavior on the titanium substrate.

FIGURE 35.

MICROSECTION OF TYPICAL BALL SHOWN IN FIGURE 33

4% Nital Etch

Mag 150 X

FIGURE 36.

MICROSECTION OF RESIDUAL PARTICLES SHOWN IN FIGURE 33

4% Nital Etch

Mag. 500X

Tee specimens (Sec. 2.1.4) brazed with Alloy 168 were tested in tension at room temperature and at 700°F, both in the as-brazed condition and after aging at 950°F for 24 hours. Individual values recorded in Table VI were computed on the arbitrary basis of ultimate load divided by cross section area of the vertical leg of the tee. Although computed on an arbitrary basis, the strength represented by Ag-Cu-Ge-Ti alloy is viewed as marginal for structural application. For comparison, two specimens in Table VI show considerably higher values for Ag-Al foil alloy which was brazed at 1625°F.

TABLE VI

MECHANICAL PROPERTIES OF BRAZED TEE-SPECIMENS

Alloy No.		Test Temperature (°F)	Ultimate Strength (psi)[1]
168	As brazed at 1100°F	R. T.	5700
168	As brazed at 1100°F	R. T.	7200
168	As brazed at 1100°F	R. T.	10000
168	As brazed at 1100°F	R. T.	8000
168	As brazed at 1100°F	700	14000
168	As brazed at 1100°F	700	14000
168	As brazed at 1100°F	700	9000
168	Aged 950°F - 24 hours	R. T.	6400
168	Aged 950°F - 24 hours	R. T.	8500
168	Aged 950°F - 24 hours	700	10000
168	Aged 950°F - 24 hours	700	4000
118[2]	As brazed at 1625°F	R. T.	24000
118	As brazed at 1625°F	R. T.	7500
118	As brazed at 1625°F	R. T.	8400
95 Ag-5Al	As brazed at 1625°F	R. T.	36000
95 Ag-5Al	As brazed at 1625°F	R. T.	32000

[1] Computed on the basis of cross section area of the vertical leg of the tee.

[2] Ag-10Ge-2Ti

To assess a possible adverse influence of copper-rich interfacial layers, Alloy 118 (Ag-10Ge-2Ti) also is represented in Table VI. The low values obtained on these specimens do not support assignment of marginal performance to the copper content in the filler alloy. Figures 37 and 38 contrast Alloys 168 and 118 with respect to filler alloy microstructure, but it is evident that a substantial interfacial film accompanied use of the copper-free alloy (118).

Throughout the tension tests on tee specimens, failure occurred in a manner which imputed the relatively low values to the interfacial phase between the filler alloy and the titanium substrate. In most cases, failure consisted of extracting the vertical leg of the tee from the fillet accompanied by brittle fracture through the interfacial phase. Figure 39 is a microsection through a typical tee specimen failure, illustrating mode of failure.

Single-shear, lap-joint specimens were brazed under the same conditions as tee specimens and tested according to the same schedule. Individual test values are listed in Table VII. Visual examination of the failed specimens indicated a failure mechanism essentially similar to that of the tee specimens.

Table VIII presents summary test information on both the lap-joint and tee specimens for room temperature and 700°F performance. In general, the lap-joint shear data are more meaningful than tee-specimen data, because behavior of the tee specimens to a large degree reflected substantial variations in fillet configuration.

On the basis of average values in Table VIII, performance of brazed specimens is somewhat better at 700°F than at room temperature. Since mechanical behavior is determined chiefly by the interfacial film, the improved performance at 700°F could be ascribed to the incidence of slight improvement in behavior of the interfacial phases. In the case of lap specimens, average strength varied from 10,750 psi for the aged specimens to 11,900 psi for specimens tested as-brazed.

2.2.4 Corrosion Tests

Salt spray corrosion resistance was evaluated by a 72-hour salt spray exposure on three tee specimens of Ti-6Al-4V which had been brazed with Alloy 168 and aged at 950°F for 24 hours. The ultimate tensile strength of these specimens was compared with the same property for comparable specimens which had not been exposed to the salt spray. The overlapping strength values indicated no degradation from the salt spray exposure, and failure mechanism was identical for the two groups. Examination after exposure showed no visible effects of the salt spray test.

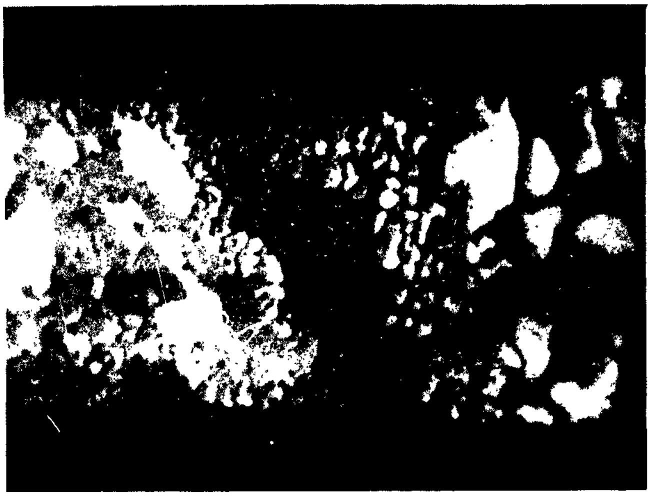


FIGURE 37.

MICROSTRUCTURE OF ALLOY 168 IN TEE JOINT (Ag-24.4Cu-19.3Ge-1.0Ti)

Unetched

Mag. 750X

FIGURE 38.

MICROSTRUCTURE OF ALLOY 118 IN TEE JOINT (Ag-10Ge-2Ti)

Unetched

Mag. 750X

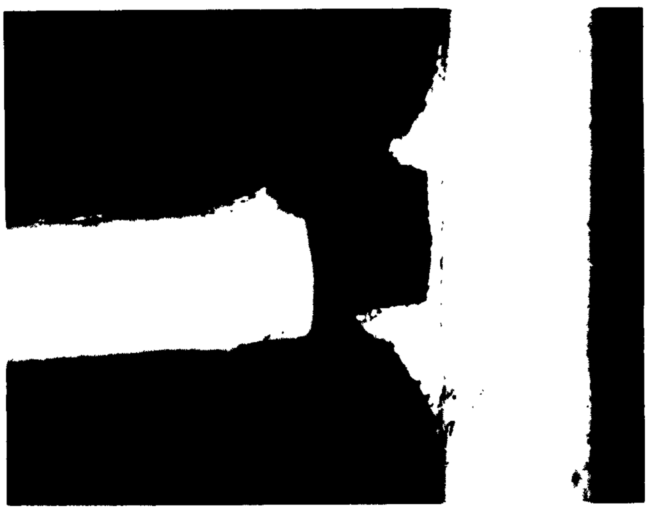


FIGURE 39.

TYPICAL FAILURE OF ALLOY 168 TEE SPECIMEN

Unetched

Mag. 100X

TABLE VII

LAP SHEAR TESTS ON ALLOY 168[1]

Description	Test Temperature (°F)	Shear Strength (psi)
As brazed	R. T.	9,500
As brazed	R. T.	7,900
As brazed	R. T.	7,000
Aged 950°F, 24 hours	R. T.	10,000
Aged 950°F, 24 hours	R. T.	8,000
Aged 950°F, 24 hours	R. T.	8,000
As brazed	700	20,000
As brazed	700	9,500
As brazed	700	6,100
Aged 950°F, 24 hours	700	11,000
Aged 950°F, 24 hours	700	11,000
Aged 950°F, 24 hours	700	10,000

[1] Ag-24.4Cu-19.3Ge-1.0Ti. Specimens (0.250 x 0.010 x 2 inches) were brazed under vacuum at 1100°F

TABLE VIII

SUMMARY OF MECHANICAL TESTS ON ALLOY 168

Testing Temperature	As Brazed		Aged (950°F - 24 hours)	
	Tee Specimen	Lap Specimen	Tee Specimen	Lap Specimen
R.T.	7700	8100	7500	8700
700°F	12000	11,900	7000	10,700

Note: The values in this table are arithmetic averages of individual ultimate strengths (psi) of tee specimens and lap-joint shear specimens in Tables VI and VII.

III. CONCLUSIONS

1. From practical consideration of applicable binary data, the Ag-Cu-Sn and Ag-Cu-Ge base alloys were investigated.

2. Ag-Cu-Sn base alloys required tin contents in excess of 30 percent to depress the melting temperature, and the resulting joints possessed inadequate toughness to justify further study.

3. Ag-Cu-Ge base alloys exhibited favorable flow characteristics below 1100°F in argon and under vacuum. Marginal strength characteristics, however, would justify only highly restricted usage of the alloys. Salt spray corrosion resistance was satisfactory.

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3. Nowotny, H., Bachmayer, K., "The Ternary System Cu-Ge-Ag", Monatshefte fur Chemie. Vol. 81 (1950), p. 669.

Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt No. ASD TR 61-313, Pt II. DEVELOPMENT OF LOW TEMPERATURE BRAZING ALLOYS FOR TITANIUM HONEYCOMB SANDWICH MATERIALS. Final report, Jan 63, 41 pp. incl illus., tables, 3 refs.

Unclassified Report

For brazing titanium under 1100°F, binary information formed the basis of selecting two promising ternary basis alloys for development, (1) Ag-Cu-Ge and (2) Ag-Cu-Sn. Melt and flow behavior was favorable with Ag-Cu-Sn base alloys, but work was discontinued because of excessive joint brittleness related to inter-

(over)

1. Brazing titanium alloy
2. Ag-Cu-Ge base alloy
3. Ag-Cu-Sn base alloy

I. AFSC Project 7351, Task 735102
II. Contract No. AF 33(616)-7249
III. Solar Aircraft Co. San Diego, Calif.
IV. W. C. Troy
V. Aval fr OTS
VI. In ASTIA collection

metallic films formed on the substrate. Alloys based on the Ag-Cu-Ge ternary also formed intermetallic films, but the joints had intermediate strength which justified evaluation. Average shear strength of lap joints varied from 10,750 psi for aged specimens to 11,900 psi for after brazing at 1100°F. These marginal properties would justify only limited application of the Ag-Cu-Ge based alloys.