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PROPOSED PROGRAM

TASK I - Mechanism of Bonding to Thermoelectric Materials

The main aim of this task of the proposed program is to determine the mechanism of bonding between Fe and PbTe and PbSnTe . An attempt will be made to distinguish between adhesion associated with atomic bonding (due to solid solution formation between the Fe electrode and the thermoelectric element) or in the case of brazing, bonding associated with the formation of an interlinked Fe mechanical eutectic structure which is metallurgically bonded to the Fe electrode through direct welding of Fe to Fe . An attempt will be made to relate electrical, chemical, metallurgical and mechanical observations so that one may obtain not only an understanding of the bond mechanism but a means to evaluate its utility in long term operational generators.

The various tasks are outlined below.

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Sub-Task I Determine the solid solubilities and eutectic composition and temperatures in the Fe-PbTe-SnTe pseudo-ternary system. An attempt will be made to determine:

(a) the path of monovariant eutectic solidification from 100 - 30% SnTe ,

(b) deviations from pseudo-ternary behavior, and

(c) solid solubilities of Fe in PbTe-SnTe solid solutions as well as in PbTe and SnTe .

Sub-Task II Investigate directly the diffusion bonding process:

(a) Prepare diffusion couples of PbTe , SnTe and $Pb_{0.7}Sn_{0.3}Te$ to Fe . This is to be done in consideration of results obtained in the constitutional investigation.

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(b) Determine the rates of diffusion in these systems by microprobe and/or tracer (using Fe^{55}) techniques.

(c) Evaluate the electrical properties of diffusion contacts, (contact resistance and its variation with temperature).

(d) Determine the mechanical characteristics of diffusion contacts in tension and shear. (A testing procedure utilizing a thin 0.050" PbTe or SnTe slab bonded to large Fe electrodes should eliminate confusion with bulk effects.)

(e) Investigate crystallographic and structural effects in diffusion - grain boundary diffusion, surface diffusion, anisotropic diffusion, etc.

Sub-Task III Study of Braze Bonding

(a) Prepare and evaluate the mechanical properties of braze bonds of the eutectic compositions of PbTe, SnTe and $Pb_{0.7}Sn_{0.3}Te$ with Fe. (Fabrication will take place in a small vertical furnace under high vacuum.) Mechanical evaluation will be made on bonds of the same configuration as diffusion bonds.

(b) Prepare and evaluate bonds as above with a series of compositions between SnTe-Fe and $Pb_{0.7}Sn_{0.3}Te$. The electrical and mechanical properties of these structures will also be evaluated.

(c) Evaluate the brazing of Fe (w/SnTe) to $Pb_{0.7}Sn_{0.3}Te$.

1. Effects of time and temperature (during the brazing process on the concentration of the constituents within the braze region.

2. Effects of time and temperature (solid) on further redistribution of constituents.

3. Investigate morphological and concentration variation of Fe in SnTe with increasing Pb content.

4. Study the effect of primary Fe in SnTe-Fe braze on subsequent brazing to $Pb_{0.7}Sn_{0.3}Te$.

5. Determine mechanical and electrical differences between brazed joints made by melting-on briefly a eutectic braze and/or by reacting the SnTe, e.g. directly with the Fe electrode to analyze differences in the Fe interface and/or mechanical interlocking of precipitates.

Sub-Task IV Determination of the effect of excess constituents (third phase metal, stannide or telluride) on each of the above mechanisms.

Explanatory Note:

The main aim of these studies is to attempt to determine the mechanism of bonding. Is it atomic bonding associated with mutual solid solubility, or is it mechanical interlocking of precipitates and then Fe to Fe welding? For example, if there is solid solubility of Fe in $Pb_{0.7}Sn_{0.3}Te$ of sufficient magnitude to yield diffusion bonds, is the braze bond substantially different in any way or is it just a diffusion bond with Fe scattered around and behind it in the braze region? Is the mixed eutectic region of importance with respect to thermal shock?

Some attention will be given to the mechanics of the brazing experiments. It has often proven difficult to cause reproducible stress patterns to be set up in the junctions even though reproducible methods apparently are used. To accomplish this we propose to use a well calibrated high precision set-up which utilizes a micrometer drive in a high vacuum furnace. The "jig" would allow setting up with the same pressure each time. The use of a dished Fe electrode would provide much better control of the braze thickness and of

"spills" which would have a disastrous effect on a careful systematic investigation.

Mechanical tests, which will be of considerable importance should avoid wherever possible the problems associated with bulk elements. Two systems which are readily workable and also yield a comprehensible state of stress are the pin-in-a-hole approach or plane interfaces with suitable Fe pieces such that they can be easily gripped for tension or torsion.

TASK II - Life Testing of Ultrasonically Cast - Bonded and Unbonded Thermoelectric Elements and Couples

In this study the major emphasis will be on the determination of the life characteristics of the metallurgically bonded and unbonded materials. The test systems will allow a careful analysis of the effect of pressure, as well as thermal gradient on the properties of bonded, as well as unbonded thermoelements. The effect of environment (O_2, argon, H_2O, H_2, etc.), will also be evaluated.

Sub-Task I Construct one 12-station life test module (bell jar type) to evaluate the long term performance of metallurgically bonded couples. (The system will be capable of producing bonding pressures up to 200 psi and will allow evacuation and introduction of various environments, O_2, H_2, N_2, etc.) Measurements of Seebeck voltage, total resistance and junction temperatures will be made as a function of time (hot junction temperature 550°C), 6000 hours of testing will be accumulated.

Sub-Task II Construct one 12-station life test module (bell jar type) to evaluate the long term performance of metallurgically bonded and unbonded (pressure) ultrasonically prepared thermoelements. The system will be used to evaluate the effect of pressure, environment (O_2, H_2, H_2O, etc.) and thermal gradient on the long term performance of 100% dense, oxygen free ultrasonically cast thermoelements. Measurements of Seebeck voltage, total

resistance and junction temperatures will be made as a function of time (hot junction temperature 550°C) 6000 hours of testing will be accumulated.

Sub-Task III Thorough evaluation, both metallurgical and chemical will be carried out when dictated by specific variations in electrical characteristics.

Sub-Task IV Continue isothermal tests under varying pressure, atmosphere and temperature. Accumulate at least 8,000 hours on bonded and unbonded samples. Evaluate critically in this segment the effect of O_2 on the bond and electrical properties as a function of pressure and temperature.

TASK III - Optimization of Ultrasonically-Prepared PbTe Thermoelements and Thorough Evaluation of Materials Characteristics

This portion of the study will concentrate on an evaluation of the new PbTe material as it refers to long term generator behavior. Such degradation processes as pore migration, thermal fracture and oxygen damage of the bulk PbTe and the contact will be evaluated. Where these studies indicate improvements in the material are necessary, process development work will be initiated. All work will be carried out using both elemental and 3 M's powder as charge materials.

Sub-Task I Study and Evaluate the Mechanism and Effect of Pore Migration.

Studies will be carried out using pressed and sintered and ultrasonically cast PbTe:

(a) Determine effect of pressure 15 - 150 psi

(b) Determine effect of initial porosity and composition

(c) Determine effect of temperature.

Sub-Task II Study and Evaluate Deformation Mechanisms in PbTe Thermoelements as They Relate to Thermal Shock and Thermal Gradient.

(a) Determine strength in tension shear and compression of PbTe under thermal gradients up to 600°C/cm.

(b) Determine effect of compressive loading on some of these properties.

(c) Determine mechanism of deformation under various stress conditions (glide planes, dislocation and stacking fault effects, grain boundary effects, etc.).

Sub-Task III Study and evaluate the effect of O_2 on the bond resistance and bulk properties of PbTe . The oxygen content of ultrasonic material will be varied by doping of the melt.

(a) Determine the effect of oxygen on the contact resistance of pressure bonded and metallurgically bonded PbTe thermoelements.

(b) Determine the effect of oxygen on the bulk properties, electrical and mechanical.

Sub-Task IV Process Development and Refinement.

Process improvements such as new crucible configuration, will be initiated where the above studies indicate improvements are desirable.

TASK IV - Produce Optimum Ultrasonic Material for Use In Systems Presently Under Development.

Material sufficient for incorporation into systems presently under development will be produced. Evaluation of the effects of 100% density, low oxygen and impurity content and high tensile strength on system performance will be made. Both PbTe thermoelements produced from elemental charge and/or 3 M's PbTe powder charge will be produced.