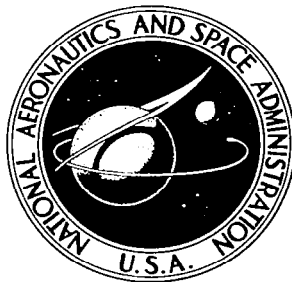
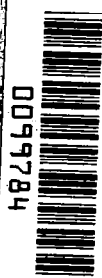


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# THERMOELECTRIC BONDING STUDY

## THE BONDING OF PbTe AND PbTe-SnTe WITH NON-MAGNETIC ELECTRODES

*by M. Weinstein and H. E. Bates*

Prepared under Contract No. NAS 5-3986 by  
TYCO LABORATORIES, INC.  
Waltham, Mass.

*for*

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## ABSTRACT

The major aim of this program is to define clearly the most appropriate system and process for the reproducible fabrication of low resistance, high strength, non-magnetic bonds to PbTe and PbTe-SnTe alloys. During this study we have investigated the applicability of the refractory metals Mo, Nb, Ta, W, and Zr as electrode materials in both diffusion and braze bonding. In conjunction with these refractory metals, SnTe, SnTe-0.1% Fe, AgSbTe<sub>2</sub>, and AgBiTe<sub>2</sub> have been studied as brazes. The Ta-SnTe electrode-braze-composite is the most promising of the various combinations studied. The metallurgical nature as well as the electrical properties of SnTe-Ta braze-bonded PbTe are discussed.

A process for the diffusion-bonding of N-PbTe and P-PbTe-SnTe with pure W has been developed. Initial results indicate that this structure is somewhat superior to the braze bond. Problems associated with diffusion and thermal expansion mismatch have been carefully evaluated. By employing a refined bonding procedure which involves a precise lapping technique, W-diffusion bonded structures have been prepared without deterioration of the electrical and mechanical properties of the "as prepared" thermoelement.

The results of measurements of the thermoelectric properties of bonded and unbonded P and N - type thermoelements are described in detail.

Results of a study to determine the rate of sublimation of cold pressed and sintered P and N - type thermoelements are presented.



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## I. INTRODUCTION

Thermoelectric generators can be incorporated in systems which require long-term stability under a wide range of environmental conditions. The extremely high temperatures in high efficiency generators, the severe mechanical vibrations in missiles and space vehicles, and the rapid temperature changes in many heat pump systems all place extreme demands on the total structure of the thermocouple module. Since reliable long-term operation is one of the main advantages of thermoelectric devices, the thermoelectric elements and bonding structures must be both physically and chemically stable. In most cases the solution of the bonding problem is far more complex than the development of the basic thermoelectric material.

The most efficient thermoelectric generators in operation at this time employ PbTe and PbTe alloys (e. g. SnTe-PbTe). The major problems of these generators are connected with the physical stability of the bulk PbTe and the chemical and physical stability of the electrode-thermoelement composite. The aim of this program is to develop a bonding approach, using non-magnetic materials, which will insure both physical and chemical thermocouple reliability.

Previously, various bonding techniques such as compression-loading of the hot junction together with soft soldering of the cold junctions<sup>(1)</sup> have been used to produce fairly stable, low resistance contacts. However, even with the mechanically complex structures necessary for this technique, the contact resistance still is a significant contribution to the total resistance of the thermocouples. During this investigation we will concentrate on the braze-bonding and diffusion-bonding techniques previously employed by the author for the bonding of Fe electrodes to N- and P-type PbTe<sup>(2)</sup>. In this section the braze and diffusion bonding techniques are discussed in terms of the general requirements of a bonded structure.

## A. Mechanical Stability of the Bond

In most cases the bond must be at least as strong as the bulk thermoelectric material. Where a high efficiency device is desired, the electrode must also provide the major mechanical support for the thermoelements. One technique which has been used to obtain maximum ductility and strength has been the use of an intermediate braze, such as SnTe or  $\text{AgBiTe}_2$ , between the electrode and thermoelement. In the case of the Fe-SnTe-PbTe structure, the bond has been shown to be significantly stronger than the bulk PbTe. This is not surprising, since it has been experimentally determined that the maximum strength of a brazed joint may be considerably higher than the yield strength of the brazing alloys, owing to an interesting phenomenon of tri-axiality of stress. In simple terms, the SnTe (or SnTe-PbTe alloy), being a material of lower yield stress than Fe or PbTe, tends to begin yielding shortly after the load is applied. However, the presence of the Fe and PbTe prevents the plastic deformation and constrains the SnTe ( or SnTe-PbTe alloy ) from yielding; thus, at each interface shear stresses are built up. Since the shear stresses act in planes normal to the longitudinal axis of the specimen, they generate tensile forces when acting within the iron. Analysis of the stresses shows that the uniaxial component of tensile stress is less than the load divided by the area of the specimen, i. e. , the imposed load.

In the normal diffusion bond such an increased bond strength is obtained when the diffusion zone (Fe-PbTe) has a similar or higher ductility than the original material (PbTe). This condition is usually met if second-phase formation and precipitation can be avoided.

When a physical bond is fabricated by alloying or other means, the expansion coefficient of the various structural components must be closely matched in order to avoid shearing stresses during thermal cycling. The braze process using SnTe tends to minimize the problems associated with mismatch in the expansion coefficient, since the alloying



of the braze SnTe with the base PbTe creates a graded region in the vicinity of the bond. A similar result, on a much smaller scale, has been obtained on the diffusion-bonding of Fe to PbTe.

### B. Electrical Conductance of Bond

Another major requirement of the metallurgical bond is that it provide good electrical conductance through the thermoelectric system; it must not introduce any resistive component compared to the volume resistance of the elements. In practice, this is seldom accomplished. The majority of the efficient thermoelectric materials employed today are intermetallic compounds and semimetals. Many of the constituents of these systems are quite reactive; therefore, very often at the electrode-thermoelement junction an intermediate layer of high resistivity or depleted carrier concentration is formed.

To eliminate this problem, non-reactive material must be selected for both electrode and braze. The direct contact of a pure metal alloy to PbTe thermoelements has met with only limited success, iron being the only metal directly bonded to PbTe satisfactorily. This technique is hampered by the need for extremely clean surfaces and by narrow tolerances as far as electrode-thermoelement parallelism is concerned. By employing an intermediate braze which forms a complete series of solid solutions with PbTe and also wets the electrode effectively, bonds of extremely low resistance can be prepared.

### C. Thermal Conductance of the Bond

The electrode-bond structure must provide good heat transfer both into and out of the thermoelectric junctions. In pressure and direct contact bonds this requirement is often lacking because of the presence of oxide layers or air gaps at the electrode-thermoelement junction. The majority of efficient thermoelectric materials, par-

ticularly PbTe and PbTe alloys, form thin, strongly adherent surface oxide layers immediately upon exposure to air, and must therefore be carefully treated to remove such oxides before good thermal contact to the electrode can be made. As in other situations where good thermal conductance is of major importance, brazing is probably the only satisfactory bonding technique. If proper preparation can be accomplished, the diffusion-bonding technique could produce suitable thermal conducting bonds.

## II. EXPERIMENTAL RESULTS AND DISCUSSION

### A. Braze Bonding

The criteria underlying the choice of a braze are that it bond (wet) independently to the electrode and P- and N-type PbTe, that it have an intrinsically high electrical conductivity, that its melting point lie between the upper operating temperature of the thermocouple and the melting point of PbTe, that it form a graded region in the vicinity of the bond to minimize strains from the mismatch in the expansion coefficients, and that it not cause chemical or electrical deterioration of PbTe at the operating temperatures. These criteria lead inevitably to the semimetals or near degenerate semiconductors with crystal structures related to that of PbTe.

Initial work was an evaluation of the wetting properties of SnTe on Mo and Ta electrodes as a function of surface treatment. Figure 1 shows the results of initial wetting experiments of SnTe on Ta. The left slice was polished on 600 grit paper. The SnTe in this case did not spread over the Ta surface. The middle Ta slice was polished with  $5.0 \mu \text{ Al}_2\text{O}_3$ . A large thin area of SnTe which adhered strongly to the slice was produced. The right slice was polished with  $0.05 \mu \text{ Al}_2\text{O}_3$ . Similar spreading was obtained. Figure 2 shows the results obtained for the wetting of Mo by SnTe. The left slice was polished on 600 grit paper, the middle slice with  $5.0 \mu \text{ Al}_2\text{O}_3$  and the right slice with  $0.05 \mu \text{ Al}_2\text{O}_3$ . Satisfactory results were again obtained for the  $0.05$  and  $5.0 \mu \text{ Al}_2\text{O}_3$ .

To evaluate the brazing materials, it was also necessary to determine the most efficient means of melting the braze and the most suitable form of braze material. Three methods of melting were evaluated:

- a. Melting in a sealed evacuated quartz tube,
- b. Melting in an evaporation chamber, and
- c. Melting in a carbon boat under an inert argon atmosphere, heat being supplied by a resistance furnace.

The carbon boat technique was found to be most suitable since 22 slices could be brazed at the same time. The carbon boat ensured that all slices were at the desired braze temperature, and allowed a slow uniform rate of cooling, which eliminated bond fracture due to thermal shock.

Both powdered and single-chunk SnTe were used as the charged braze. The single chunk was found to be most efficient, since it allowed removal by H<sub>2</sub> reduction of most of the surface oxide. The powdered charge also caused a large amount of gas porosity to be present in or near the interface:

The following procedure was carefully followed in the brazing of the refractory metal electrodes:

- a. Slice preparation:
  - 1) surface polish with 5  $\mu$  Al<sub>2</sub>O<sub>3</sub>
  - 2) degrease in boiling N-propanol (twice)
  - 3) wash ultrasonically in Alconox and de-ionized water
  - 4) rinse in de-ionized water (twice)
  - 5) rinse in boiling methanol (twice)
  - 6) keep in methanol until immediately prior to loading into carbon boat.
- b. Braze preparation:
  - 1) scrape surface of large SnTe ingot section
  - 2) break into large chunks
- c. Boat preparation  
fire boat in high purity argon 1 hour @ 950°C prior to each run.
- d. Brazing techniques:
  - 1) flush furnace at least 5 minutes with high purity argon
  - 2) place loaded carbon boat into furnace at 250°C or less
  - 3) introduce argon (5 CFM) up to 425°C

- 4) introduce hydrogen (5 CFM) from 425<sup>o</sup> - 650<sup>o</sup>C
- 5) introduce argon from 650<sup>o</sup>C to maximum temperature of 840<sup>o</sup>C. Hold at 840<sup>o</sup> for 5 minutes. Cool to 825<sup>o</sup> and hold for 15 minutes.
- 6) allow to slow-cool to 250<sup>o</sup>C or less

(All results reported on braze bonding were obtained using this procedure, with only slight modifications in some specific cases.)

Figure 3 shows typical surfaces of braze on Mo and on Ta before and after grinding. In the lower figure sample 1 is a Mo slice from which the braze separated on grinding. The light area is where the braze had adequately wet the surface. Sample 2 is again a Mo surface which has retained its physical integrity after being ground down to a 5 mil thickness. Sample 3 is braze on Mo slice after the polishing and cleaning operation. In this case the dark area is braze; the gray area is the region where the braze did not adequately adhere and cracked off when ground. Sample 4 is SnTe on a Ta slice after grinding, polishing, and cleaning. This sample, like the majority of other SnTe-Ta bonds, shows no sign of bond fracture on grinding.

The following observations and conclusions have been made on the brazing of Mo and Ta with SnTe (46 samples):

- a. SnTe-Ta :
  - 1) braze spreads over entire surface
  - 2) braze surface appears dull; however, each slice that has been brazed is strongly bonded.
  - 3) brazed composite dropped 6 ft. onto concrete slab remained intact.
- b. SnTe-Mo :
  - 1) braze spreads over entire slice
  - 2) braze appears well bonded; however, structure separates when dropped 4 ft. onto a concrete slab. Braze appears to have wet only a few points on the surface.

3) grinding causes fracture of the brazed joint.

All attempts to obtain adequate braze joints between W and SnTe have met with failure.

Figure 4 shows rather unsuccessful attempts to braze Mo and Ta with  $\text{AgBiTe}_2$  and  $\text{AgSbTe}_2$ . An apparently clean bond was formed between  $\text{AgBiTe}_2$  and Mo. (Sample 1) On bending or scratching, the brazed electrode readily separated from the braze. The  $\text{AgSbTe}_2$  bond with Mo (Sample 2) was similar to Sample 1 in all respects. In the braze bond between  $\text{AgBiTe}_2$  and Ta (Sample 3) the surface appeared oxidized and the braze did not wet the Ta.  $\text{AgSbTe}_2$  did wet Ta (Sample 4), but again this braze bond fractured under limited stress.

Figures 5 and 6 show the  $\text{AgBiTe}_2$ -Zr and  $\text{AgSbTe}_2$ -Zr bonds. Neither structure showed satisfactory wetting. However, the  $\text{AgSbTe}_2$  appeared to be extremely well bonded in the wetted areas.

In order to increase the N-type conductivity of the SnTe braze, 0.1% Fe was introduced. Figure 7 shows the strong mechanical adherence of the braze to a Ta slice. The Ta did not shear away from the braze on grinding. However, it can be seen that the Ta-SnTe (0.1% Fe) bond (left samples, Figure 8) does not adhere to Ta as well as pure SnTe (samples on right, Figure 8). The perfect wetting of the SnTe-Ta samples is again evidenced in Figure 8.

In order to bond to the N- or P-type thermoelement the SnTe braze was normally ground down to 0.012 - 0.017 in. , and the Ta or Mo electrodes were maintained at 0.008 in. thick. Bonding was accomplished by placing into a cylindrical hole in the carbon block a brazed electrode, thermoelement, brazed electrode, and a W weight in that order. Bonding took place at  $810 \pm 5^\circ\text{C}$  for 15 minutes in an argon atmosphere.

A typical SnTe-Mo bond is shown in Figure 9. (200 X) It can be seen that a second phase formed adjacent to the junction. This allowed the propagation of multiple microcracks in the junction region.

(A polishing effect causes the junction interface to appear as a broad black line.) This polishing effect is shown in Figure 10 which is a photomicrograph (200X) of the SnTe-Ta bond.

Figure 11 is a photomicrograph (200X) of this junction focused into the recessed bond region. Interdiffusion of Ta and SnTe is evident.

A SnTe braze between Ta and PbTe (either N- or P-type) in most cases produced thermoelements of low resistance and extremely stable bonding. Two such typical bonded thermoelements are shown in Figure 12. In some cases, however, high resistance, mechanically unstable thermoelements were produced using the SnTe-Ta combination. Figure 13 (50X) shows the precipitation and fracture structure found in the PbTe-SnTe region of one of these high resistance thermoelements. Problems such as these have been traced to improperly zone-leveled SnTe. The excess Sn normally found in SnTe is probably the cause of the precipitated substructure.

#### B. Diffusion Pressure Bonding

In order to clearly define the effect of the braze on the electrical properties of the thermoelement, control samples of PbTe were placed in the carbon-bonding jig. On heating to the bonding temperature, the tungsten bonding weights adhered to the PbTe thermoelement. As can be seen in Figure 14 (lower section) the W bonded to the thermoelement only in certain sections. This result indicated that W could be bonded directly to PbTe, but that extremely critical evaluation of such things as electrode and element smoothness and boat loading techniques would be necessary.

Employing more accurate control of surface preparation and boat loading, the adhesion shown in Figure 15 was obtained. The W electrode made direct diffusion contact to the entire PbTe surface with both N- and P-type PbTe. Elements of N-type and P-type PbTe-SnTe bonded with W electrodes are shown in Figure 16.

## 1. Bonding Procedures

A new method of preparing the surfaces of the metallic electrodes and thermoelement for diffusion bonding has been developed. Grinding and polishing produced slightly convex surfaces, which made a poor bond after subsequent diffusion. This was evidenced by the rim of poor adhesion or the absence of adhesion on the outside of such elements. The new method consists of lapping both element and electrode on a flat glass plate to the same degree of finish as had been achieved by polishing. The lapping sequence is as follows:

- 180 grit - SiC
- 240 grit - SiC
- 320 grit - SiC
- 400 grit - SiC
- 600 grit - SiC
- 1800 grit - Al<sub>2</sub>O<sub>3</sub>

The cleaning procedure after lapping is as follows:

- (1) degrease in boiling N-propanol (twice),
- (2) wash ultrasonically in Alkonox and de-ionized water,
- (3) rinse in de-ionized water (twice),
- (4) rinse in boiling methanol (twice); keep in methanol until immediately prior to loading into carbon boat.

The diffusion-bonding technique is:

- (1) place thermoelements and electrodes into carbon jigs employing a dead-weight pressure,
- (2) flush furnace at least five minutes with high purity, low oxygen argon,
- (3) place loaded boat into furnace at 250<sup>o</sup> or less, introduce argon (5 cfm) up to 425<sup>o</sup>C,
- (4) introduce hydrogen (5 cfm) from 425<sup>o</sup> to 650<sup>o</sup>C,
- (5) introduce argon from 650<sup>o</sup>C to the maximum temperature of approximately 850<sup>o</sup>C. Hold at 835<sup>o</sup> to 850<sup>o</sup>C



for 20 min. This is considerably higher than that proposed initially, 825<sup>o</sup> to 840<sup>o</sup>C for 5 min. The longer time and higher temperature appear to give extremely well behaved and reproducible bond structures,

- (6) allow to cool slowly to 250<sup>o</sup>C or less (cooling rate  $\approx$  6<sup>o</sup>C/min).

## 2. Electrode Configuration

During this period we have normally employed electrodes of tungsten and tantalum approximately 0.125 in. x 0.25 in. in diameter cut from 0.250 in. rods. These are being used to alleviate the problem of flaking of the elements under the tungsten voltage probe needles used for making direct resistivity measurements of the element. In this case contact is made to the large electrode near the bond. Although there was some hesitation about using thicker electrodes because of their "stiffness" during thermal deformation, so far there have been no indications of thermal cracking. Another reason for the use of large electrodes is that the technique employed for diffusion-bonding is extremely sensitive to the surface flatness and parallelism of the electrodes. The 10 mil sheet originally used for electrodes normally retains some of the cupping produced during the punching process in fabrication; it is, therefore, much easier to obtain a flat highly polished surface on the larger electrodes. Having more perfect parallel faces on the electrodes avoids unequal distribution of the force provided by the dead-weight loading, making it possible to get a more accurate estimate of the reliability of the diffusion-bonding process.

### III. ELECTRICAL MEASUREMENTS

A schematic diagram of the apparatus used for measuring the resistivity of thermoelectric materials as a function of temperature is given in Figure 17. During initial experimental work it was found that although an A.C. measuring technique is employed (as shown) the furnace had to be wound non-inductively to avoid stray pick-up. During this work all resistivity measurements were made on bonded elements with the voltage probes on the electrodes, due to the flaking of the element under the tungsten voltage probe needles of the resistivity jig. For comparison, data supplied by Minnesota Mining and Manufacturing Corporation was used for unbonded material. Measurements of Seebeck coefficient and resistivity from room temperature to 500°C were made to compare bonding methods, and to determine the relations of changes in resistivity and Seebeck voltage produced by prolonged time at high temperature. Results of these studies are given in the next section.

#### A. Resistivity Measurements

Figure 18 is a plot of the resistivity as a function of temperature for W diffusion-bonded N-type PbTe thermoelements. The reported value for unbonded material obtained from 3 M Corporation is shown for comparison. The resistivity of the diffusion-bonded element is lower at low temperatures than that reported for unbonded material, and approaches the value reported by 3 M at 500°C. Figure 19 again shows the resistivity of W diffusion-bonded PbTe; however, in this figure the value of resistivity as a function of temperature is compared with that of an N-type element bonded with brazed tantalum electrodes. The brazed tantalum electrodes give approximately the same value over the entire temperature range as that reported by the 3 M Corporation for unbonded material. Direct Ta diffusion-bonding gave very poor results and therefore has been discontinued. Figure 20 is a plot of the resistivity as a function of temperature for P-type lead telluride thermoelements bonded by the tungsten diffusion-bonding process.

This plot agrees in character with that for the N-type bonding process in that the resistivity of the bonded element approaches that of the unbonded PbTe at 500°C. The excellent reproducibility of the bonding approach is shown in this figure. Figure 21 again demonstrates the excellent bonds produced by both the Ta-SnTe brazing process and the tungsten diffusion-bonding process. For P-type bonding Ta diffusion-bonding appears to be relatively effective. The similarity of the W diffusion-bonded structures on N- and P-type thermoelectric material, and Ta-diffusion bonded structures on P-type thermoelectric material contrasted with the behavior of brazed tantalum on N- and P-type material is the salient feature of these measurements, as well as the fact that neither process increases the resistivity of the material over the unbonded resistivity.

#### B. Seebeck Voltage

Measurements of the Seebeck voltage of the various bonded thermoelectric structures were made from room temperature to 500°C. Figure 22 is a plot of the Seebeck voltage as a function of temperature for N-type unbonded PbTe. These elements are from two different lots from the 3 M Corporation. The excellent reproducibility of the results denotes reasonably good quality control for the N-type material. Figure 23 shows the average values of Seebeck voltage as a function of temperature, obtained from approximately 25 bonded electrodes. The values obtained for Seebeck voltage as a function of temperature for W diffusion-bonded electrodes are almost exactly the same as those obtained for the average of unbonded material. The slight deviation in these two values may be associated with the temperature drop across the metallic electrodes. There appears to be a slight deterioration in the Seebeck voltage of N-type PbTe elements brazed with SnTe and bonded to Ta electrodes. As was reported previously, the effect is associated with the relatively large amount of braze utilized in the initial SnTe bonding experiments. The SnTe alloy formed at the bond interface appears to have an excessively detrimental effect upon the Seebeck

voltage. As can be seen from Figure 24, all measurements on new, unbonded P-type SnTe-PbTe agree very closely with the values published by 3 M Corporation. The W diffusion-bonded elements do not deviate significantly from unbonded material. This was checked by removing the bonds from one of the elements and checking this voltage output with that of the bonded element. An unbrazed Ta diffusion-bonded element showed a significant loss in voltage output. This effect has been assigned to the tendency of tantalum to oxidize before bonding actually takes place. For Ta diffusion-bonding to be as satisfactory as W diffusion-bonding, careful preparation of the system and electrodes, with particular reference to atmospheric control must be carried out. No extensive measurements have yet been made on SnTe brazed, Ta bonded P-type SnTe-PbTe alloys.

### C. Life Tests

A few limited life tests were run during this quarter to determine whether there is a variation in thermoelectric properties or in the stability of the bond with time at temperature. Thermoelement 64N was maintained at 500°C for 112 hours in argon atmosphere. Figure 25 shows the resistivity before and after the life test. A slight increase in resistivity was observed, accompanied by a slight increase in Seebeck voltage as a function in temperature. In Figure 26 are shown the average Seebeck voltage as a function of temperature for unbonded, bonded, and the life tested W electrode-bonded N-type PbTe. It is suggested that this increase in voltage which is accompanied by an increase in resistivity, is associated with annealing recovery phenomena and not with the diffusion of tungsten into the thermoelement. Further examination of this problem is necessary. Included in the 115 hour test were three Ta-SnTe brazed N-type elements. These electrodes were heavily oxidized and the considerable depth of 50 mils had to be ground away to make proper electrical contact. One element broke; the crack in the bulk was highly oxidized, so it probably existed before the test. Figure 27 shows the catastrophic effect oxygen can have on the

Seebeck voltage of the bonded thermoelectric material. Major deterioration appears to occur at the electrode thermoelement interface and in the voids of the thermoelement.

#### IV. SUBLIMATION RATES IN VACUO OF PbTe AND 0.5 PbTe-0.5 SnTe

A series of experiments was undertaken to measure the rate of sublimation of PbTe, and SnTe, from pressed and sintered thermoelements. Experiments were performed in an NRC vacuum evaporator under pressures ranging from 1 to  $4 \times 10^{-6}$  mm Hg. Elements (1/4" x 1/4" diam.) were unbonded and had either no or only low ( $< 500^{\circ}\text{C}$ ) temperature exposure. The element surfaces were polished lightly with 210 emery paper, cleaned ultrasonically in methanol, rinsed, boiled in methanol and dried with a hot air blower. This treatment was sufficient to remove dirt, grease, and other volatiles as shown by no detectable ( $< 0.1$  milligram) change in weight of an element held at room temperature for 17 hours at  $\approx 1 \times 10^{-6}$  mm. After degreasing the elements were measured and weighed. The elements were heated by radiation from an Mo strip heater positioned above the elements which sat on a small square of stainless steel sheet whose upper surface had been coated with boron nitride. The steel sheet sat on a tube of steel foil to minimize the heat loss to the base-plate of the evaporator. Temperatures were determined by the setting of the variable transformer powering the heater; calibration of the transformer was done by measuring the temperature of an element in the apparatus with a thermocouple set in a hole drilled to the center of the element.

##### A. Results

The rate of sublimation for cold-pressed and sintered thermoelements of PbTe and 0.5 PbTe-0.05 SnTe (approximately) in vacuum as a function of temperature is shown in Figure 28. The points plotted represent the average of at least two measurements and in some cases more. The uncertainty of the measurements is on the average of about  $\pm 15\%$ . There is probably a small systematic error due to the real surface of a sintered compact being of greater area than the apparent or geometric surface. This would tend to give rates higher than would be measured for a dense, smooth sample. Such an error is

not important, however, in applying these data to similar elements. Use of the data in Figure 28 for a cast element would require an estimate of the error due to surface roughness and correction of the sublimation rate. It is important to note also that the temperature was uniform over the element, and does not represent a hot junction temperature. Application of these data to an element operating in a gradient would require knowledge of the temperature profile and subsequent integration of the varying sublimation rate over the surface of the element.

It is of interest to note that although the vapor pressure of SnTe is somewhat higher than that of PbTe (see Figure 29), the rate of sublimation of 0.5 PbTe - 0.5 SnTe elements is lower above 500<sup>o</sup>, implying a lowered vapor pressure for both compounds in the solid solution. It is also possible that the lower sublimation of 0.5 PbTe - 0.5 SnTe elements were due to the formation of a loose, fine black surface deposit after appreciable sublimation ( $> 4 \text{ mg/cm}^2$ ). The nature or origin of this powder layer is not known; it could be oxide which was on the surface of the powder particles before compaction. Once again, while such an occurrence prevents these data from accurately indicating the sublimation rate of pure, dense 0.5 PbTe - 0.5 SnTe, they still give a reasonably precise measure of the behavior of PbTe-SnTe elements which might be incorporated into a device.

It was found that the Seebeck voltage of the samples used to measure sublimation was not affected by their exposure, even when the volume of element which was porous due to sublimation was about 25% of the total. In a number of cases the Seebeck voltage was slightly increased, which may be due to annealing effects. No measurements of the resistivity were made.

The vapor pressures of PbTe and SnTe are presented in Figure 29. All three investigations<sup>(3-5)</sup> used the Knudsen effusion technique to measure the vapor pressure in equilibrium with the solid compound at temperatures from 500<sup>o</sup> to 700<sup>o</sup>C. The data from our measurements of the sublimation of PbTe were used to calculate the

vapor pressure of PbTe using the Langmuir equation

$$P_i = \frac{m}{t \cdot A} \sqrt{\frac{2 \pi RT}{M i}} \quad (\text{atm})$$

where  $m$  (gm) is the mass of vapor of molecular weight  $M$  which evaporates from an area  $A$  ( $\text{cm}^2$ ) in time  $t$  (sec). The systematic difference between our values and those of Pashinkin<sup>(3)</sup> is probably partly due to a lowering of the activity of PbTe in the element by the present of the dopants and "promoters". There is, however, good agreement between the slopes of the lines, a measure of the heat of sublimation.



## V. CONCLUSIONS

From the experimental results the following conclusive statements can be made:

- 1) SnTe wets Mo and Ta effectively. An extremely tenacious bond is obtained between SnTe and Ta.
- 2) The wetting of Nb, W, and Zr by SnTe is not satisfactory.
- 3) AgSbTe<sub>2</sub> and AgBiTe<sub>2</sub> do not wet the refractory metals as effectively as does SnTe.
- 4) SnTe-Ta is the most practical and effective braze-electrode combination.
- 5) Metallurgically sound, low resistance (200  $\mu \Omega$ ) bonds have been prepared using SnTe-Ta on N- and P-type PbTe. The bonding procedure is relatively simple and applicable to large scale production.
- 6) A diffusion-bonding procedure which employs a W electrode has been developed for the bonding of PbTe (P- and N-). Low resistance ( $< 10 \mu \Omega$ ) bonds have been prepared by this technique.
- 7) The total resistivity including contact resistance of W diffusion-bonded N-type PbTe is always lower than that reported by MMM for unbonded material at low temperatures, and tends to approach the unbonded value at 500°C.
- 8) The total resistance of Ta-SnTe braze bonded N-type PbTe is identical to that of unbonded material from R. T to 500°C.
- 9) Behavior similar to that reported in (1) and (2) is observed for P-type PbTe-SnTe.

- 10) The Seebeck voltage of W-bonded N-type PbTe does not differ significantly from that of unbonded N-type PbTe.
- 11) The Seebeck voltage of Ta-SnTe braze-bonded N-type PbTe is somewhat lower than that of unbonded N-type PbTe .
- 12) The Seebeck voltage of W diffusion-bonded P-type SnTe-PbTe thermoelements is similar to that of unbonded P-type material.
- 13) A Ta diffusion-bonded P-type element shows some loss in Seebeck voltage relative to unbonded P-type SnTe-PbTe.
- 14) Life tests of 112 hours for W-bonded N-type PbTe have shown an increase in total resistivity with a corresponding increase in Seebeck voltage. No deterioration of the thermoelectric figure of merit could be ascertained.
- 15) Oxygen was found to cause catastrophic failure of Ta diffusion and braze-bonded elements.
- 16) The rate of sublimation for cold-pressed and sintered thermoelements of PbTe and 0.5 PbTe-0.5 SnTe (approximate composition) in vacuum as a function of temperature is presented.

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5. C. Hirayama, Y. Ichikawa, and A. DeRoo, J. Phys. Chem. , 67, 1039 (1963)





FIGURE 1 Spreading of SnTe on Ta as a function of surface treatment.

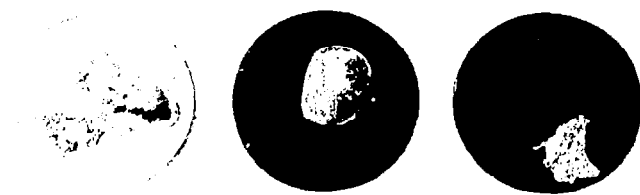


FIGURE 2 Spreading of SnTe on Mo as a function of surface treatment.

SnTe BRAZE





on Mo		
on Ta		



FIGURE 3 SnTe on Mo and Ta before and after grinding.

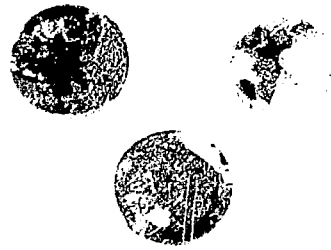


FIGURE 4

- 1.) AgBiTe<sub>2</sub> on Mo
- 3.) AgBiTe<sub>2</sub> on Ta

- 2.) AgSbTe<sub>2</sub> on Mo
- 4.) AgSiTe<sub>2</sub> on Ta

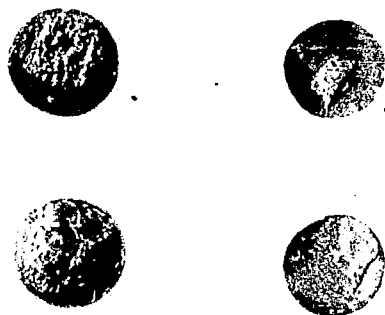


FIGURE 5 Uneven spreading of  $\text{AgBiTe}_2$  on Zr.

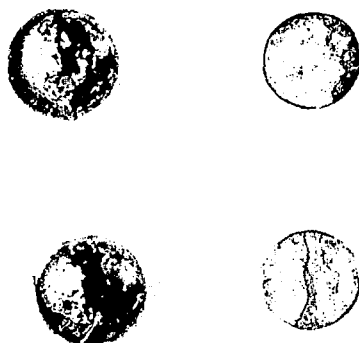


FIGURE 6 Uneven spreading of  $\text{AgSbTe}_2$  on Zr.



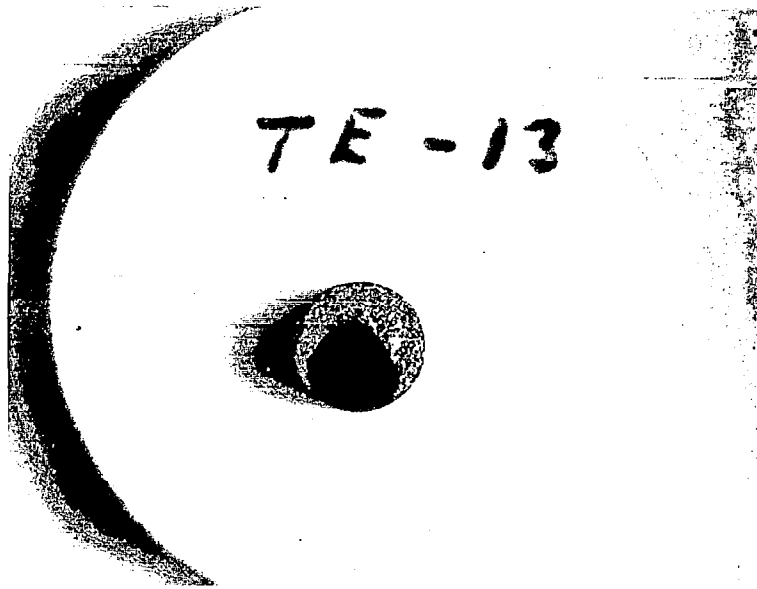


FIGURE 7 Strong mechanical adherence of SnTe + 0.1% Fe to Ta.

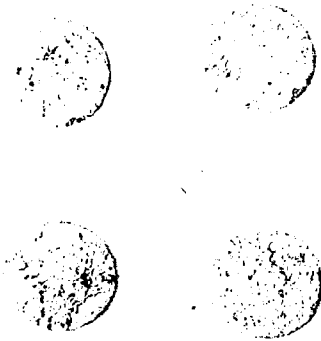


FIGURE 8 Comparison of brazing characteristics of SnTe + 0.1% Fe and pure SnTe on Ta.

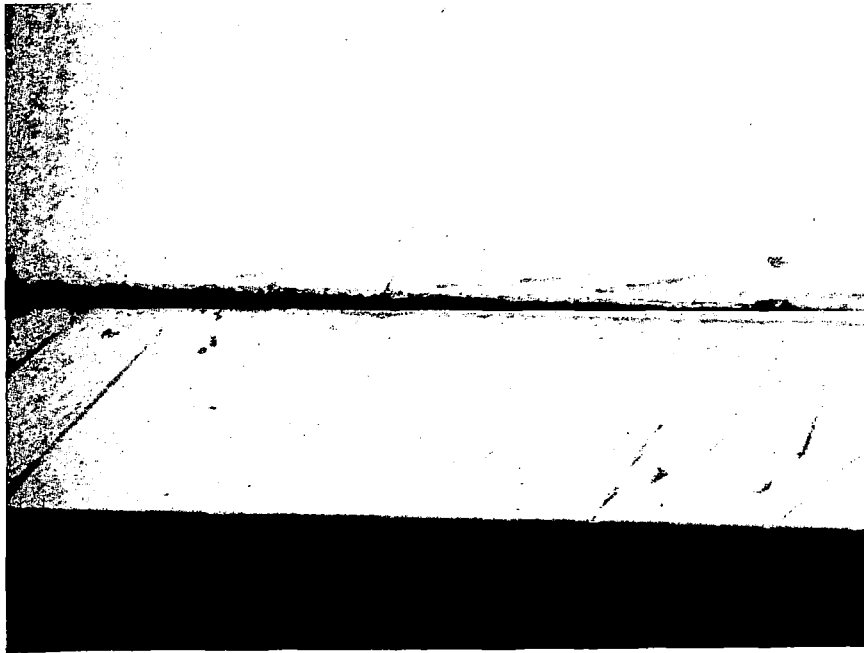


FIGURE 9 SnTe-Mo bond. Second phase formation with the propagation of grain growth and fracture.

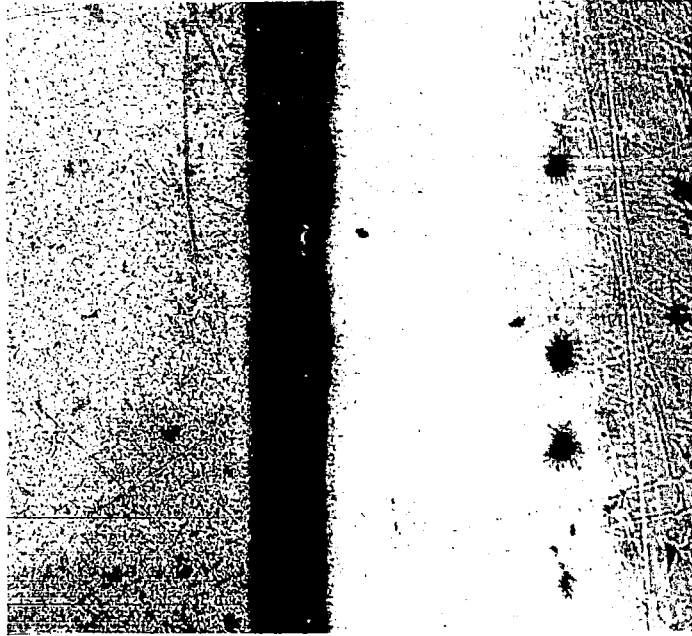


FIGURE 10 SnTe-Ta bond showing polish effect.

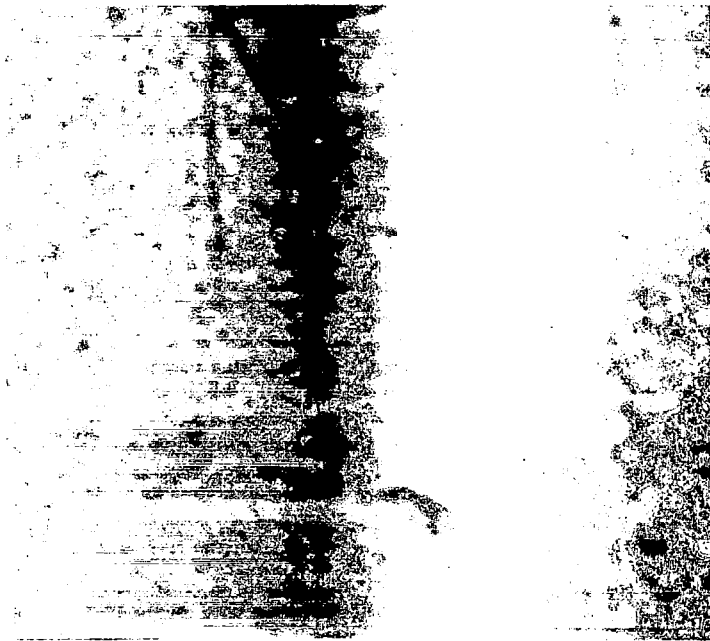


FIGURE 11 SnTe-Ta composite. Focused into recessed bond region. Interdiffusion of Ta into SnTe and SnTe into Ta is evident.

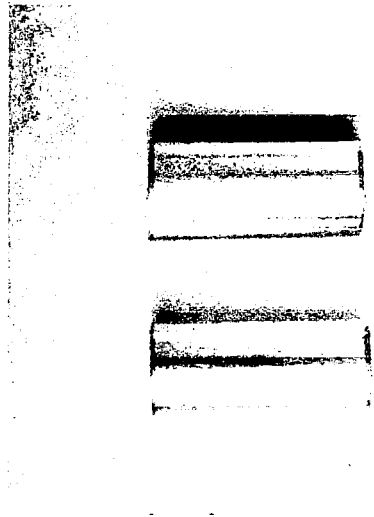


FIGURE 12 Typical braze-bonded N-type PbTe thermoelements.

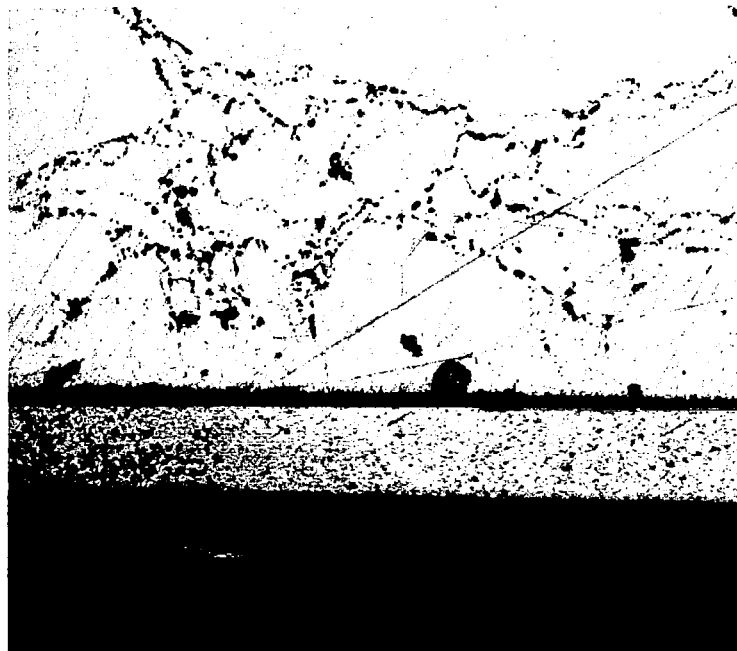


FIGURE 13 Precipitation and fracture of PbTe in vicinity of PbTe-SnTe mixture.

TE - 18



FIGURE 14 PbTe bonded to W weight. Surface of W weight after PbTe has been pulled away.

TE-45



FIGURE 15 W electrodes broken off PbTe. Strong adhesion characteristic is evident.

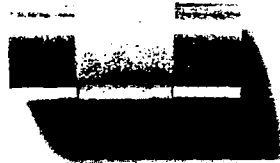
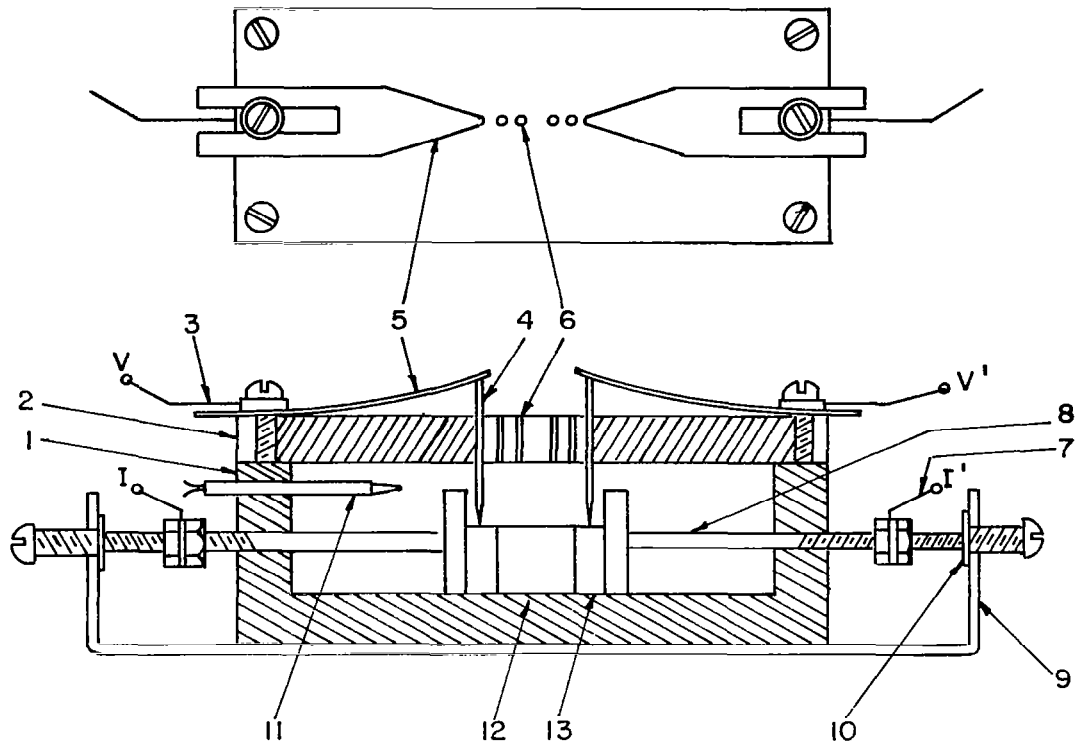


FIGURE 16 N-and P-type elements diffusion bonded to W.



- |  |                                  |
|--|----------------------------------|
| 1. FIRED LAVA BASE                             | 7. CURRENT LEAD                  |
| 2. FIRED LAVA COVER                            | 8. CURRENT CONTACT               |
| 3. VOLTAGE LEAD                                | 9. CURRENT CONTACT TENSION CLAMP |
| 4. VOLTAGE PROBE (W NEEDLE)                    | 10. INSULATING WASHER            |
| 5. VOLTAGE PROBE TENSION SPRING<br>(INCONEL-X) | 11. THERMOCOUPLES                |
| 6. VOLTAGE PROBE (VARIABLE SPACING)            | 12. BONDED THERMOELEMENT         |
|  | 13. ELECTRODE                    |

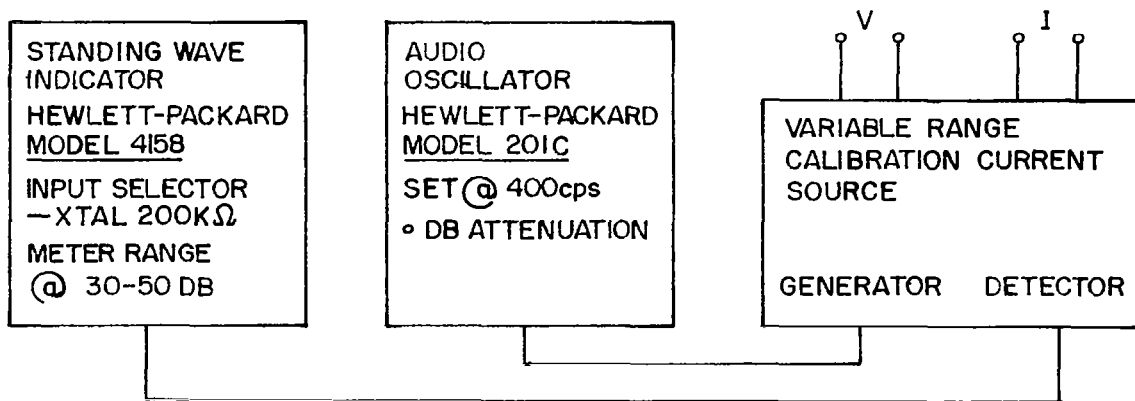


FIG. 17 - Schematic diagram of resistivity jig

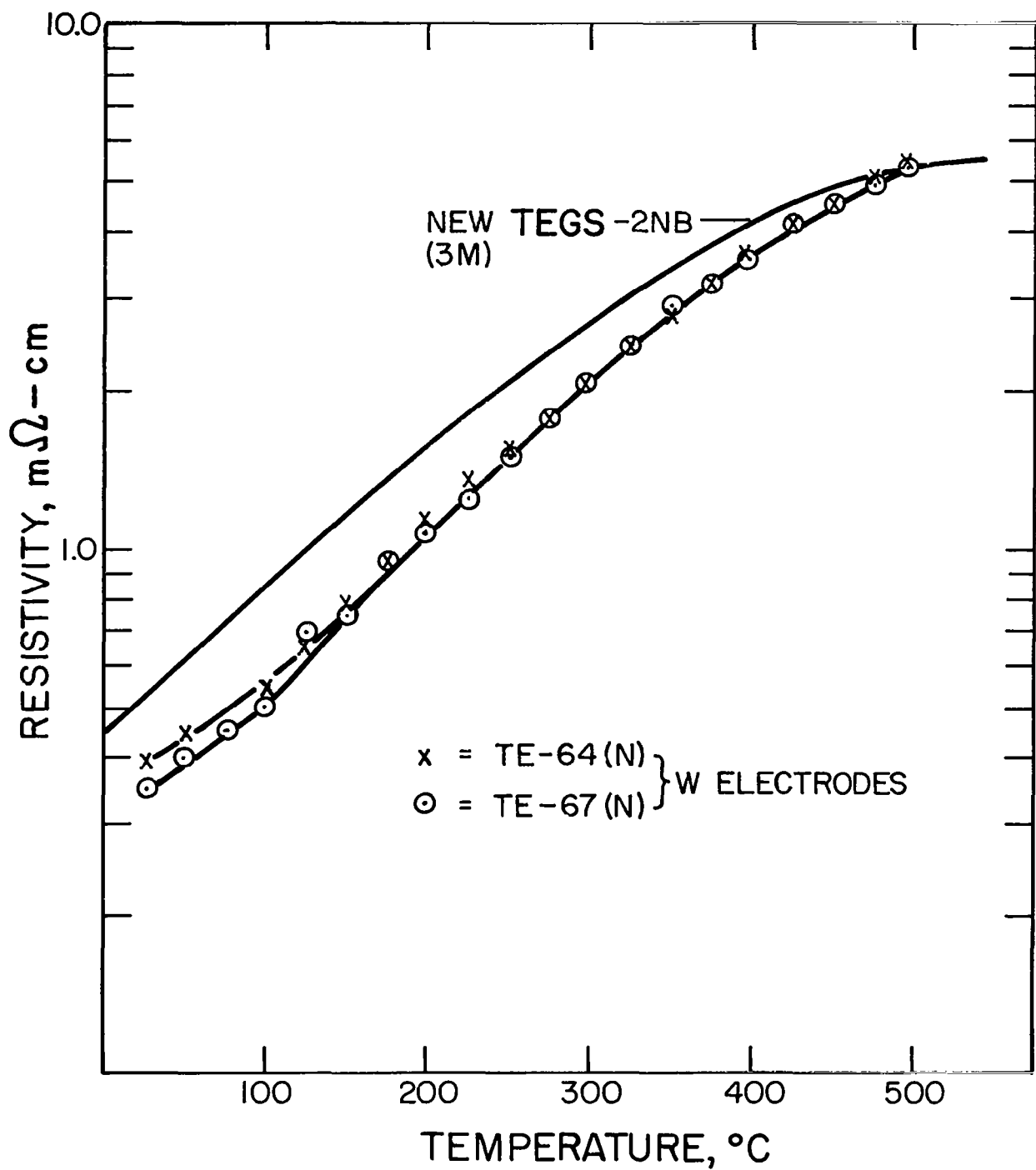


FIG. 18 - Resistivity as a function of temperature for W diffusion-bonded N-type PbTe



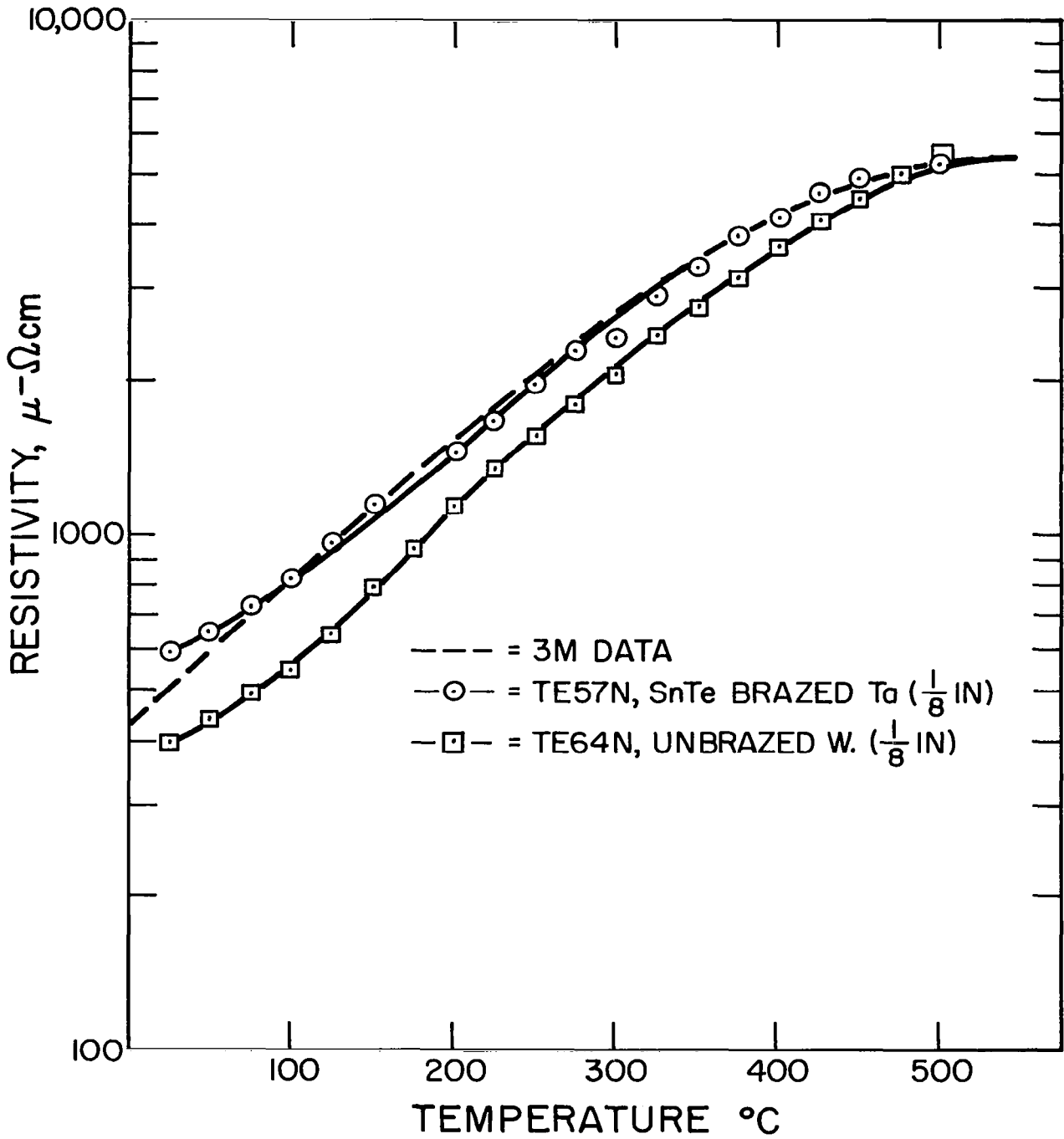


FIG. 19 - Comparison of resistivity as a function of temperature for SnTe-brazed, W diffusion-bonded and unbonded N-type PbTe

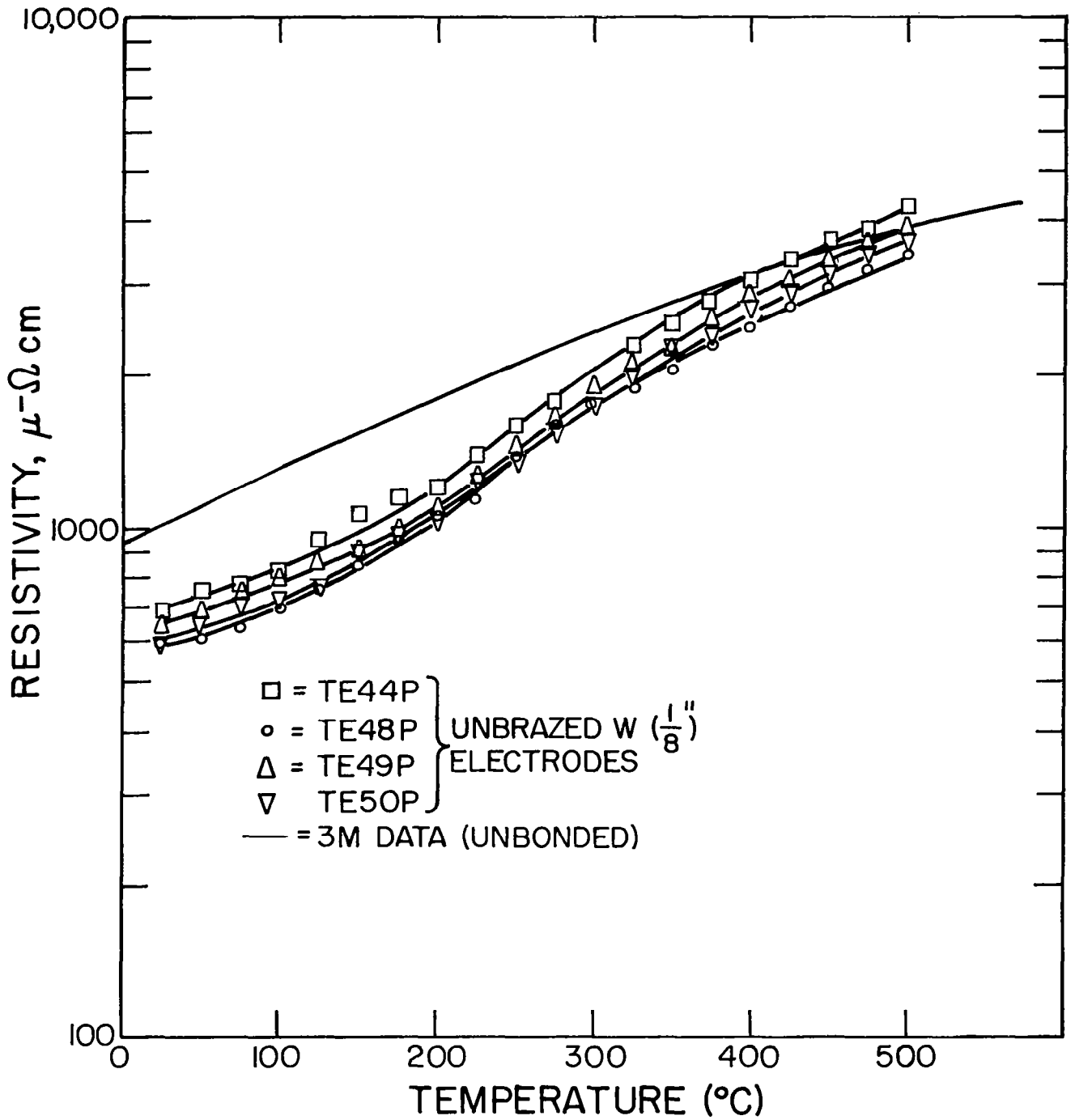


FIG. 20 - Resistivity as a function of temperature for W diffusion-bonded P-type PbTe-SnTe

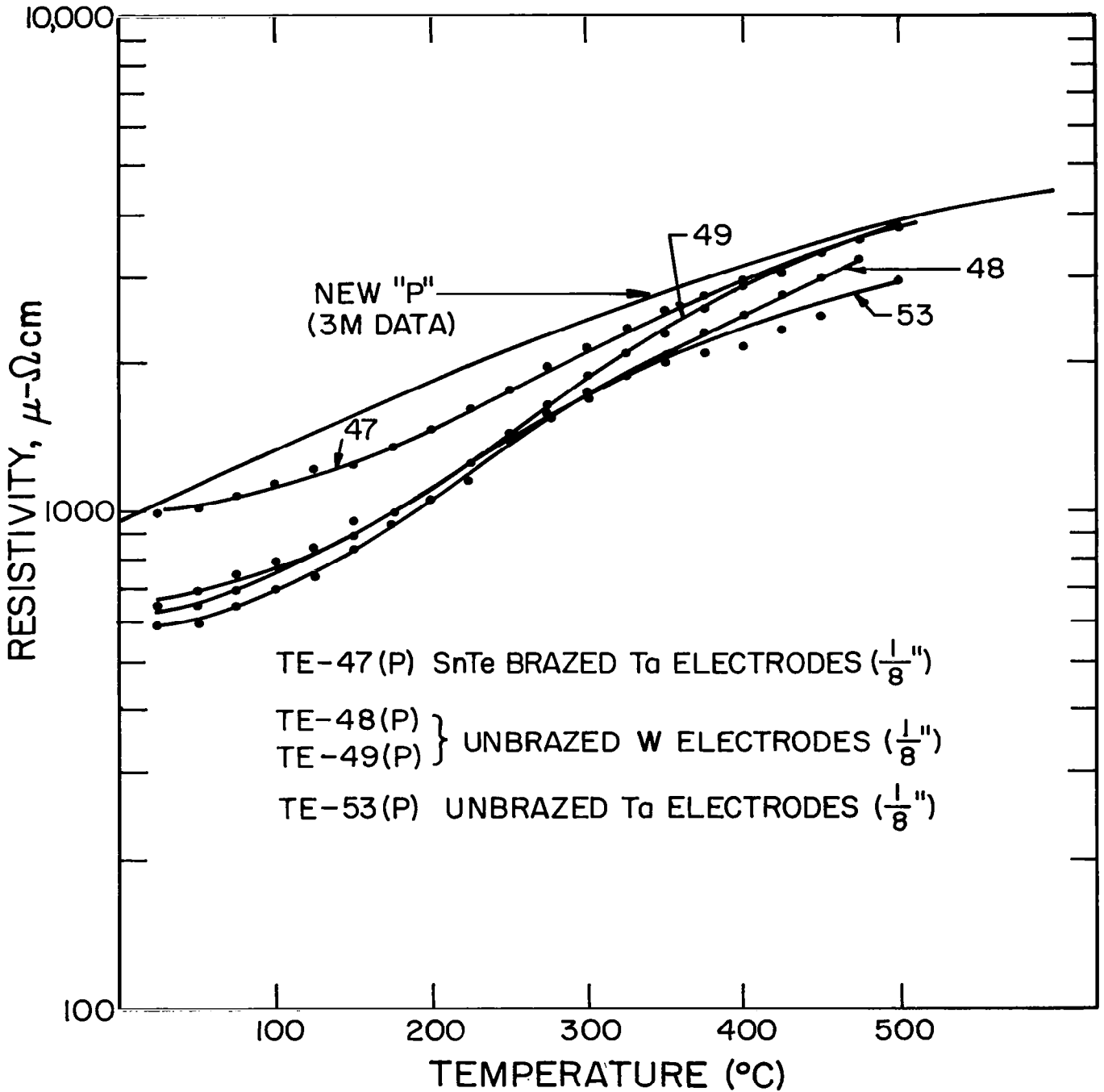


FIG. 21 - Comparison of resistivity as a function of temperature for SnTe-brazed, Ta-bonded, W diffusion-bonded, and Ta diffusion-bonded P-type PbTe-SnTe

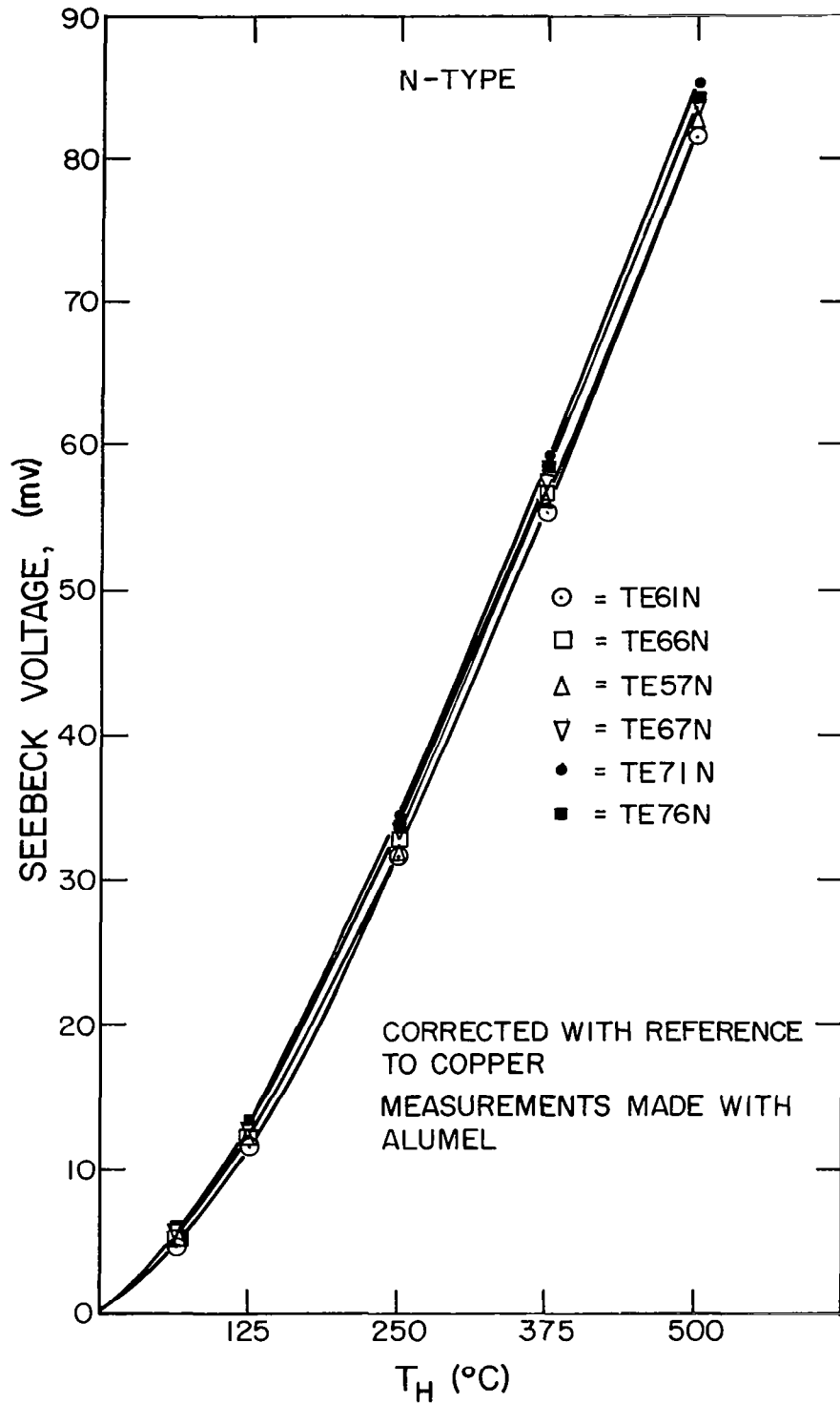


FIG. 22 - Seebeck voltage as a function of temperature ( $T_H$ ) for unbonded N-type PbTe

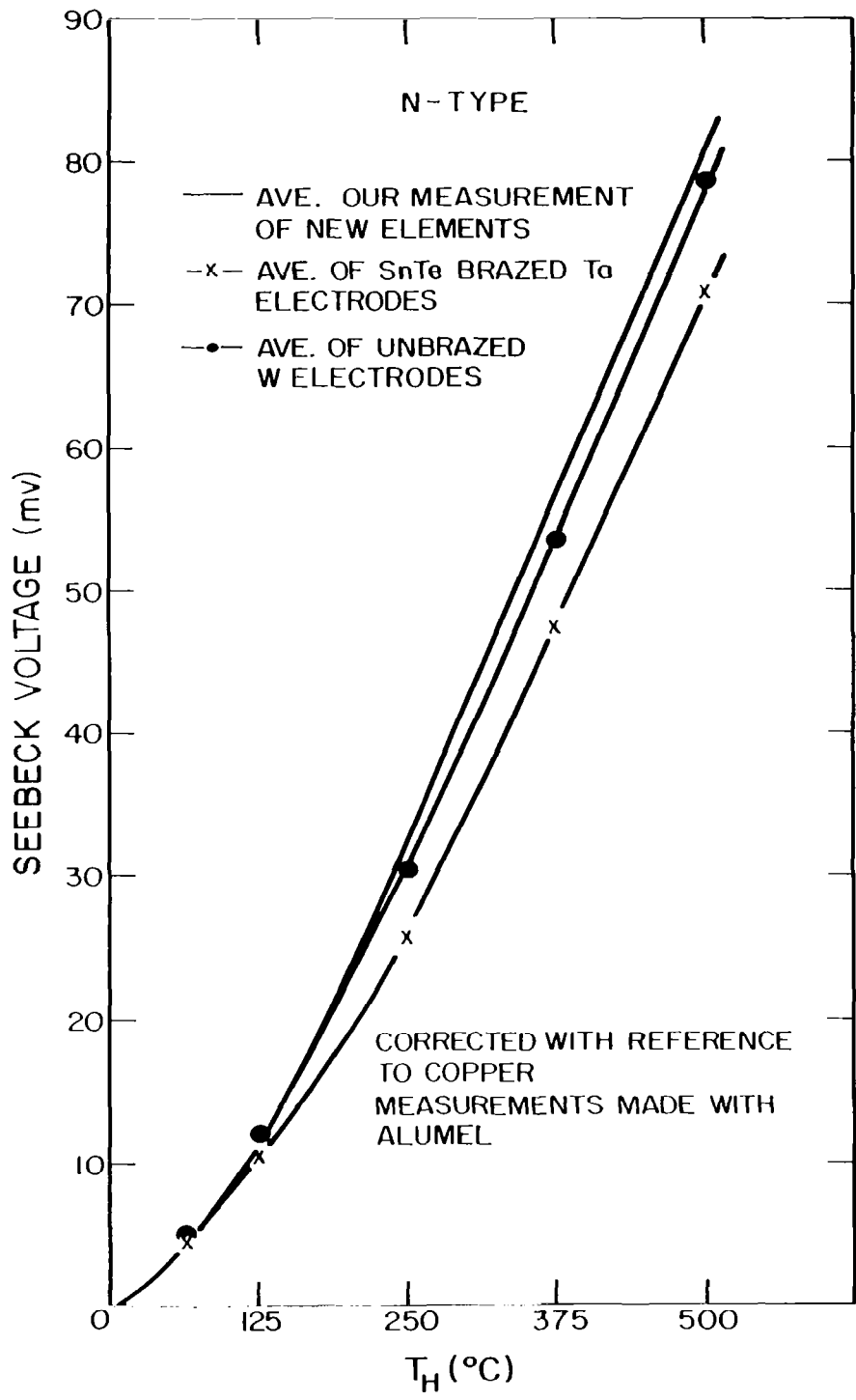


FIG. 23 - Comparison of Seebeck voltage as a function of temperature ( $T_H$ ) for unbonded, SnTe-braze, Ta-bonded, and W diffusion-bonded N-type PbTe

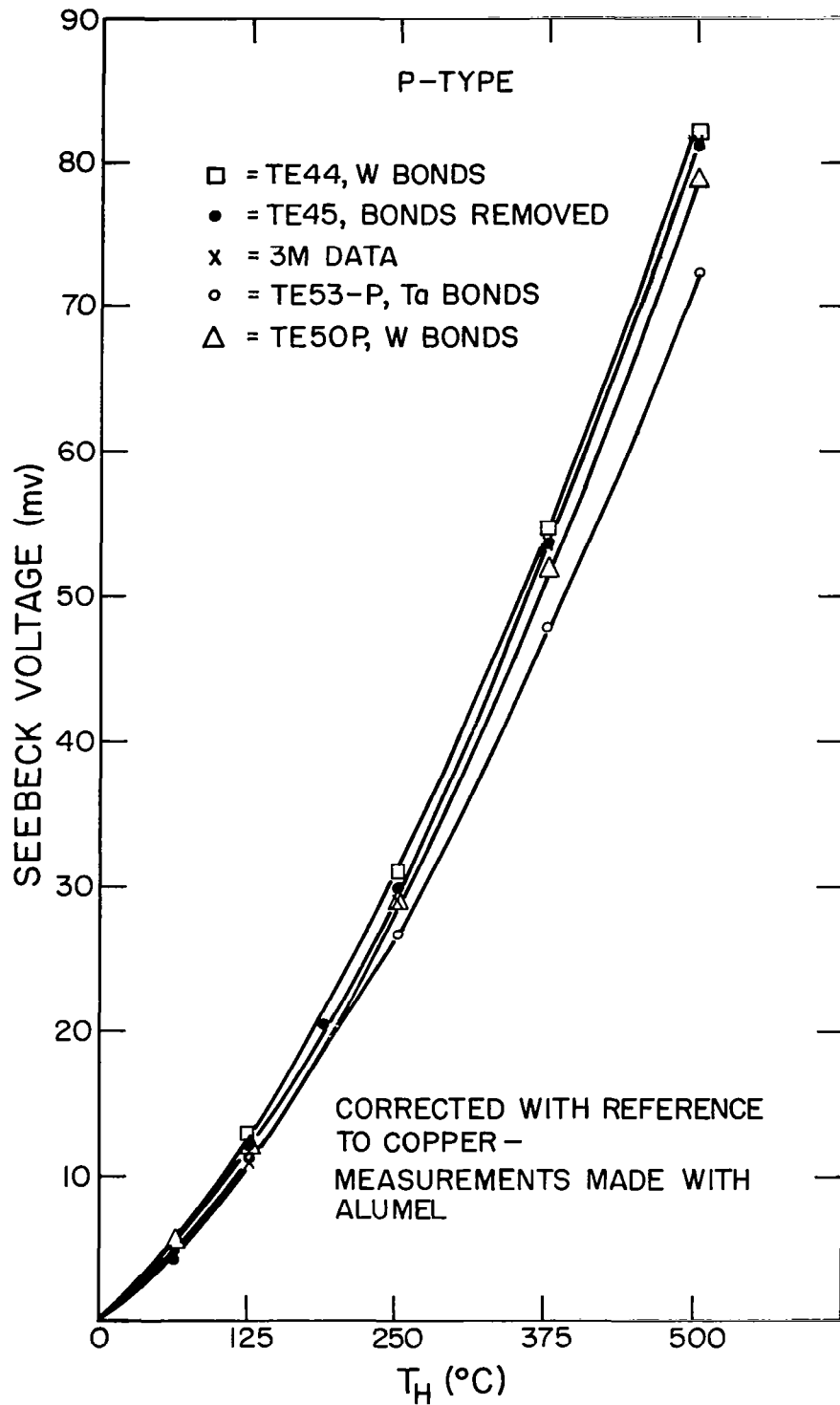


FIG. 24 - Seebeck voltage as a function of temperature for unbonded and W diffusion-bonded P-type SnTe-PbTe

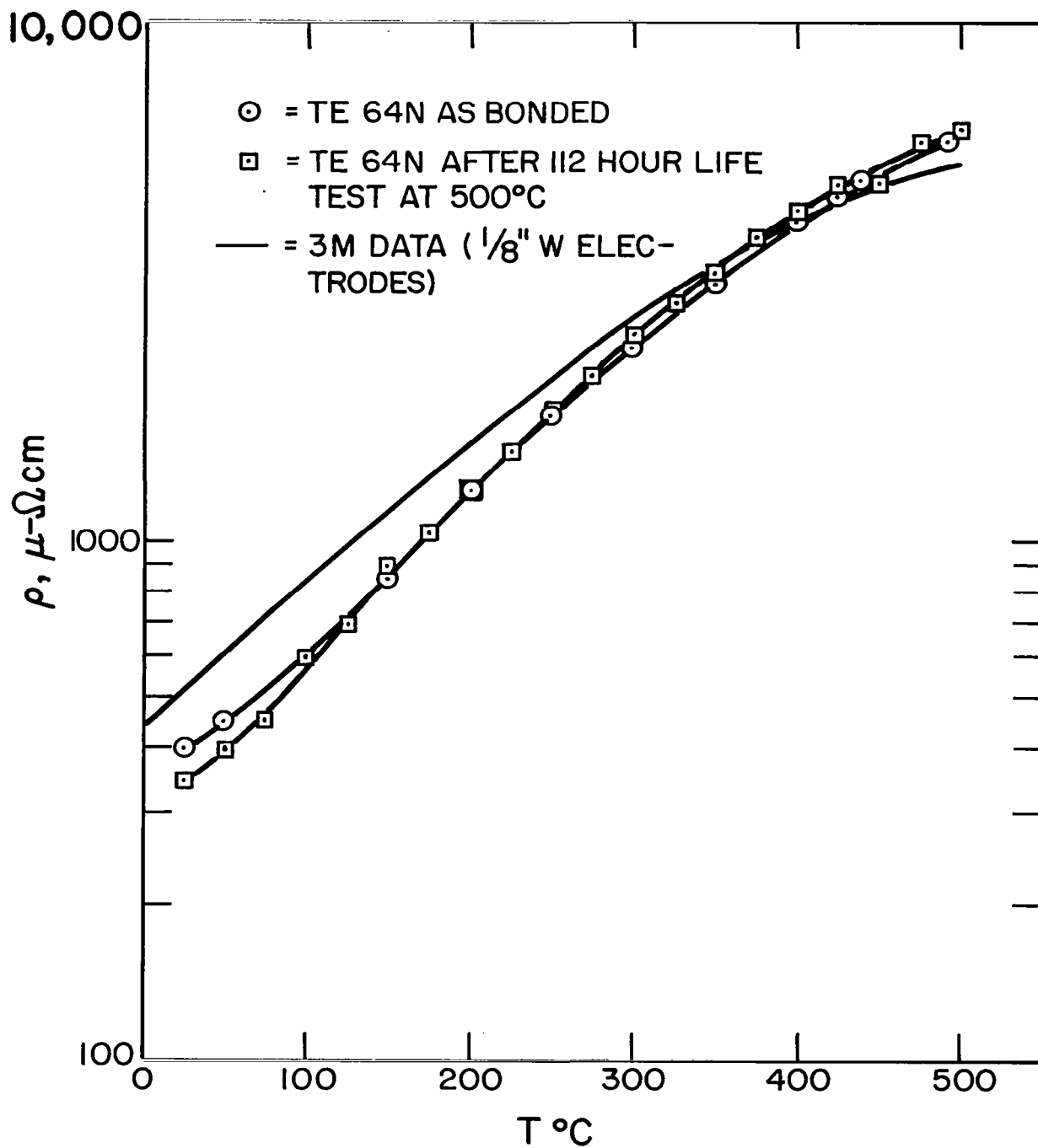


FIG. 25 - Resistivity as a function of temperature for N-type PbTe before and after 112 hour life test

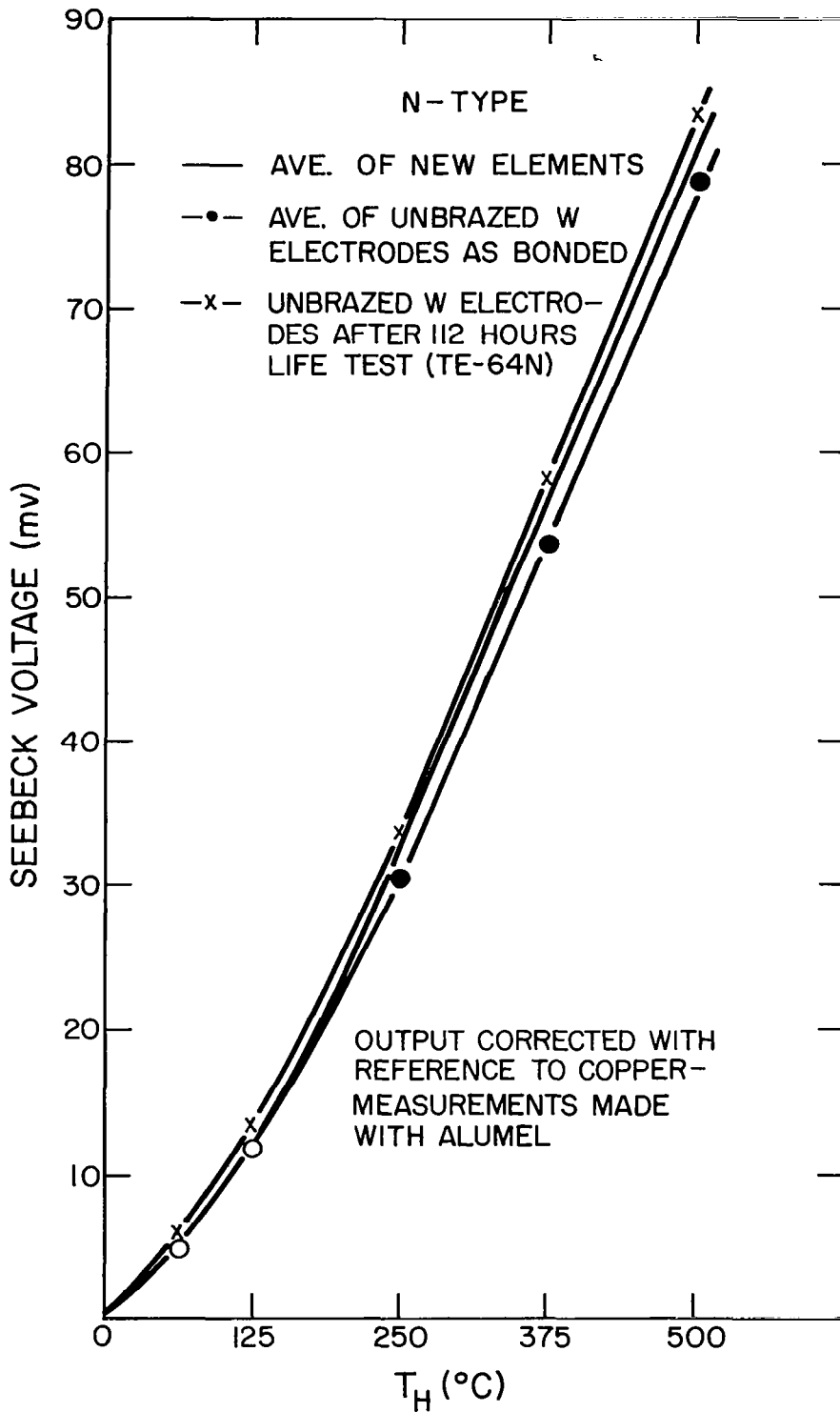


FIG. 26 - Seebeck voltage as a function of temperature for N-type PbTe before and after 112 hour life test



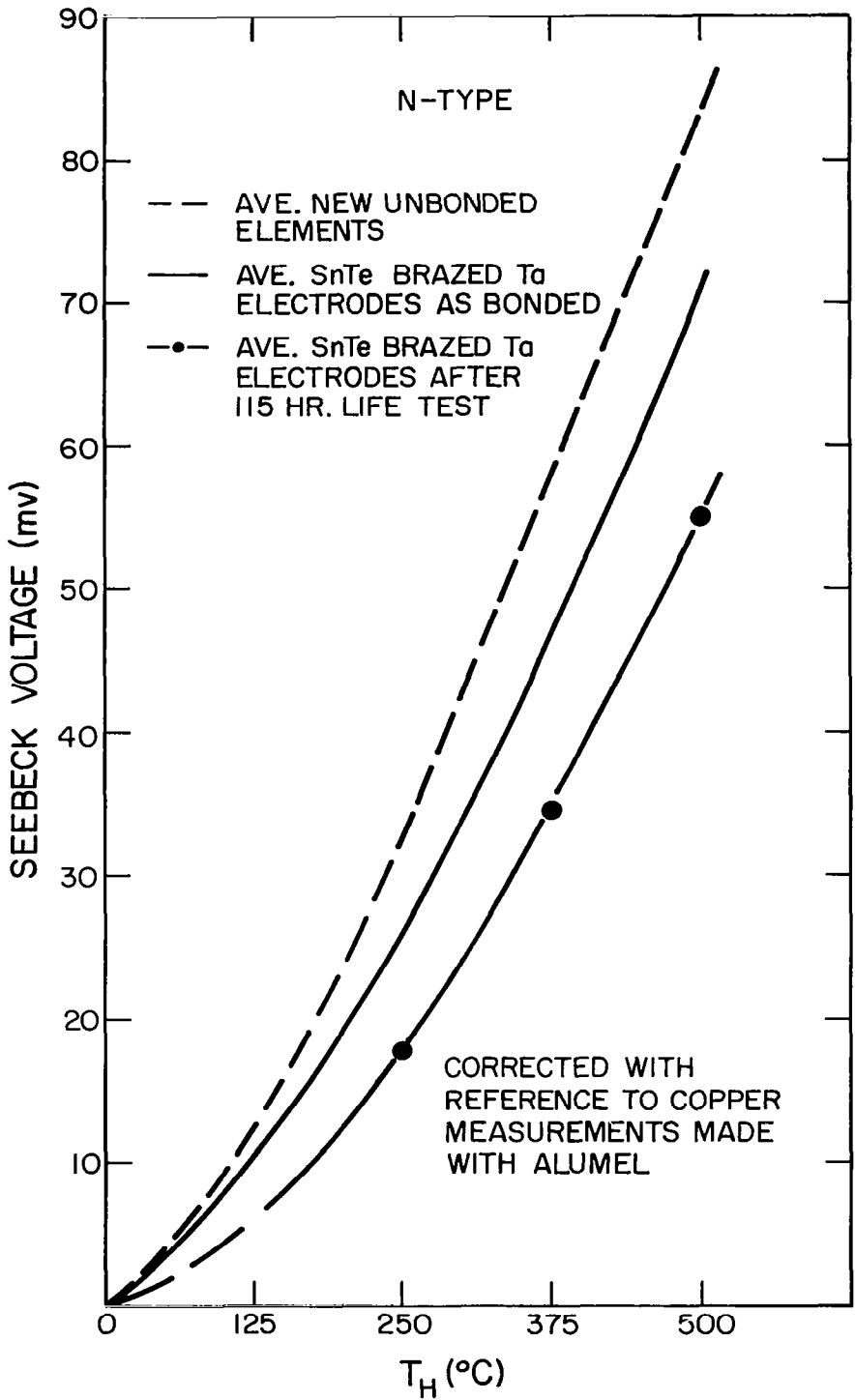


FIG. 27 - Comparison of Seebeck voltage as a function of temperature for unbonded, SnTe-brazed Ta as bonded, and SnTe-brazed, Ta-bonded after 115 hour life test

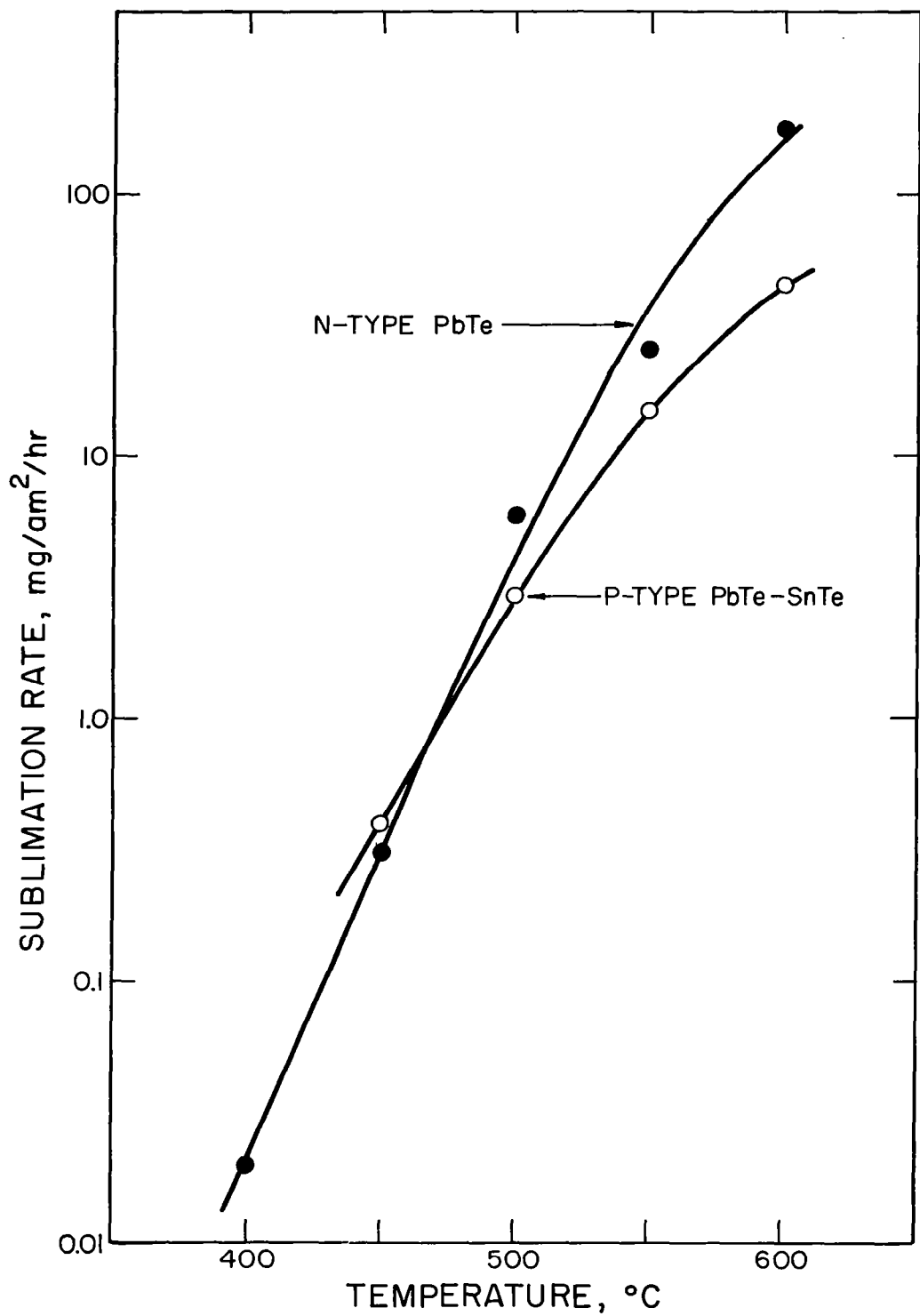


FIG. 28 - Sublimation rate as a function of temperature for cold-pressed and sintered N-type PbTe and P-type PbTe-SnTe elements.

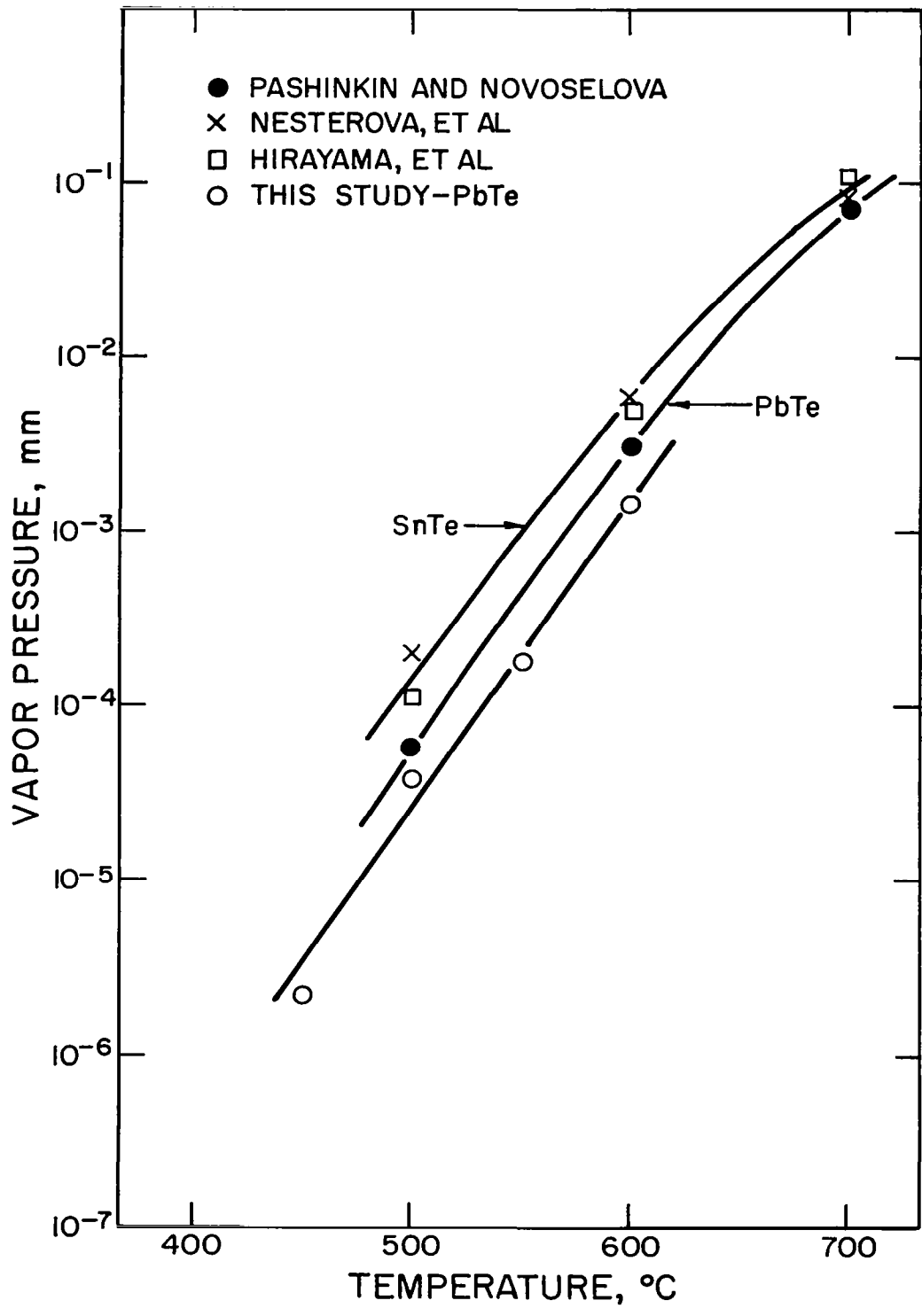


FIG. 29 - Vapor pressure as a function of temperature of PbTe and SnTe.

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