Semiannual Phase Report No. 5

LEAD TELLURIDE BONDING AND SEGMENTATION STUDY

(1 AUGUST 1969 - 31 JANUARY 1970)

CONTRACT NO.: NAS 5-9149

Prepared by

TYCO LABORATORIES, INC.
BEAR HILL
WALTHAM, MASSACHUSETTS 02154

for

National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland 20771

Semiannual Phase Report No. 5

LEAD TELLURIDE BONDING AND SEGMENTATION STUDY

(1 August 1969 — 31 January 1970)

Contract No.: NAS 5-9149

Goddard Space Flight Center

Contracting Officer: Kathleen G. Williams, Code 245

Technical Monitor: Joseph Epstein, Code 716

Prepared by

Tyco Laboratories, Inc.

Bear Hill

Waltham, Massachusetts 02154

Authors: S. Mermelstein, S. Michalik, and F. Wald

for

Goddard Space Flight Center

Greenbelt, Maryland 20771

SUMMARY

Metallurgical investigations during the present reporting period centered around the high Co-end of the Co-Ge-Si system, where we hope to find a eutectic suitable for brazing $MoSi_2$ to Si-Ge thermoelectric material. Since phase relationships in all other parts of the Co-Ge-Si diagram are relatively favorable, success in locating a eutectic with a suitable melting point would immediately make bonding studies feasible.

The second part of this report describes bonding of the segmented Si-Ge/PbTe couples which are to be used in the submodules. Furthermore, preliminary mechanical and thermal tests on submodule components are described, and the module assembly procedures are outlined.

Finally, redesign and rework required on the thermoelectric test fixture for submodule testing are described. The Appendix presents a literature study of binary systems which might be pertinent for Si-Ge hot shoe brazing.

Table of Contents

List of Illustrations

List of Illustrations (Cont.)

I. INTRODUCTION

The widespread use of thermoelectric power generation as the solution to a number of specialized power supply problems has been anticipated for some years. However, the application of thermoelectrics has been hindered by a number of major materials problems. These problems can be divided into those associated with (1) the physical characteristics, (2) the chemical behavior, or (3) the low conversion efficiency of thermoelectric materials.

The predominantly covalent nature of most thermoelectric alloys results in materials which are generally weak and brittle. In addition, PbTe alloys have a high thermal expansion coefficient which leads to susceptibility to thermal shock and thermal stress cracking. The mismatch in expansion coefficient between PbTe and metals also causes a fundamental physical incompatibility which must be dealt with in contacting these materials at the hot side. The vapor pressure of PbTe alloys precludes operation in vacuum or requires encapsulation. Porosity in sintered PbTe not only contributes to its mechanical instability, but may also pose a substantial long term hazard to the integrity of metallurgical bonds by migration of the pores in the temperature gradient. The high temperature mechanical properties of PbTe alloys are very poorly defined, and there is an almost complete lack of understanding as to what role they may have in generator design.

The reactive nature of one or more elements in all thermoelectric materials places severe limitations on the materials for use as hot side contacts. Reaction between the metal contact and the thermoelectric material can produce electrically active or mechanically destructive phases at the interface. Interactions between the dopants and contacts, which can drastically affect the electrical properties, are also possible. In fact, the consequences of reaction between the thermoelectric material and any of the several materials which constitute its environment are such

that extreme care must be exercised in the choice of all such materials. However, without a basic knowledge of the interactions of the thermoelectric materials with metals, potential brazes, insulations, etc., selection of these materials can only be by a trial and error process.

The low efficiency of thermoelectric generating materials has been the main impediment to their wider application as power sources. The search for new materials has been largely abandoned; however, the need for higher efficiencies still exists. The most feasible means for achieving higher efficiencies appears to be the combination of existing materials over extended temperature ranges. The best known thermoelectric power generation materials, PbTe and Si-Ge, have optimum temperature ranges which complement each other for operation over a temperature interval of 800 to 1000 °C to 200 to 50 °C. Devices utilizing these materials over such a temperature interval should exhibit higher conversion efficiency than either material alone.

This program comprises a study of: (1) the bonding of PbTe thermoelements to nonmagnetic electrodes, (2) the behavior of the elements and contacts at operational temperatures, (3) the compatibility of PbTe and SnTe with metals and the interactions of Si-Ge thermoelectric materials with potential hot contact materials and brazes, and (4) the physical and chemical characteristics of the PbTe thermoelements. Other aspects of the program include a study of the segmenting of Si-Ge thermoelements with PbTe for higher efficiency, life testing of PbTe thermoelements and couples, design and construction of a prototype test device for Si-Ge/PbTe thermocouples, and the design of modules incorporating tungsten bonded PbTe and segmented Si-Ge/PbTe.

The general aims of the program are to define the most appropriate system and process for the preparation of low resistance, high strength bonds of nonmagnetic electrodes to PbTe alloys and to study the factors and processes involved in the degradation of thermoelements and contacts during extended service.

II. METALLURGICAL INVESTIGATIONS

Two primary areas of study were set forth for metallurgical development during the present contract. The first was to show the feasibility of commercially available $MoSi_2$ ("Kanthal Super") as a hot shoe in segmented thermocouples. This hot shoe would be capable of withstanding temperatures up to 1200 °C at its heated end and ≈1000 °C in the brazed region between the shoe and the Si-Ge thermocouple material. The second major area of investigation was to be the development of an elevated temperature braze material for bonding the hot shoe and the Si-Ge thermoelements. The preferred braze alloy would be a metal-Si-Ge ternary eutectic with a melting point near 1100 °C. The latter investigation comprised the present work in the metallurgical studies.

A. Co-Rich Ternary Alloys

The Co-rich end (>50 at. % Co) of the Co-Si-Ge system was the first candidate for study. A ternary eutectic in this compositional region seemed reasonable in the following respects. First, Co-rich eutectics exist in both binary systems between cobalt s.s. and the first Co-rich intermediate phases. In the Co-Ge system, the eutectic falls at 25 at. % Ge, 1110 °C, between Co s.s. and Co_2Ge. The Co-Si eutectic is at 23 at. % Si, 1195 °C, between Co_3Si and the solid solution phase of cobalt. Second, the major Co-rich intermediate phase — Co_2Si* and Co_2Ge — are not, in their normally existing form, isostructural. A complete solid solution pseudobinary section between the two compounds is not expected. Since

---

*The first compound at the Co end is actually Co3Si. This compound, however, is reported[1] to exist only between 1170 and 1212 °C. It is not generally retained upon quenching, but transforms readily to α-Co2Si and cobalt s.s. upon cooling. Co2Si, therefore, is regarded as the first stable compound which exists at the Co-rich end of the equilibrium diagram.

this pseudobinary section could be eutectic in form, a ternary eutectic in the com-
position range bounded by Co, Co_2Si, and Co_2Ge was probable.

Several Co-Si-Ge alloys (>50 at. % Co) were prepared by arc melting to
determine the composition of a Co-rich ternary eutectic. (The 760 °C isothermal
section of the Co-Si-Ge ternary system[2] is presented in Fig. 1 for reference pur-
poses. The alloys prepared and studied during the present phase of the investiga-
tion are designated by ⊗). The initial series of alloys had the following composi-
tions (given in atomic percent):

Co	Si	Ge
80	10	10
70	15	15
70	10	20
60	05	35
75	25	0

The first three ternary alloys between 70 and 80 at. % Co showed no evidence
of ternary eutectic formation. All three alloys showed primary phases. The pri-
mary phase in the 80 at. % Co alloy is ϵ'-Co solid solution.

A photomicrograph of this alloy in its as-melted condition is shown in Fig. 2.
The primary phase in the 70 at. % Co alloys was not readily determined. X-ray dif-
fraction studies indicate the presence of both the Co_2Si and Co_2Ge phases. Fig. 3
shows the cast structure of $Co_{70}Si_{10}Ge_{20}$. It should be noted that the primary phase
in the 80 at. % Co alloy, i.e., ϵ'-Co, is not the same as that in the 70 at. % Co al-
loys. This is readily emphasized by the metallographic structure of the cast
$Co_{76}Si_{11}Ge_{13}$ shown in Fig. 4. This alloy is an intermediate composition between
the 70 and 80 at. % Co alloys, and lies directly on the linear tieline between the two
binary eutectics. It is an important alloy for the following reasons: (1) it has re-
latively small amounts of primary phase, indicating that the primary phases in the
80 and the 70 at. % Co alloys, with their relatively large volumes, cannot be the
same constituent; and (2) it shows that no consistent eutectic structure exists be-
tween the two binary eutectics. Instead, areas of the $Co-Co_2Ge$ eutectic, as well as
the eutectoid decomposition structure of Co_3Si, are seen quite separately.

The binary alloy Co-25 at. % Si was prepared as a standard for ternary
metallographic structures in this compositional area. The 60 at. % Co alloy, as-
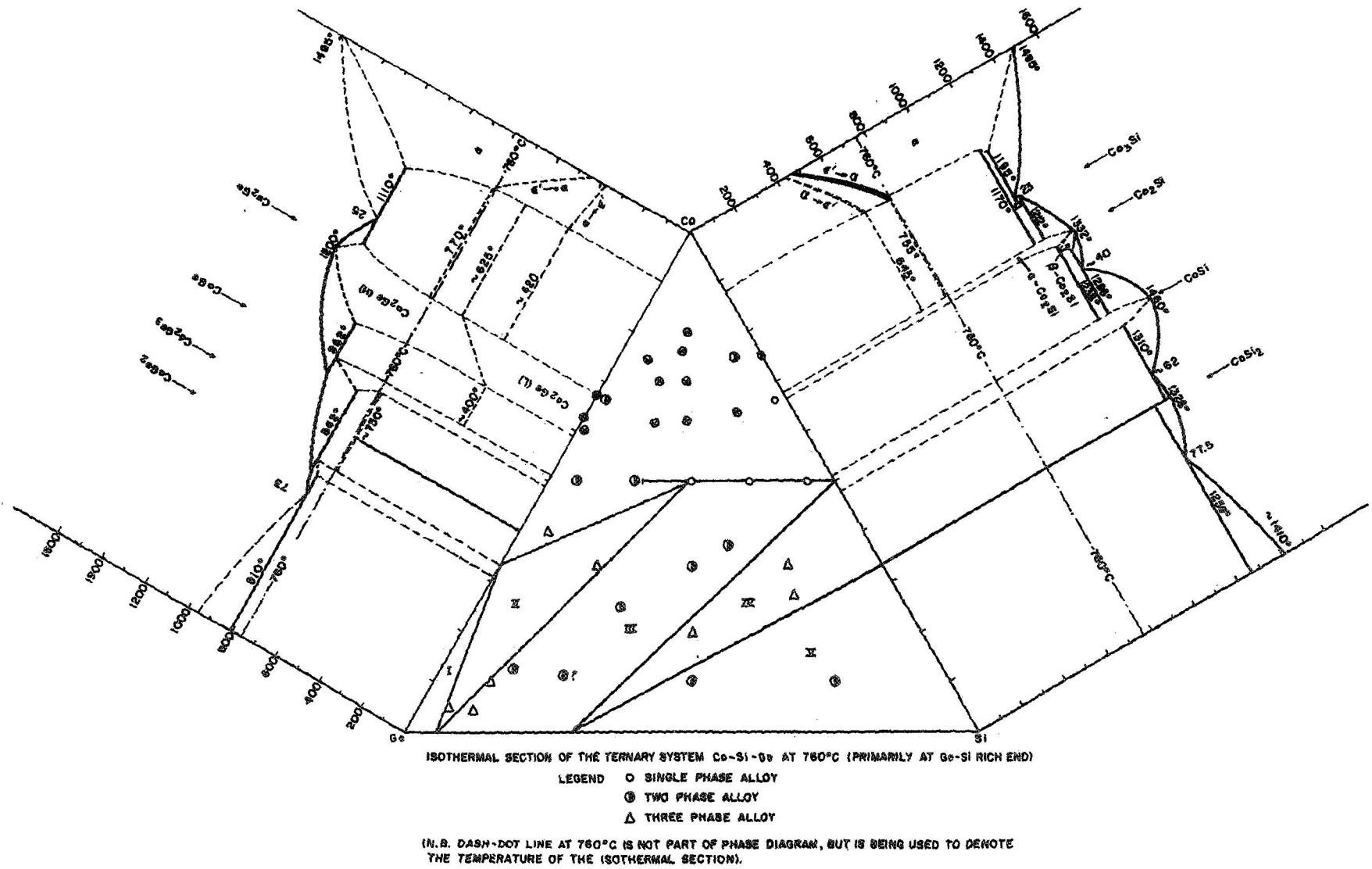
ISOTHERMAL SECTION OF THE TERNARY SYSTEM Co-Si-Ge AT 760°C (PRIMARILY AT Ge-Si RICH END)

LEGEND   O SINGLE PHASE ALLOY

          ⊕ TWO PHASE ALLOY

          △ THREE PHASE ALLOY

(N.B. DASH-DOT LINE AT 760°C IS NOT PART OF PHASE DIAGRAM, BUT IS BEING USED TO DENOTE
THE TEMPERATURE OF THE ISOTHERMAL SECTION).

Fig. 1. 760 °C isothermal section of Co-Si-Ge system (new alloys prepared
and studied for the present report are designated ⊗)

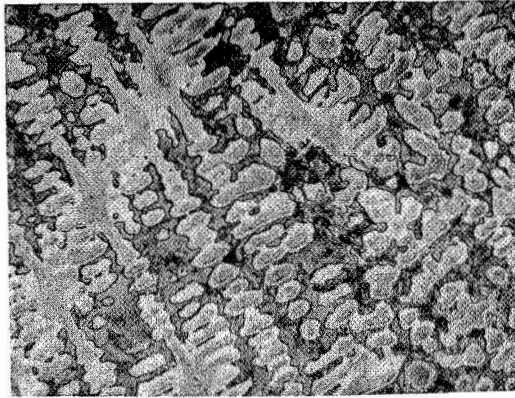Fig. 2. $Co_{80}Si_{10}Ge_{10}$, as melted (primary phase is ϵ'-Co s.s.; matrix is essentially Co_3Si decomposition product with traces of the Co-Co_2Ge eutectic; 300X)
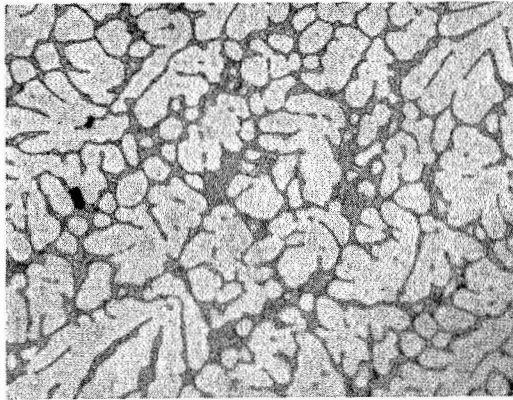

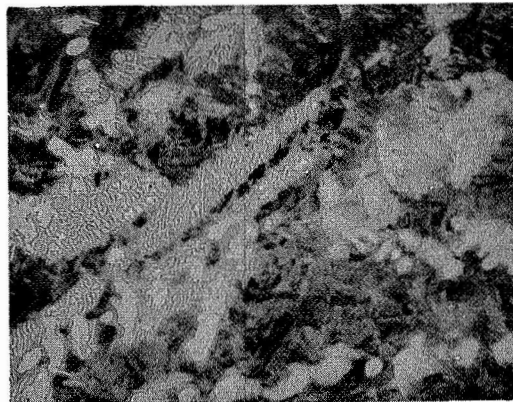Fig. 3. $Co_{70}Si_{10}Ge_{20}$, as melted (primary phase may be either Co_2Si or Co_2Ge s.s.; matrix is essentially Co-Co_2Ge eutectic; 300X)

Fig. 4. $Co_{76}Si_{11}Ge_{13}$, as melted [very small amount of primary phase; major portion of the structure appears to be the Co_3Si decomposition product ($Co_3Si \rightarrow \alpha$-$Co_2Si$ + ϵ'-Co solid solution) and the Co-Co_2Ge eutectic; the primary phase appears to be associated with the eutectic, and could be Co_2Ge solid solution; 500X]

- 6 -

melted, was found to be a single-phase alloy, and is more relevantly discussed below.

B. The Co_2Si-Co_2Ge Section

Since the possibility of a ternary eutectic between 70 and 80 at. % seemed questionable, a second series of alloys was arc-melted in the pseudobinary section between Co_2Si and Co_2Ge. The normally existent crystalline forms of these two compounds are not isostructural. α-Co_2Si has been reported as an orthorhombic structure isostructural with δ-Ni_2Si, and has a distorted Ni_2In structure.[1] The high temperature form of the germanium compound, Co_2Ge (H), is a "filled-up" NiAs structure according to Hansen[1] ($B8_1$ structure type), but is classified by Pearson[3] as a $B8_2$-type isostructural with the β-phase in the Fe-Ge system. Both structural classifications are essentially simple hexagonal close-packed crystals. (The crystalline form of β-Co_2Si, the high temperature allotrope of the compound which exists between 1238 and 1332 °C, is not known. The low temperature polymorph,[2] Co_2Ge, reportedly has an hcp superstructure.[1]) On this basis, it was probable that a two-phase region would exist between the two compounds, with a possible pseudobinary eutectic reaction. The next series of alloys had the following compositions (given in atomic percent):

Co	Si	Ge
63	11	26
64	18	18
65	25	10
66 2/3	0	33 1/3
64	0	36

The two binary alloys were made principally for the purpose of metallographic and X-ray standards for the Co_2Ge phase.

1. Ge-rich end

The as-melted alloys: $Co_{63}Si_{11}Ge_{26}$, $Co_{60}Si_{05}Ge_{35}$, and $Co_{64}Ge_{36}$, are single-phase on the basis of X-ray diffraction and metallographic analyses. The X-ray diffraction data from these cast alloys were quite simply indexed according to the hcp β-phase in the Fe-Ge system, and had the following parameters:

Alloy	c, Å	a, Å	c/a
$Co_{60}Si_{05}Ge_{35}$	4.981	3.872	1.286
$Co_{63}Si_{11}Ge_{26}$	4.989	3.887	1.284
$Co_{64}Ge_{36}$	5.018	3.940	1.274

Fig. 5 shows the single phase microstructure of $Co_{63}Si_{11}Ge_{26}$ in its as-melted condition.

In contrast, the stoichiometric binary compound Co_2Ge is not a single phase compound in the as-melted state. Its X-ray diffraction data are not characteristic of the simple hcp structure of the above single-phase alloys. The metallographic analysis of this compound showed some evidence of a possible transformation structure, which could account for the more complex X-ray diffraction pattern of this alloy.

The $Co_{64}Ge_{36}$ and Co_2Ge alloys were heat treated at 950 °C for 24 hr in evacuated quartz ampoules and quenched. The $Co_{64}Ge_{36}$ alloy, after the 950 °C anneal, remained single phase with an hcp structure, and essentially the same lattice parameters as in the as-melted alloy. The Co_2Ge alloy, heat treated at 950 °C, was apparently equilibrated. It showed a two-phase structure with evidence of a transformation structure in the primary phase. Fig. 6 (a and b) is a series of photomicrographs showing these effects in the heat-treated Co_2Ge. The X-ray diffraction pattern was almost identical with that of the as-melted alloy.

The X-ray diffraction data for Co_2Ge have not yet been indexed. However, the following observations are worth noting. It does appear that the Co_2Ge phase undergoes a solid state transformation at its Co-rich end, which does not occur at higher Ge concentrations within the phase field. Further, the Co_2Ge phase field does not appear to include the stoichiometric composition, but exists only at higher Ge concentrations as does the Fe-Ge β-phase. Lastly, the Co_2Ge phase definitely exhibits a high solubility for Si ($\geq$10 at. %) and extends significantly into the ternary Co-Si-Ge cross section. These points will hopefully be more fully detailed with further investigation, since they do affect the nature of the ternary system.

Fig. 5. $Co_{63}Si_{11}Ge_{26}$, as melted (single-phase alloy based upon Co_2Ge; 115X, polarized light)
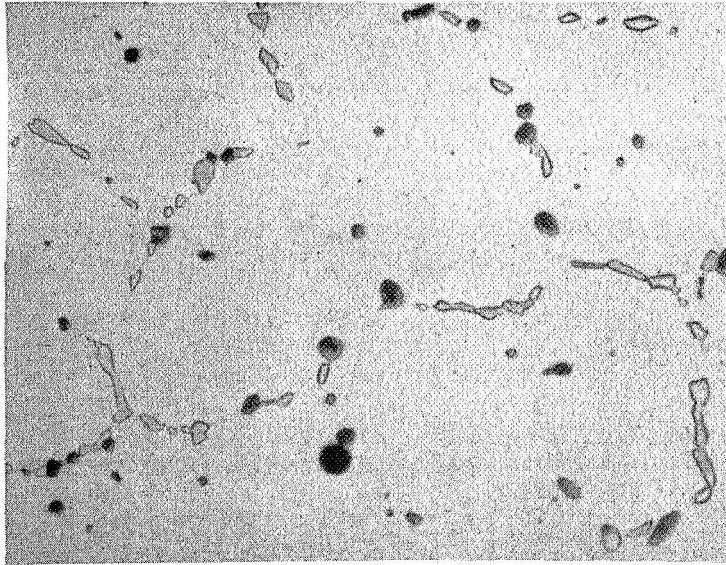
(a) Under regular light, a grain boundary precipitate is seen in the heat-treated compound of stoichiometric composition
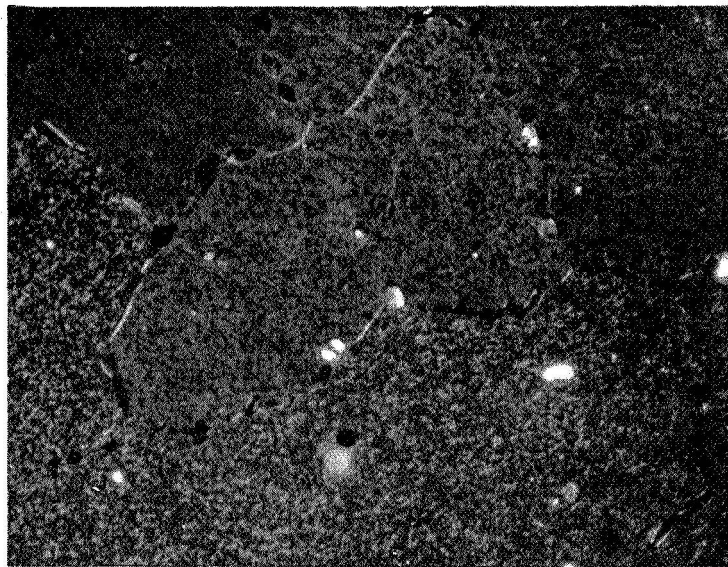
(b) Under polarized light, the primary phase in the same area displays distinct markings which are probably associated with a solid state transformation

Fig. 6. Co$_2$Ge (950 °C in vacuum, 24 hr, quenched; 225X)

2. Si-rich end

The as-melted alloys, $Co_{65}Si_{25}Ge_{10}$ and $Co_{64}Si_{18}Ge_{18}$, have X-ray patterns whose d-parameters are satisfied by a combination of the orthorhombic Co_2Si and the hcp $Co_2(Ge, Si)$ phases. (It is interesting to note that the X-ray data from these two alloys show a definite similarity to those of the two 70 at. % Co ternary alloys noted above, both in d-spacings and intensities. It would be premature, however, to hypothesize any phase relationships in the ternary equilibrium diagram on the basis of these initial data.)

The metallographic analysis of these two alloys is complex and, in contrast, not readily related to the 70 at. % Co alloys. The structure of $Co_{65}Si_{25}Ge_{10}$ appears to have been a single-phase structure which underwent a total solid state transformation, e.g., β-$Co_2Si \rightarrow \alpha$-$Co_2Si + CoSi$. These structures are seen in Fig. 7 (a and b). The etching behavior of $Co_{64}Si_{18}Ge_{18}$, as-melted, has been problematic, but distinct areas of a similar transformation structure have been observed. No eutectic structure is evident in either sample.

The overall pseudobinary section Co_2Ge-Co_2Si does not appear to possess a eutectic reaction. The section is dominated by a large ternary solid solution based upon Co_2Ge, and a transformation phase structure at its Si-rich end.

The form of the Co_2Ge-Co_2Si pseudobinary section lends itself to some further consideration. Co_2Ge (H) exists[1] above 625 to 400 °C (varying with composition), and has been experimentally retained at room temperature at a composition of 36 at. % Co. As noted above, Co_2Ge (H) is reported to be $B8_2$ structure type, which is isotypic with Ni_2In. Orthorhombic α-Co_2Si, the common form of this compound, has a distorted Ni_2In structure, also referenced above. If β-Co_2Si, the elevated temperature form of the compound, exists in the normal crystalline Ni_2In structure before transforming into the orthorhombic α-form, then Co_2Si may be a $B8_2$ structure type at elevated temperatures, and consequently isostructural with Co_2Ge (H). If this were true, then a high temperature region of complete solid solution between β-Co_2Si and Co_2Ge (H) is possible, with regions of limited solubility between the low temperature polymorphs. The high solubility of Si in the Co_2Ge (H) phase, as in the cast $Co_{63}Si_{11}Ge_{26}$ alloy, offers some evidence for this possibility. Equilibrium heat treatment and differential thermal analysis of the alloys in this composition range will eventually establish the complete form of the pseudobinary section.
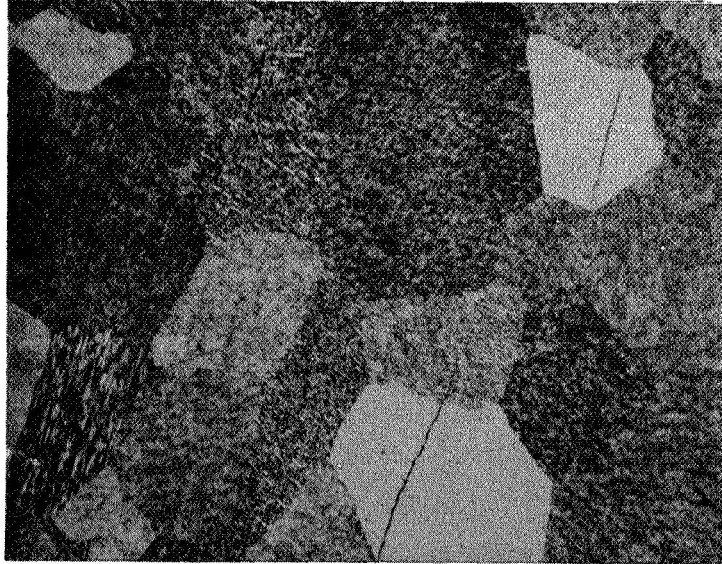
(a) At **125X,** the alloy appears to have been a single phase which underwent a transformation upon cooling (e.g., β-Co$_2$Si $\rightarrow$ α-Co$_2$Si + CoSi)
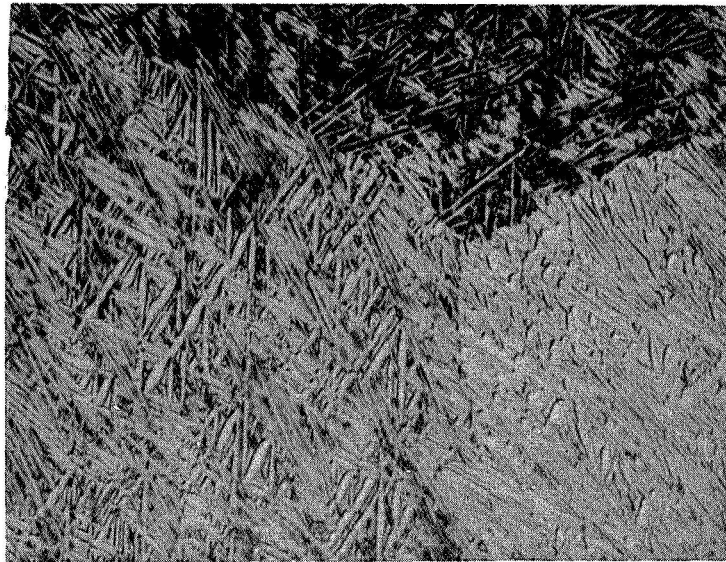
(b) At **1200X,** oil immersion, the nature of the transformation product is seen

Fig. 7. Co$_{65}$Si$_{25}$Ge$_{10}$, as melted (polarized light)

C. The $Co\text{-}Co_2Ge$ Eutectic With Si

It is apparent that no pseudobinary or ternary eutectic exists in the composition range between Co, Co_2Ge, and Co_2Si. The melting points of alloys in this area of the ternary section, however, seem appropriate for the given temperature requirements of the proposed high temperature braze. The melting point of commercial $MoSi_2$ ("Kathal Super") is 1980 °C, with a maximum continuous operating temperature of ≈1700 °C. The commercial Ge-Si thermoelements used in the hot end of the segmented thermocouples are about 70 at. % Si with a solidus temperature of approximately 1210 °C. The desired melting point of the high temperature braze would be about 1100 °C.

The eutectic between Co and Co_2Ge occurs at 1110 °C and 25 at. % Ge. The eutectic as such would be unacceptable due to the absence of silicon. An Si-free braze material in contact with the Si-Ge thermoelements could result in a high degree of solid state interdiffusion at 1000 °C, causing localized compositional deviations in the couple material near the vicinity of the braze. The effects of small amounts of Si on the Co-Ge eutectic, with respect to its melting point, was not experimentally known; the high solubility of Si in the Co_2Ge phase, one component of the eutectic, has been shown in the present investigation.

An alloy $Co_{75}Si_{05}Ge_{20}$ was arc melted. Essentially one-fifth of the Ge has been replaced by silicon. Metallographic analysis of the as-melted alloy, as seen in Fig. 8, shows that a complete eutectic structure is retained. Three differential thermal analysis runs showed an average melting point of 1107 ± 5 °C. (The binary eutectic reportedly melts at 1110 °C, as noted above.) It is quite probable, then, that the $Co\text{-}Co_2Ge$ eutectic with Si added will function acceptably as a high temperature braze in segmented thermocouples. The Si addition should retard the development of major compositional gradients by diffusion at the interface of the braze and the Si-Ge thermoelements

Further investigation will be carried out on 75 at. % Co alloys with varying amounts of Si and Ge to determine the amount of Si which can be added without (1) modifying the eutectic structure, and (2) raising the eutectic melting point too far above that of the binary eutectic. Those alloys showing acceptable eutectic characteristics and melting points will later be tested for wettability with the necessary thermocouple components.
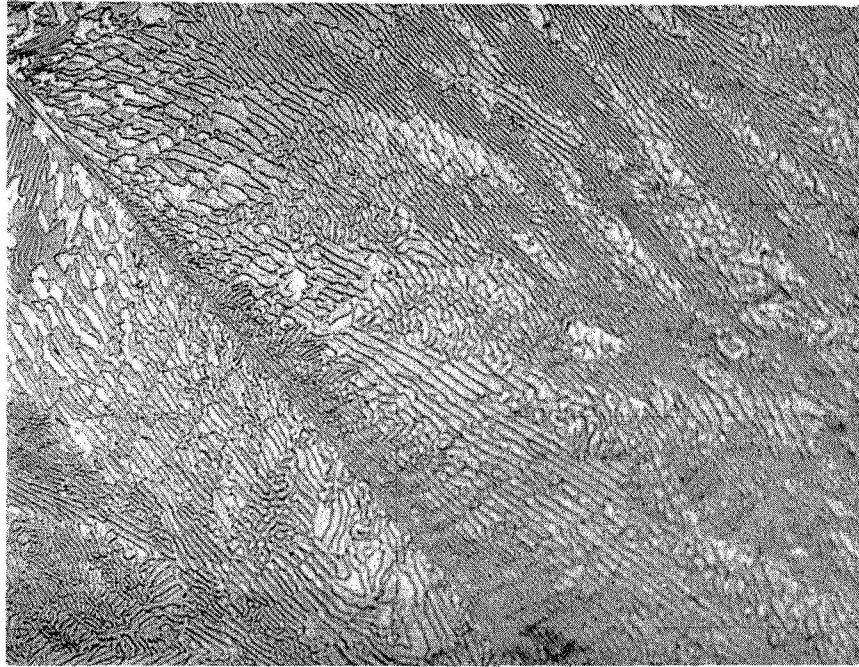
Fig. 8. $Co_{75}Si_{05}Ge_{20}$, as melted (the $Co-Co_2Ge$ eutectic with Si addition; mp = 1107 ± 5 °C; 500X)

D. Other Co-Si-Ge Alloys

In addition to the development of a high temperature braze from the Co-Si-Ge systems, other alloys have been prepared by arc melting in order to clarify the overall ternary phase diagram. These are (in atomic percent):

Co	Si	Ge
58	32	10
60	20	20
55	10	35
45	09	46

Metallographic and X-ray diffraction analysis of these alloys has been initiated, and results will be detailed in subsequent reports.

E. Metal-Si-Ge Systems

A limited literature survey was initially carried out on other metallic systems with Si and/or Ge which could be pertinent to high temperature brazes for thermoelectric segmented thermocouples. The systems reviewed include those of the Pt metals (Pt, Pd, Rh, Ir, Ru, and Os), the remaining Group VIII metals (Ni and Fe), as well as Cr, Ti, and V. The results of this review are presented in the Appendix.

From this compilation, the choice of ternary systems of the metal-Si-Ge type applicable to high temperature braze material is seen to be rather limited. The most promising alternative material for the necessary high temperature braze would be the $Rh-Rh_2Ge$ eutectic with silicon additions. The binary eutectic in this system has an approximate melting point of 1080 °C and a composition of 22 at. % Ge. (These data points would need further experimental investigation, since they are only tentatively reported.[4]) If the Rh_2Ge phase exhibits a high degree of solubility for Si, as does Co_2Ge, there should be little or no modification to the eutectic with small additions of silicon.

III. DESIGN OF SEGMENTED COUPLE MODULES

A. Synopsis

Some preliminary testing was done on modules with couples installed. So far, breakage has been encountered in the ceramic side plates where a temperature gradient of about 400 °C is applied from hot to cold shoe with maximum load springs installed. It is not clear whether faulty test equipment or excessive stress is responsible.

Bonding work on the couples is well underway, as well as work on improving the test equipment.

B. Bonding

We are somewhat behind in bonding work due to delays in ordering and receiving materials and in training new people. We fully expected to have all the couples bonded by now, but instead find ourselves midway toward completion.

It was necessary to machine two new bonding fixtures (Fig. 9) to accommodate the new couples, which have a considerably smaller center-distance. Both fixtures were fired twice in vacuum at 900 to 1000 °C for pretreatment. The shoe soldering fixtures will not have to be remade for center-distance accommodation, because the clamp pistons are oversize.

In starting up bonding again, three runs had to be made to establish power settings, rise and fall time, and furnace profile. Material preparation was carried out in the manner previously established: the PbTe element is finish lapped and cleaned just prior to bonding or, if storage of the finished element is required, then it is immediately placed in a methanol holding bath.

It was previously reported that a temperature of 830 °C for 30 to 45 min created good bonds. For the new couples, this is true for the n type but not for the p. After the first few attempts resulted in failure to bond the p type element, the bonding time was extended to 60 min, which resulted in what appeared to be a good
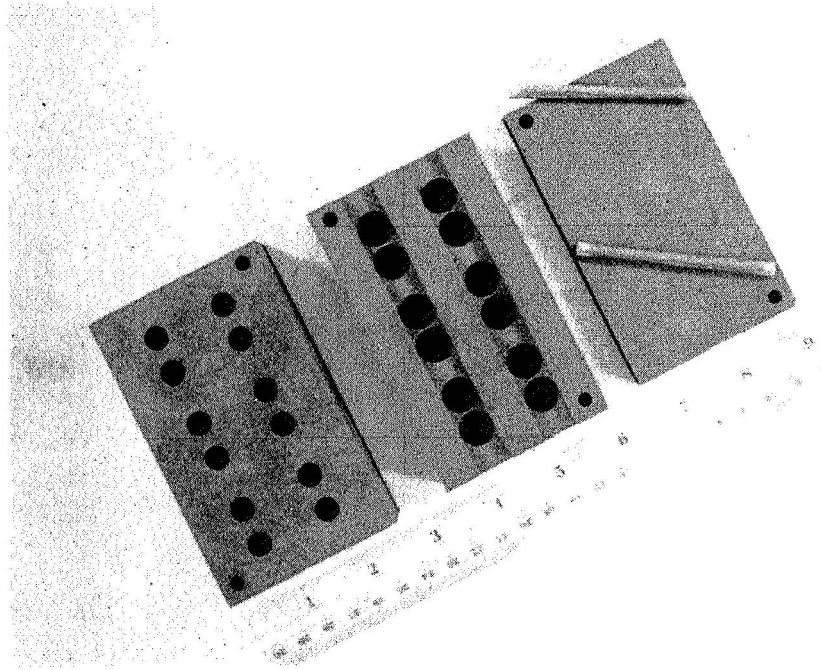
Fig. 9. New bonding fixtures to accommodate new couples

bond.

The resistivity of the combined p type leg (end of PbTe element to hot shoe) was 0.0009 ohm or 0.9 mohm, which indicates a good bond. The n type leg showed unduly high resistivities, and an investigation into possible causes will have to be made.

A bonded couple is shown in Fig. 10. The steps in bonding follow (and will be adhered to unless the new couple material requires further procedural changes).

Follow steps 1 through 6:

1. Hold SiGe couple and PbTe elements in a vacuum desiccator or under methanol before and after lapping.

2. Lap PbTe parallel, perpendicular within 0.001 in., and flat within 0.0002 in. using 320 and 600 silicon carbide in a methanol vehicle on a plate glass lap. Ultrasonically clean in methanol between grit changes and do all rinsing in methanol. Finished piece should be about 0.001 in. or less oversize in length.

3. Pretreat PbTe element by heating to 820 to 825 °C for 30 min in a hydrogen atmosphere.

4. Lap to finished length dimension using 1000-grit silicon carbide. Ultrasonically clean and hold under methanol.

5. Assemble SiGe and PbTe into graphite bonding fixture and load into bonding furnace.

6. Heat slowly at about 6°/min for about 2 hr to reach the bonding temperature of 830 °C. Hold for 60 to 75 min at 810 to 830 °C, and cool at about 6°/min to room temperature (substitute argon for hydrogen below 400 °C).

C. Preliminary Testing of Module Components

In reviewing areas of possible long term material deterioration under conditions of stress and temperature, it was felt that the hot shoe merited some investigation. The hot shoe is formed from one piece of molybdenum 1/16 in. thick, and the cold formed bend is of a generous radius. The possibility of premature recrystallization and large grain formation is more prevalent here due to the "severe" cold working. The chances of material failure at stresses well under those allowed are therefore greater.

To reassure ourselves, we obtained samples of the same kind of material
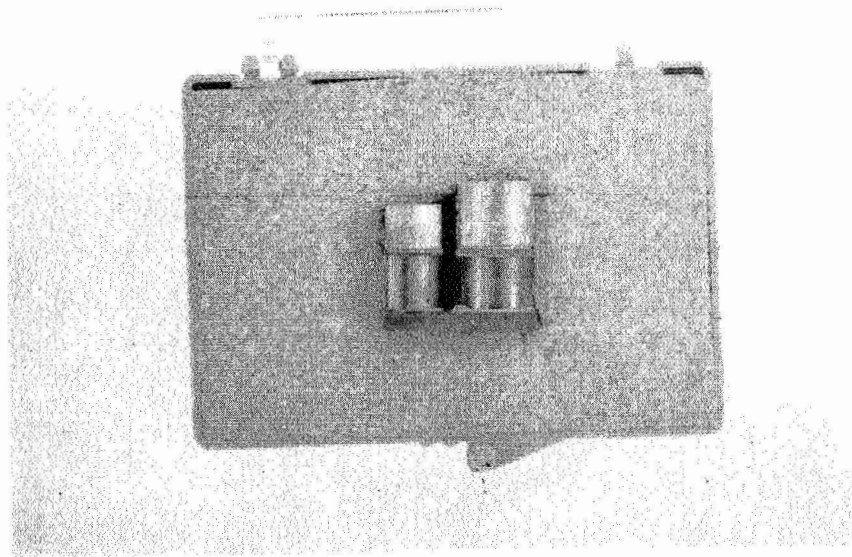
Fig. **10.** Example of bonded couple

formed in the same way and subjected these to a heat cycle of 950 °C (1742 °F) for 2 days in an argon atmosphere. Then, metallurgical preparation of an area not in the zone of bending and one of the bend itself was done in the usual manner, and photographs (Fig. 11) were made for comparison.

The grain size and distribution of both sample areas indicated that recrystallization had not taken place or had been corrected by the heat treatment (which is close to but below the recrystallization temperature of molybdenum).

All 25 finished hot shoes were then subjected to an identical heat-treatment cycle, and a section within the bend was polished to check grain size. This is shown in Fig. 12 (note there are no signs of any recrystallization evident).

D. Module Assembly

The first module assembly work, using actual components, was undertaken using a dummy couple (scrapped out couple material). As previously reported, block MIN-K insulation could not be used because of the requirement for thin sections and the structural weakness of the material.

We tried packing in micro-quartz in place of the MIN-K, but found this method sloppy and not efficient in filling voids. Also, assembly became cumbersome since the part of the insulation between the couple legs had to be installed before mounting the side plates and tended to shift and drop out of place.

The system finally chosen uses a precut blanket of micro-quartz which is compressed between platens to remove some spring-back quality in the material. This flattened blanket is then wrapped around the couple in a B-like path, starting in between the couple legs and terminating at the same spot.

Almost no voids are left with this style of lagging, and a very neat package is produced with accurate and reproducible dimensions. Another advantage is that the one-piece construction prevents material from falling between the couple leg and the interconnecting strap or piston, and leaves a neat entrance for the interconnecting strap insertion.

Other steps in the assembly are as follows (see Figs. 13 and 14):

1. Ultrasonically clean all parts.

2. Mount snap rings in cold shoe block and drop in spring thrust washers.

3. Nest springs in pistons and fit to cold shoe block using draw-in
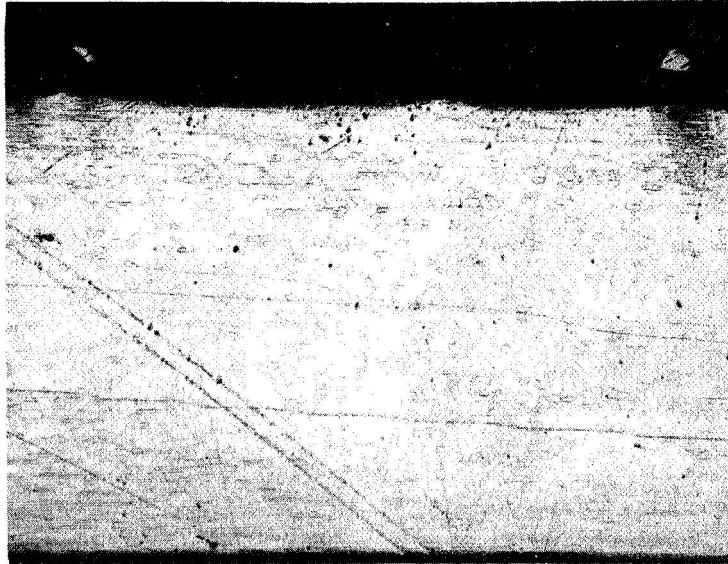
(a) Unworked, used as standard for recrystallization comparison
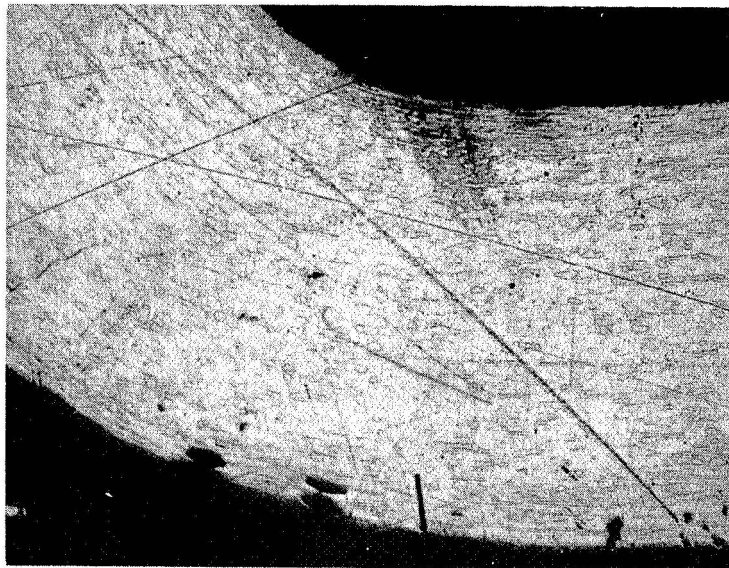
(b) Worked in area of 90° bend (shows no recrystallization or agreement with above structure)

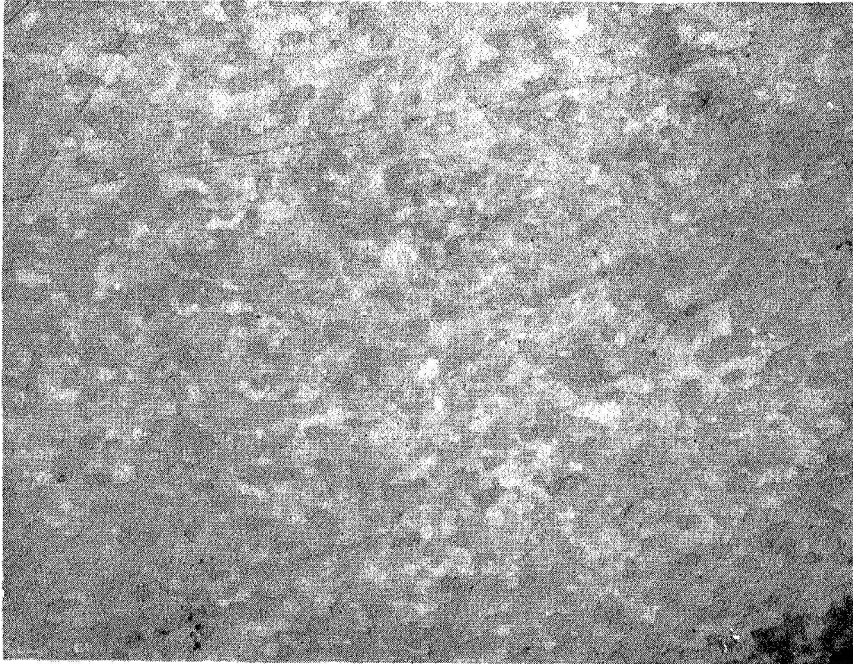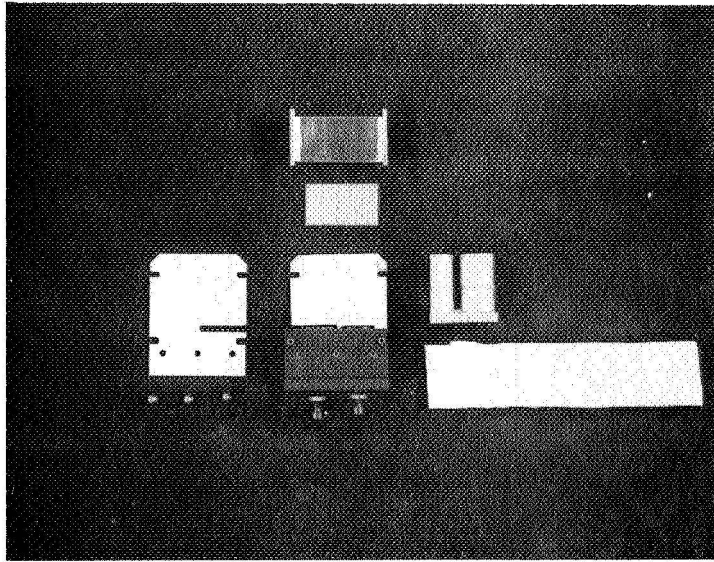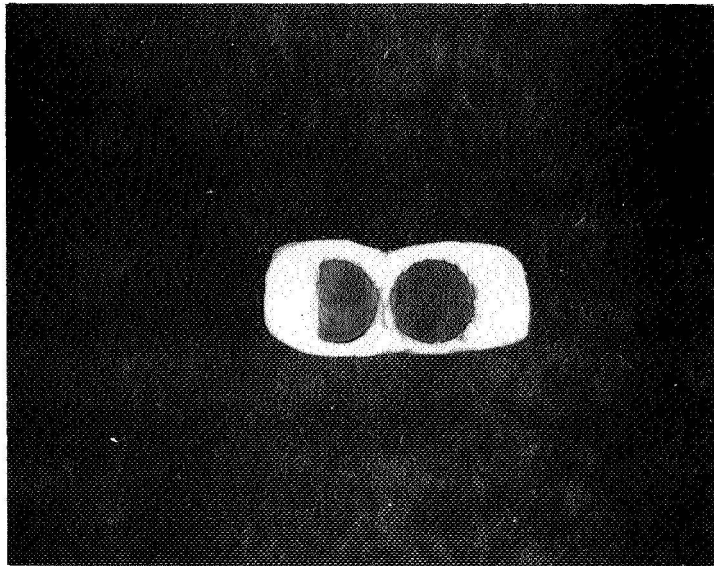Fig. 11. Grain structure of molybdenum hot shoe

Fig. 12. Grain structure of actual molybdenum hot shoe in area of 90°
bend (shows no recrystallization at end of 950 °C, 48-hr, heat-
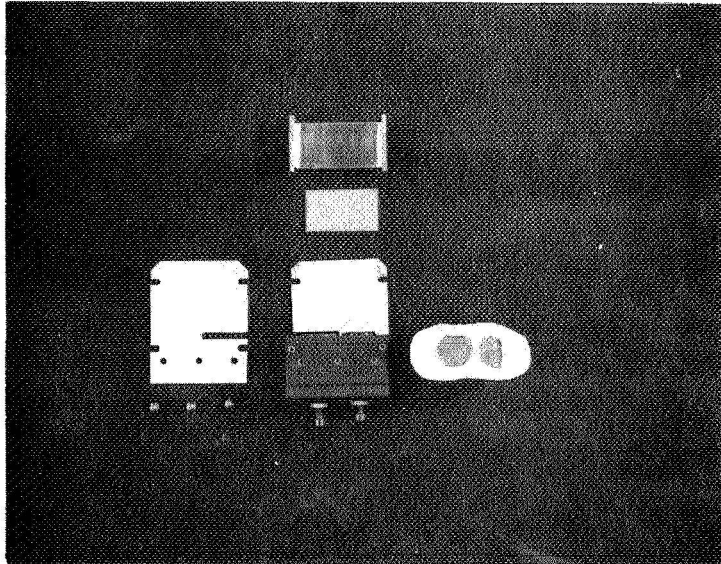treatment cycle; 90X)

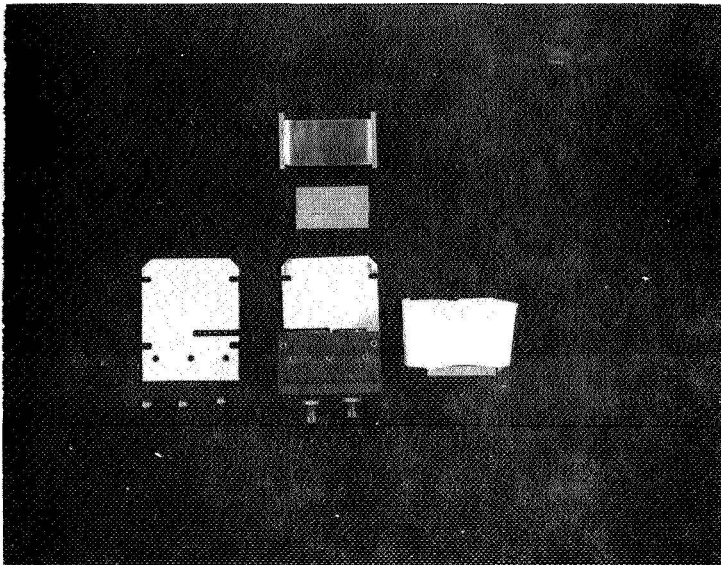(a) No couple subassembly

(b) Blanket wrapped couple

Fig. 13. Module parts ready for assembly step 5

(a) Top view of couple subassembly

(b) End view of couple subassembly

Fig. 14. Module parts at assembly step 5

screws and washers to keep piston in place when spring is compressed.

4. Fit one side plate and screw down using copper washers under screw heads. Torque screws only moderately.

5. Lay unit on side and place interconnecting straps over pistons followed by blanket wrapped couple.

6. Fit hot shoe and alumina insulator, and locate and screw down second side plate.

7. After seeing that hot shoe is well centered in side plates, slowly back off draw-in screws and remove entirely.

8. The module is now ready to be mounted on the copper pedestal of the test apparatus once a resistance reading is made.

Preliminary Module Testing: One module (Figs. 15 and 16) was assembled in the manner prescribed above using a no. LC032D14 spring which applies the maximum rated load to the structure. The assembly was stored at room temperature under load for 1 day with no discernible ill effects.

The module was then placed into the existing test equipment (Fig. 17) without the benefit of other external insulation so that its behavior under temperature could be observed. The heater was spring-loaded against the hot shoe of the module. Cooling of the cold shoe was accomplished with a liquid-to-air heat exchanger.

As heat-up progressed, data were recorded as follows over a 3-hr period:

Preliminary Run No. 1

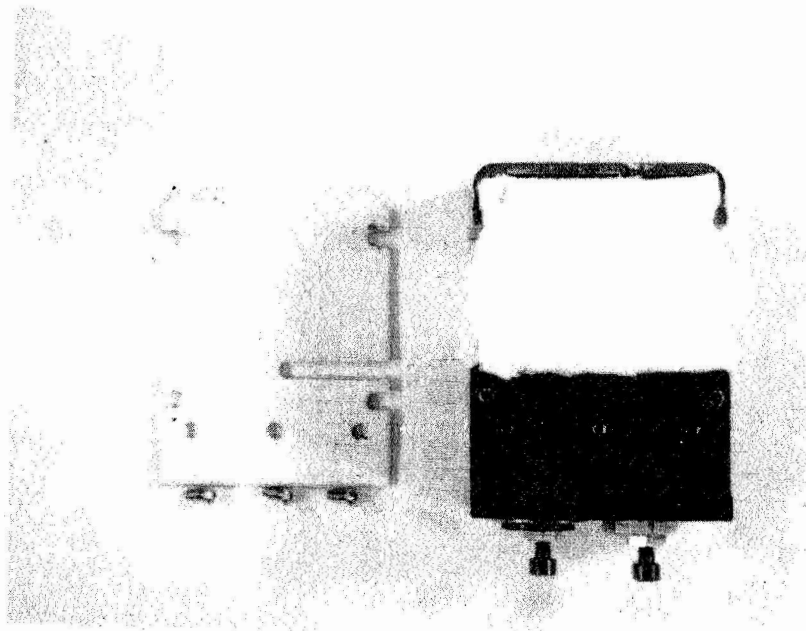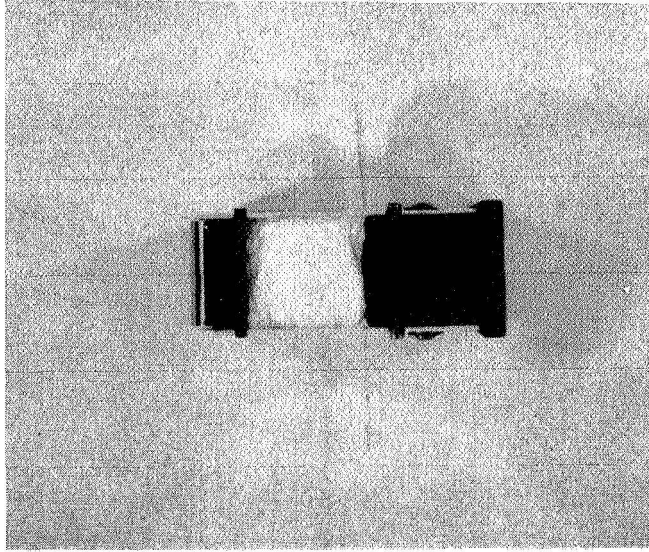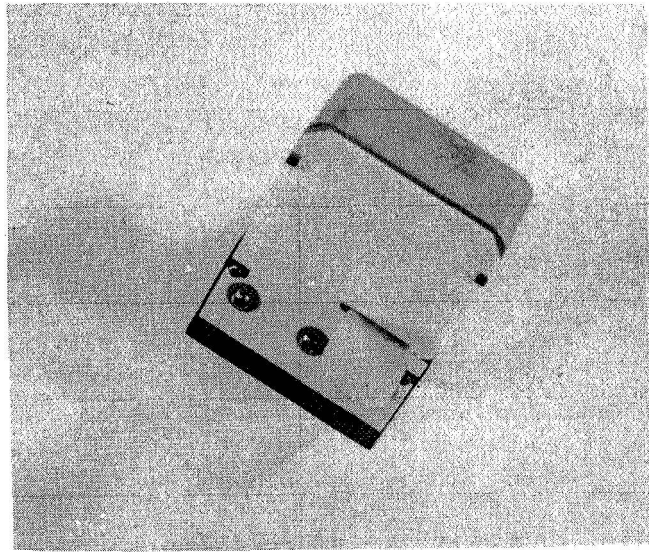|	Temperature, °C			Heater	
Time	Heat Flow Legs	Cold Shoe	Heater (Hot Shoe)	Volt	Ampere
10:30	—	66	139	20.0	8
11:00	—	74	171	—	—
11:15	60	81	195	—	—
11:30	60	85	218	—	—
11:45	61	88	244	22.0	0.9
12:00	61	93	275	—	—
12:15	—	—	295	26.0	1.0
12:30	62	100	337	—	—
1:00	—	—	—	30.0	1.21
1:40	62	129	486	—	—

Fig. 15. Module at assembly step 6

(a) Side view
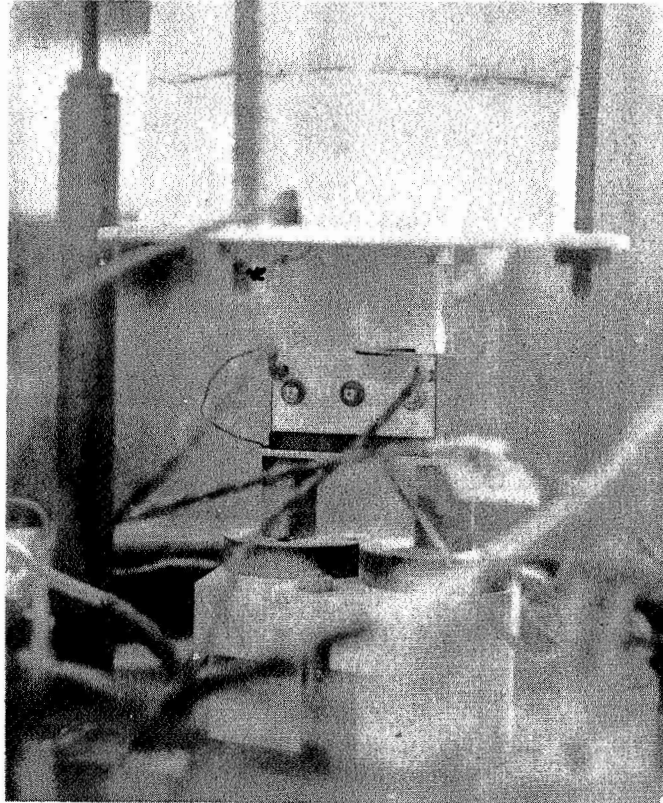

(b) End view

Fig. 16. Assembled module

Fig. 17. Module mounted in original test fixture

As the heater and hot shoe approached **486** °C, it was readily observed that the side plates had flared out considerably at their free ends, and it was not surprising to have one of the plates fail at the hot shoe notch (Fig. **18**). The reasons for the side plate flare are not clear at this time, but it is felt that expansion of the wrapped insulation may be responsible.

The module was fitted with a new side plate and brought up to temperature (605 °C) again. The flaring effect was not very noticeable this time, and the unit was kept at temperature overnight. The next morning it was found that a side plate had failed in the deep lower notch area and the module had jacknifed out of its pedestal upsetting the heater and the copper heat flow rods.

Since no one was in attendance at the time, it is hard to explain exactly what happened. Since the setup was a flimsy one (the module was not bolted down and the copper rods were not fixed), it is possible that someone may have shocked the setup and caused the failure that way.

Testing was suspended until an improved setup could be designed and built. When testing is resumed, lower spring pressures will be tried and the blanket insulation will not be installed initially. Also, a mechanically sound thermal analog dummy couple will be used to obtain uniform loading of the side plates.

Test Equipment Rework: The old SiGe test equipment was found to be mechanically inadequate for testing modules, and extensive revision was required to properly support the module and ensure the ability to produce good vacuum easily and often. Fig. **19** shows the modified equipment less vacuum, thermocouple glands, and power feedthrough. The heater assembly now rests upon the module insulation stack.

Since the Waltham industrial area is known for occasional interruptions in utilities such as electricity and water, this was considered in modifying the test equipment. Convection cooling of the cold shoe is used to ensure that such failures do not result in unduly high temperatures within the module (the heater is well insulated and cools down very slowly when power is removed).

A 1.5-in.-diameter OFHC copper rod (Anaconda alloy **101**) extends from the bell jar chamber through the baseplate and has a large extruded aluminum convection heat sink bolted to it (heat sink compound is used in the joint). The geometry is such that the cold shoe of the module can be kept at 50 °C or lower by conduction and convection heat transfer. The heat sink can be shrouded to raise the cold shoe
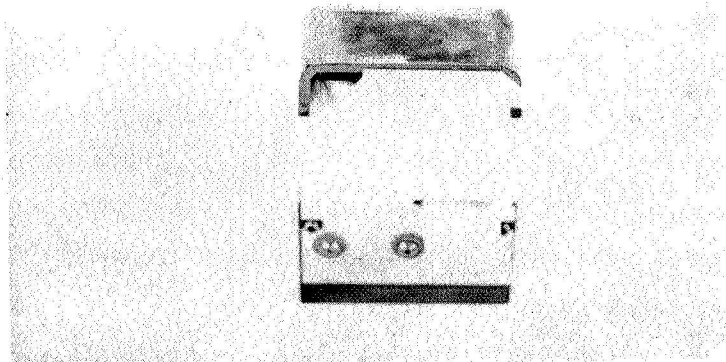
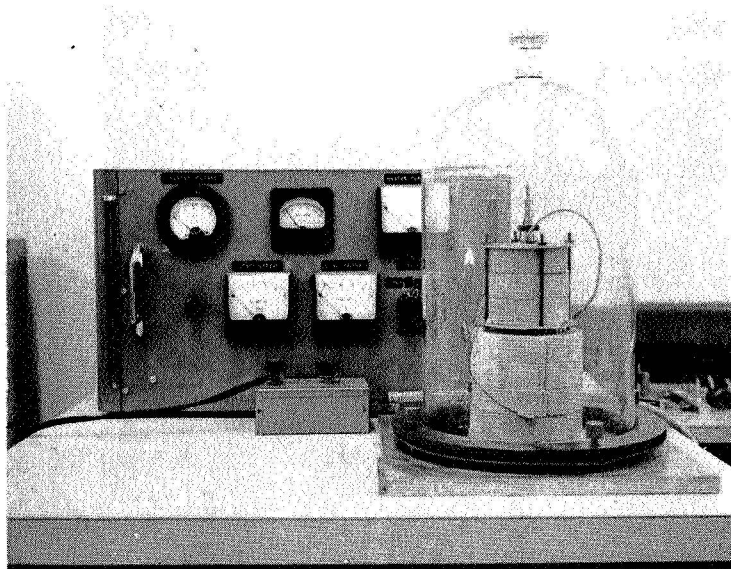Fig. 18. Failure of side plate after initial heat-up to 486 °C

Fig. 19. Modified test equipment minus vacuum, thermocouple, and
power feed-through glands

temperature.

The module bolts directly to the chambered end of this rod. Just below the module is an integrally machined, right circular cylinder of a precise diameter (or precise cross-sectional area) with machined thermocouple pads that allow couples to be clamped along the rod axis, spaced precisely apart. Since the OFHC alloy is certified, its thermal conductivity value can be ensured at a particular operating temperature. Fig. 20 shows the complete assembly removed from the vacuum gland.

Chromel-constantan couples (large output per degree) of a small gage (40 gage) with ISA beads and leads which are coated with a thin layer of Teflon will be used for measurements of the utmost reliability which are dependent on the nature of couple-surface contact geometry and ground loops. By using a bucking circuit to obtain the net difference in couple output, and chromel-constantan wire throughout up to the input terminals of a recorder, it should be possible to make measurements to hundredths of a degree.

The module and the heat flow leg are insulated with MIN-K (Fig. 21) to prevent heat loss. Heat flow losses in the thermocouple wire and power output leads of the module will be minimized by small conductor area where possible, and will be accounted for in the heat balance analysis. It should be possible to measure and calculate the heat flow through the module within 0.1%, or an amount of error which will not bear on efficiency calculations.
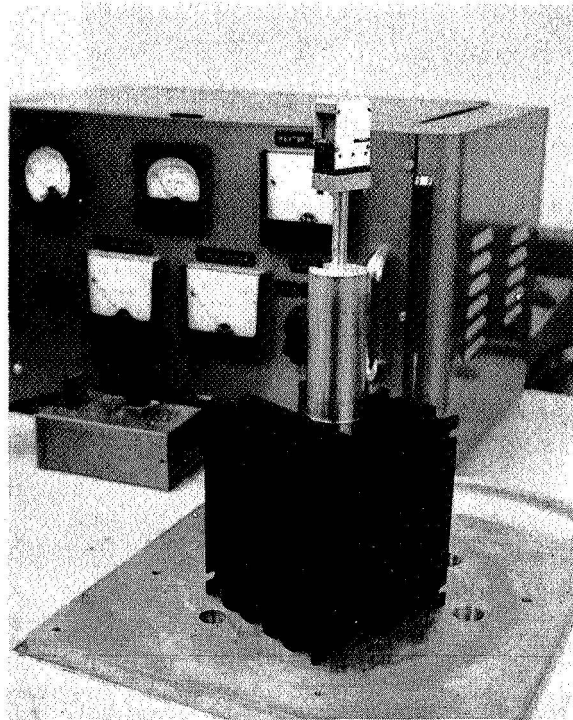
Fig. 20. Cold end assembly of module, heat flux pedestal, and heat sink
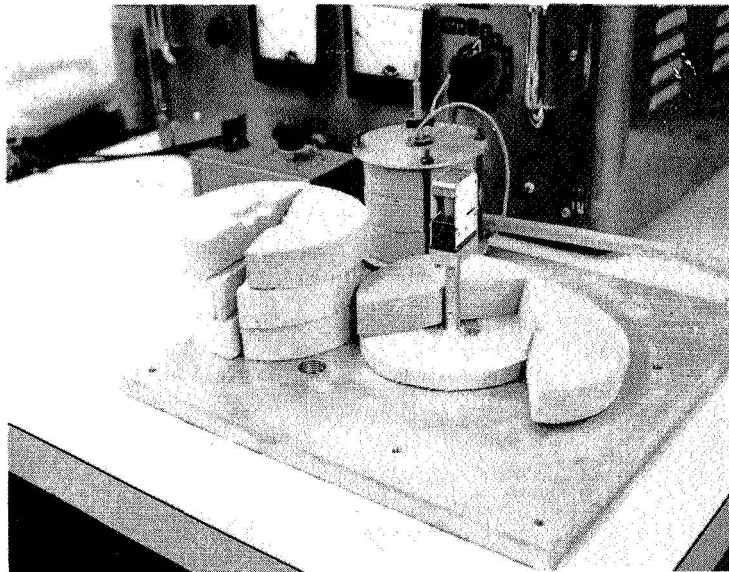

Fig. 21. Module and heat flux pedestal on baseplate with insulation partially removed

IV. REFERENCES TO TEXT AND APPENDIX

1. M. Hansen (with K. Anderko) "Constitution of Binary Alloys," Second Edition, McGraw-Hill Book Company, Inc., New York, 1958.

2. Semiannual Phase Report No. 4, "Lead Telluride Bonding and Segmentation Study," Contract No. NAS 5-9149, Tyco Laboratories, Inc., July 1969.

3. W. B. Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys," Pergamon Press, New York, 1958.

4. R. P. Elliott, "Constitution of Binary Alloys, First Supplement," McGraw-Hill Book Company, Inc., New York, 1965.

5. K. C. Jain and S. Bhan, The System Pt-Ge, Trans. Indian Inst. Metals, 19, 49-52 (1966).

6. F. A. Shunk, "Constitution of Binary Alloys, Second Supplement," McGraw-Hill Book Company, Inc., New York, 1969.

7. Semiannual Phase Report No. 3, "Lead Telluride Bonding and Segmentation Study," Contract No. NAS 5-9149, Tyco Laboratories, Inc., January 1969.

8. C. J. Raub, et al., Superconductivity of Some New Pt-Metal Compounds, J. Phys. Chem. Solids, 24, 1093-1100 (1963).

9. W. Jeitschko and E. Parthe, The Crystal Structure of $Rh_{17}Ge_{22}$: An Example of a New Kind of Electron Compound, Acta Cryst., 22(3), 417-30 (1967).

10. E. Raub and W. Fritzche, Germanium-Ruthenium-Legierungen, Z. Metall., 53, 779-81 (1962).

Appendix

METAL SYSTEMS WITH GERMANIUM AND/OR SILICON

PLATINUM

Jain and Bhan[5] have investigated the Pt-Ge system. No eutectic exists between Pt and Pt_3Ge. The latter forms peritectically at 915 ± 5 °C. The first eutectic at the Pt-rich end of the diagram exists between the compounds Pt_3Ge and Pt_2Ge at 725 ± 6 °C. The Ge-rich eutectic occurs at 802 ± 6 °C and 80 at. % Ge.

The Pt-Si system, recently reviewed by Shunk,[6] exhibits a eutectic between Pt and Pt_3Si at 830 °C. The exact composition of the eutectic is 23 at. % Si. The Si-rich eutectic occurs[1] at 67.5 at. % Si and 979 ± 4 °C.

The relatively low eutectic temperatures in the binary systems would not allow the use of a Pt-Si-Ge alloy as a high temperature (1100 °C) braze.

PALLADIUM

The $L \rightleftharpoons Pd + Pd_3Si$ eutectic is reported[6] as 782 °C, 15.5 at. % Si. The Si-rich eutectic occurs[1] at $\approx$ 58 at. % Si and 850 °C.

The Pd-Ge system has been studied as part of this contract.[2,7] Although the Pd-rich section has not yet been accurately defined, melting has been observed in alloys between 75 and 85 at. % Pd at 750 °C through differential thermal analysis. The Ge-rich eutectic is at approximately 735 °C and 67 at. % Ge.

As in the case of the Pt, this system would probably not lend itself to high temperature braze alloys due to its eutectic temperatures.

RHODIUM

Recent work has emphasized the structure of the compounds in the Rh-Ge system.[8,9] A tentative outline of the phase diagram has been reported[4] which shows a eutectic reaction between Rh and Rh_2Ge at $\approx$ 1080 °C and 22 at. % Ge (all dotted lines).

The Ge-rich eutectic, according to this diagram, occurs at about 850 °C and 23 at. % Ge.

In the Rh-Si system, a eutectic grain boundary network in the 5.3 at. % Si alloy was observed[1] to melt at 1389 °C. Again, most of the recently reported work on this system has generally involved structure determination of its compounds.

The structure of Rh_2Ge is orthorhombic, with lattice parameters of a = 5.44 Å, b = 7.57 Å, c = 4.00 Å, and 12 atoms per unit cell. It has a distorted Ni_2In-type structure. The Rh_2Si compound is also orthohombic, $PbCl_2$-type, a = 5.413 Å, b = 3.921 Å, and c = 7.384 Å. It is quite probable that these two compounds would form a continuous series of solid solutions across their pseudobinary section.

A ternary eutectic in the Rh corner of the system would not be anticipated on the basis of these data. However, the $Rh-Rh_2Ge$ eutectic with Si additions might be distinctly useful as a high temperature braze due to its extremely favorable melting point (1080 °C). The high cost of Rh, on the other hand, could be a financial deterrent.

IRIDIUM

Extensive work[1, 4, 6] has been carried out on the structural determination of the many intermetallic compounds in the systems Ir-Ge and Ir-Si. Few data are available with respect to the phase diagrams of these binary systems. A eutectoid (or eutectic) structure has been reported[4] to appear at 40 at. % Ge, probably between Ir and IrGe.

RUTHENIUM

The Ru-Ge system has been investigated by Raub and Fritzsche.[10] A eutectic exists between Ru and GeRu at 41 at. % Ru and approximately 1200 °C. Two compounds exist in the system: RuGe and Ru_2Ge_3.

In the Ru-Si system, a eutectic grain boundary phase in the 10 at. % Si alloy melted[1] at about 1488 °C. Three compounds exist in the system: Ru_2Si, RuSi, and Ru_2Si_3 (or $RuSi_{1.8 \pm 0.3}$). The latter two compounds are most likely isotypic with the corresponding Ge compounds.

The probability of an Ru-rich ternary eutectic is low; the melting temperatures in the system are also prohibitively high.

OSMIUM

A compound $OsGe_2$ has been reported.[1, 4] No other information is available.

Many compounds are reported to exist in the Os-Si system.[6] The Si-rich eutectic melts at 1360 ± 15 °C. High Os alloys melt[6] at >1690 °C.

Ternary alloys from these systems seem quite improbable for use in the present investigation.

NICKEL

The Ge-Ni and the Ni-Si system are reported in accurate detail.[1] In the Ni-Ge system, no eutectic exists between Ni s.s. and the β-phase (22.9 to 24.8 at. % Ge). A eutectic exists at 29 at. % Ge and 1130 °C between the γ and δ phases, but both constituents decompose eutectoidally at 1100 and 970 °C, respectively. The Ge-rich eutectic is at 62 at. % Ge and 775 °C.

The Si-Ni system has a eutectic between Ni solid solution and the β_3-phase at 21.4 at. % Si and 1152 °C. The β_3 constituent, however, undergoes two polymorphic transitions to β_2- and β_1-phases. An Si-rich eutectic exists between Ni-Si and $NiSi_2$ at 966 °C and 56.2 at. % Si. There is no eutectic between Si and any Si-rich compound.

A ternary eutectic could occur in the Ni-rich corner of this system, and at a fairly reasonable temperature for the braze material. However, the allotropic transformations of its possible constituents would probably cause distortional volumetric changes in the high temperature braze which would be completely undesirable.

IRON

The most recently reported version of the Fe-Ge system[6] shows no eutectic between Fe and Fe_3Ge. A eutectic does exist between Fe_3Ge and the β-phase (35 to 43 at. % Ge) at 1130 °C and 34 at. % Ge. The Ge-rich eutectic occurs at 859 °C and 75.5 at. % Ge.

The Fe-Si system, reported by Hansen[1] and supplemented in Shunk,[6] is extremely complex. No eutectic exists between Fe s.s. and the Fe-rich intermediate phase, α'. The existence of a eutectic between the dubious α'' phase and the FeSi is even questionable. If this eutectic exists, it occurs at approximately 34 at. % Si and 1200 °C. The Si-rich eutectic is at 73.5 at. % Si and 1208 °C.

The only suggested use of a eutectic alloy from these systems would be in the Fe-Ge system, which exists between Fe_3Ge and the β-phase. Si additions would be necessary. There is one negative aspect, however; both components of this eutectic are brittle compounds, which would make the resultant material mechanically

undesirable.

CHROMIUM

The Cr-Ge phase diagram has not been fully defined, although many of its compounds have been reported.[1,4,6] Cr_3Ge is the first compound to appear at the Cr-rich end. It has a "β-W" (A15) structure with a = 4.623 Å,[1] or a = 4.612 Å.[6]

The Cr-Si phase diagram has recently been reviewed.[6] A eutectic exists at 1700 ± 10 °C and 15.5 at. % Si between Cr s.s. and Cr_3Si. The Si-rich eutectic occurs at 85 at. % Si and 1335 ± 10 °C between Si and $CrSi_2$. Cr_3Si is also a "β-W" structure whose parameter varies from 4.576 to 4.563 Å over its solubility range.[4]

A ternary eutectic is not probable in the Cr-rich corner of this system, because Cr_3Ge and Cr_3Si are likely to be mutually soluble in all proportions. The temperature of the Cr-Cr_3Si eutectic is prohibitively high, and it is anticipated that the melting point of the Cr-Cr_3Ge eutectic would probably be the same.

TITANIUM

A eutectic exists at 13.4 at. % Ge and 1360 °C in the Ti-Ge system. This eutectic[1,4] is between β-Ti and Ti_5Ge_3. Ti_5Ge_3 has an Mn_5Si_3 structure (D8$_8$ type).[1]

Hansen[1] reports a eutectic between β-Ti and Ti_5Si_3 at 13.7 at. % Si and 1330 °C. Ti_5Si_3 is identified[1,4] as having an Mn_5Si_3 structure (D8$_8$ type), making this compound isotypic with Ti_5Ge_3. A compound Ti_3Si has been more recently reported[6] which would negate the simple eutectic construction between β-Ti and Ti_5Si_3. The Si-rich eutectic occurs at 86 at. % Si and 1330 °C.

It is most probable that a ternary eutectic does not occur in the Ti-rich corner of this system because of the isostructural nature of Ti_5Ge_3 and Ti_5Si_3. Secondly, the eutectic temperatures in the binary systems are well in excess of 1100 °C, which immediately negates the use of these alloys.

VANADIUM

The phase diagram of V-Ge has not yet been established. Data have been reported on V-Ge intermetallic compounds.[1,4,6] V_3Ge has been reported[6] to exist in equilibrium with V solid solution. V_3Ge has a "β-W" (A15) type of structure a = 4.769 Å,[1] or a = 4.792 Å.[6]

The V-Si phase diagram has been reported[1] and confirmed.[6] The V-rich eutectic occurs at 1840 °C and ≈ 13 at. % Si. The eutectic lies between V s.s. and V_3Si. V_3Si also has a "β-W" structure and a slight homogeneity range (its parameter

varies from **4.726** to **4.725** Å).

Again, a ternary eutectic in the V-rich corner of this system is improbable, because V_3Ge and V_3Si are isotypic and would probably exhibit complete solid solution in their pseudobinary cross section. Eutectic temperatures in these systems are far above the desired 1100 °C range.