

FABRICATION OF MILLIWATT MODULES

N.B. Elsner, J.C.Bass, S.Ghamaty, C.C.Morris, N.Baker, and J.A.Bass
 Hi-Z Technology, Inc., 7606 Miramar Road, Suite 7400, San Diego, CA 92126-4210

Introduction

Hi-Z is fabricating milliWatt modules for the DOE that will be used in power supplies for NASA's space exploration missions and the DARPA that will be used to power micro air vehicles (MAVs). Separate papers are available that describe the used of milliWatt modules in these applications. This paper deals with the factors that influence the selection of the thermoelectric materials that go into these modules, the fabrication of the modules and performance and life test data.

Technical Approach

1.1 Adaption of Presently Available Bridgman Cast Alloys to Powder Metallurgy Form

1.1.1 The Need for Powder Metallurgy Prepared Alloys

The $(\text{Bi,Sb})_2(\text{Se,Te})_3$ alloys are normally prepared by Bridgman casting which causes the material to grow in oriented columnar grains. These cast forms are not mechanically strong and cleave very easily between the columnar grains as well as trans-granularly on planes parallel to the columnar growth. The reason for the weak mechanical properties in the one direction is shown schematically in Fig. 1. The crystal growth is approximately 130° to the axis of growth of the casting. Although elements could be cut to $0.020 \text{ in.} \times 0.020 \text{ in.}$, the scrappage rate would be high and the reliability of the device would not be acceptable. Fortunately, however, the columnar growth is oriented parallel to the current flow and if a large (in cross-sectional area) thermoelectric element does delaminate, the mechanical separation is not noticeable electrically or thermally since the resulting two elements are in parallel. If a small (in cross-sectional area) thermoelectric element delaminates, a high resistance or open circuit can occur as shown in Fig. 2.

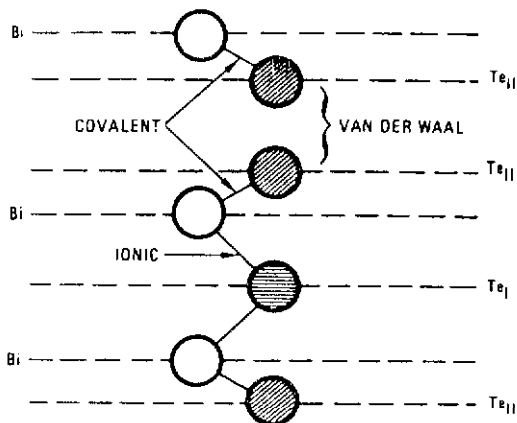


Fig. 1: Bismuth telluride structure
 The weakest bonds occur between layers Te_{II} and Te_{II}

As the need for thermoelectric elements of small cross-section and/or high strength has developed, it was apparent that Bridgman cast alloy could not be used since the small

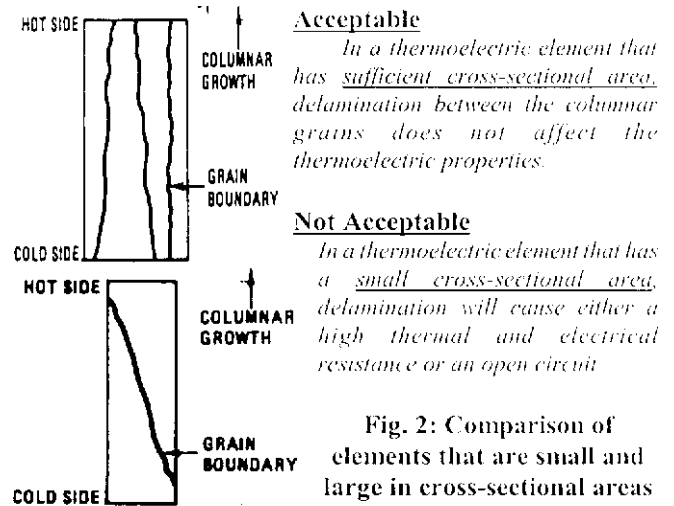


Fig. 2: Comparison of elements that are small and large in cross-sectional areas

elements have little strength and produce high-resistance anomalies.

The development of fine grain $(\text{Bi,Sb})_2(\text{Se,Te})_3$ alloys has allowed elements of very small cross section to allow fabrication of high voltage high-strength devices that either produce high voltages when used for power or can make use of high voltages when used for cooling.

While powder metallurgy alloys allowed a breakthrough in device technology, the figure of merit of the N type material was decreased by approximately 25% at room temperature; at an elevated temperature (T_{II} of 280°C), the powder metallurgy alloys are equal to or better than the Bridgman cast materials because the powder metallurgy alloys have a proportionately lower thermal conductivity at high temperatures.

1.1.2 The Powder Metallurgy of Fine Grain $(\text{Bi,Sb})_2(\text{Se,Te})_3$ Alloys

In converting the $(\text{Bi,Sb})_2(\text{Se,Te})_3$ family of alloys into a powder metallurgy product, special processing techniques and quality control procedures are necessary to ensure a high quality product. A material is required that has:

- A fine grain size
- High strength
- Low levels of O_2 contamination
- Acceptable thermoelectric properties

The problems the fabricator can expect to encounter are:
 -- The $(\text{Bi,Sb})_2(\text{Se,Te})_3$ alloys are sensitive to the way in which they are ground and sieved. From the work of Ref. 1, shown in Fig. 3, various sintering times and temperatures must be optimized to obtain the most favorable thermoelectric properties.

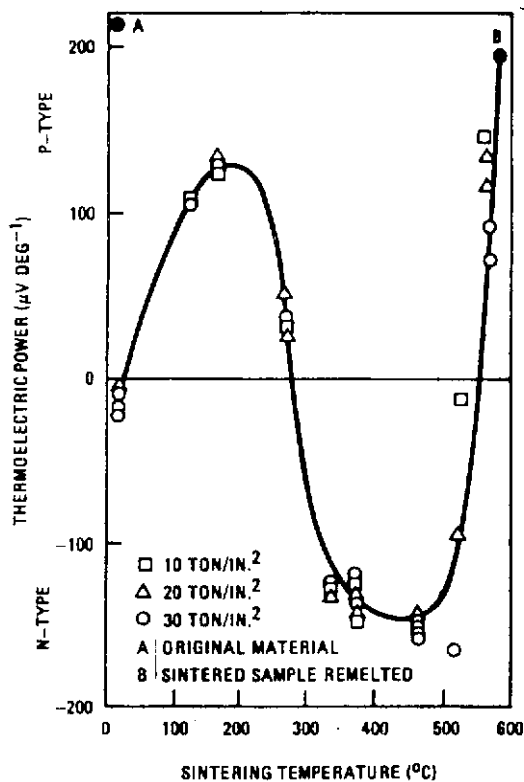


Fig. 3: The variation of the thermoelectric power of bismuth telluride with sintering temperature (Ref. 1).

- To maintain a fine grain size, low sintering temperatures must be used or grain growth as well as swelling can occur.
- The grinding of the alloys to a fine powder is difficult mechanically and the fine powder has an affinity for getting oxygen and water vapor.
- Melts must be prepared that are homogeneous and of the desired composition.
- With the N-type $(Bi,Sb)_2(Se,Te)_3$ alloys a unique problem exists. The thermoelectric properties are anisotropic and it is possible that elements with abnormally high resistance will be produced if the grain size is not controlled. As shown in Fig. 4, if elements of small cross sectional areas are required (which is often the case), the grain size must be much smaller than the cross sectional area. P-type alloys do not exhibit this behavior. If the grain size is the same size as the cross sectional area, then, the chances are that some of the grains will be oriented in the wrong direction and the thermoelectric element will exhibit a high resistance. Therefore, the powder metallurgy fabricating process must be tightly controlled to ensure consistently acceptable material.

With a coarse grain powder metallurgy material, the grain size can equal the cross-sectional area. Chances are one or more of the grains will be unfavorably oriented and high resistance will result.

With a fine grain powder metallurgy material, enough grains are randomly oriented in a favorable manner so the element resistance is acceptable. The finer grain size also increases the strength of the material.

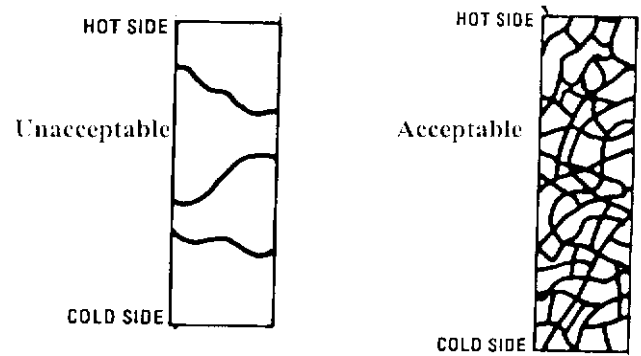


Fig. 4: Effect of grain size in element of small cross-sectional area fabricated with size N type $(Bi,Sb)_2(Se,Te)_3$ alloys

Module Fabrication Techniques

2.1 Introduction

A fabrication procedure has been developed to fabricate very small elements into a rigid high strength module.

The manufacturing process is shown schematically below. It is important to note that the Bridgman cast prepared materials, while of a slightly higher figure of merit, are not structurally strong to be sliced into thin plates. Therefore, to fabricate thermoelectric elements <0.030 in \times 0.030 inches in cross section, fine grained powder metallurgy alloys of high mechanical strength must be employed.

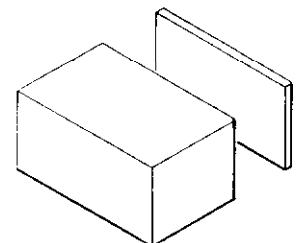
Modules constructed in this manner have been evaluated in two different power generators producing good results. For the $500\mu W$ generators, the modules were quality control resistance checked at 400 g side on load (typical failure of modules was often at 2000 g). Any fluctuation in resistance during the test was cause for rejection. In another program, 75-mW modules successfully passed 80-g loadings in all axes as well as Mil Std 810C vibration criteria.

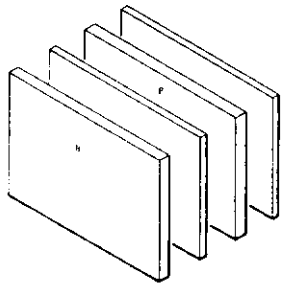
2.1.2 Assembly of Modules

The processing steps for assembling an 18×18 array module incorporating very small elements is as follows:

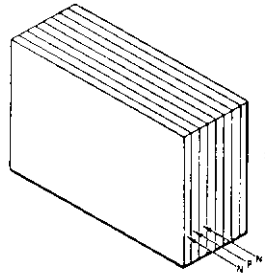
- The powder metallurgy-prepared blocks are oriented so that the material is sliced perpendicular to the pressing direction. The $(Bi,Sb)_2(Se,Te)_3$ type alloys are anisotropic (especially the N material) and the most favorable direction is perpendicular to the pressing direction. For Bridgman cast material, the favorable direction is parallel to the direction of growth.

Step 1- Blocks of N and P $(Bi,Sb)_2(Se,Te)_3$ Are Sliced into Plates.



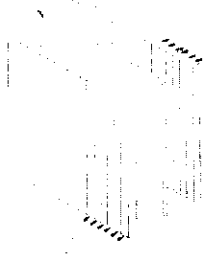


Step 2- The N and P Plates from Step 1 Are Stacked with self-bonding Kapton Between the Plates.



Step 3- The Plates and Kapton

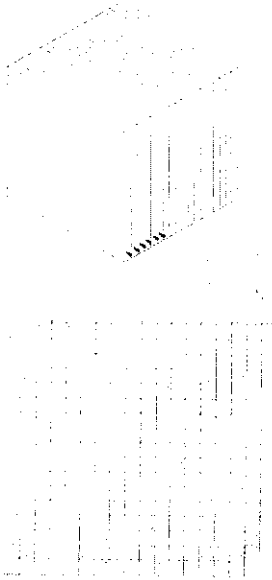
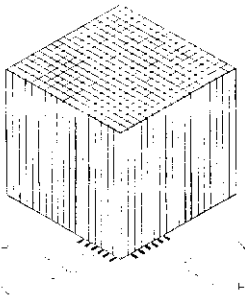
Self-Bonding Kapton



Are Bonded into One Composite.

Step 4- The Stack of Step 3 Is Sliced to Form Plates of N And P Elements. The Plates Are Alternately Layered With a 1 Mil Layer of Self-bonding Kapton.

Step 5- The Assembly of Step 4 Is Bonded Into an Array of 324 Elements. The Matrix Is Then Lapped to Length.



Step 6- A Mask Is Laid Over The Matrix And Au Is Deposited to Join the N And P Elements in a Series Circuit.

A satisfactory assembly or matrix is produced when the mask used for depositing the Au (by evaporation) can be aligned without shorting any matrix elements. Typical problems encountered were:

1. Spacing between the elements was not consistent.
2. Rows of elements were not parallel.
3. The slices and plates varied slightly in thickness.

In all cases, it was apparent that the error accumulation (or tolerance build up) in stacking the greater number of elements was causing the misalignment. This condition could

not be permitted because the overlay mask for evaporation of the contacts would not align for the desired circuitry.

The amount of misalignment was approximately 10 mils over the length of the modules. Thus, the tolerance level on each component had to be regulated to 0.1 mils to 0.2 mils to obtain tolerable assemblies.

Three approaches were taken that proved satisfactory:

1. Assemble smaller portions of the module at one time and then join these sub-modules together.
2. Modify the existing tooling to afford better alignment of the elements.
3. Utilize slices with closer thickness tolerances.

2.1.4 Contacting Methods

The initial joining of the N and P elements into a series circuit for each stage was accomplished by evaporating a layer of Au through a mask. The mask openings formed the series circuit. A typical coating layout for an 18 x 18 array is shown in Step 6.

Shown in Figs. 5, 6, and 7 are photographs of completed modules with 0.023" square, 0.015" square and 0.010" square legs respectively with Au contacts.

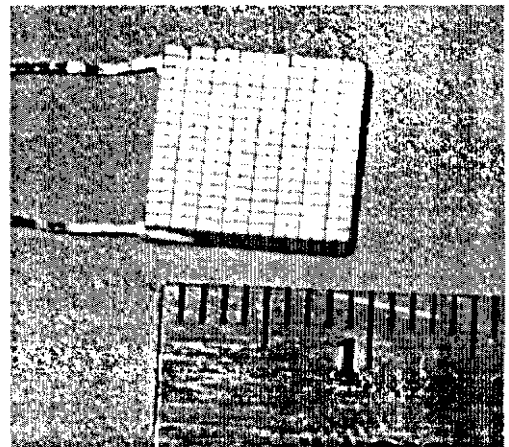


Fig. 5: Micro Air Vehicle module is a 16x16 array of 0.023" square legs. Module is 0.070" thick and produces 0.8 Watts at 5V.

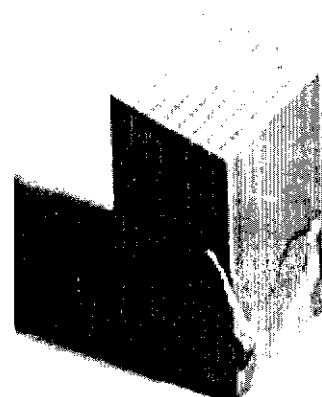


Figure 6: 40mW, 5V Module for Space Applications. Contains 324 legs 0.015" square and 0.9" long in an 18x18 array.

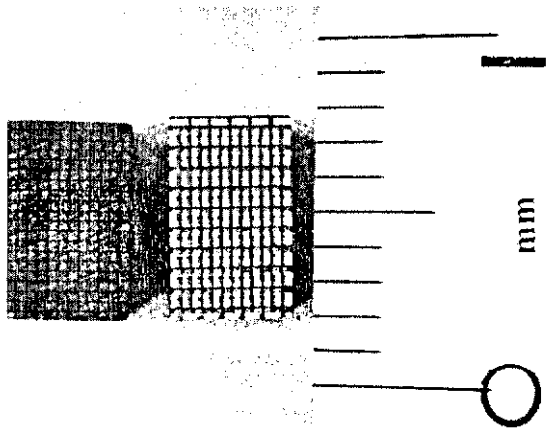


Fig. 7: Module contains 240 elements in a 20 x 12 matrix. The elements are 0.010 x 0.010 in. on cross section. Module is shown with and without contacts.

For the modules with 0.015" square and 0.010" square legs, (their length is relatively long) the resistance of the legs is quite high, thus, only a few microns of Au are sufficient for the electrical contacts and the extraneous circuit resistance is negligible.

For the 0.023" square elements (which are also relatively short), their resistance is quite low and it is desirable to have relatively thick Au contacts for joining the N and P elements and thereby minimize the extraneous circuit resistance. Thicker contacts can also endure more rugged handling and are being pursued for the DOE and DARPA modules.

Performance and Life Testing of Modules

Modules fabricated in a similar fashion but with thicker Au contacts have demonstrated very long lifetimes of >90,000 hrs. These modules operated with nuclear heat sources and the performance for four modules is shown in Figure 8.

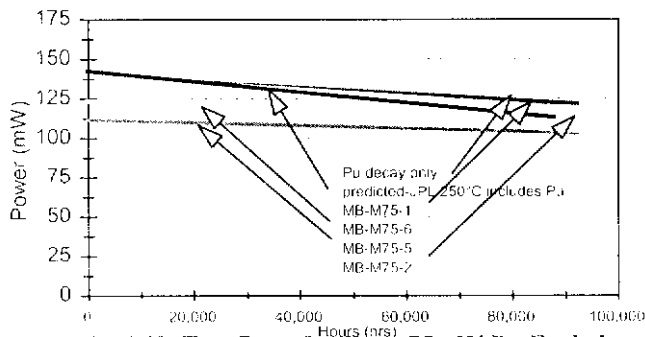


Fig. 8: Life Test Data for Four 75mW Pu Fueled Generators that Operated for >10 Years.

The modules being developed for the DOE will require 18 years of operation on Mars. Life testing of these higher density modules is underway (Fig. 9) and a degradation model will be developed to predict performance vs. lifetime.

For DARPA, the lifetime requirements for the micro air vehicles are only a few hours. Therefore, modules will be operated above their normal operating temperature to further improve the efficiency and/or power density of the power supply.

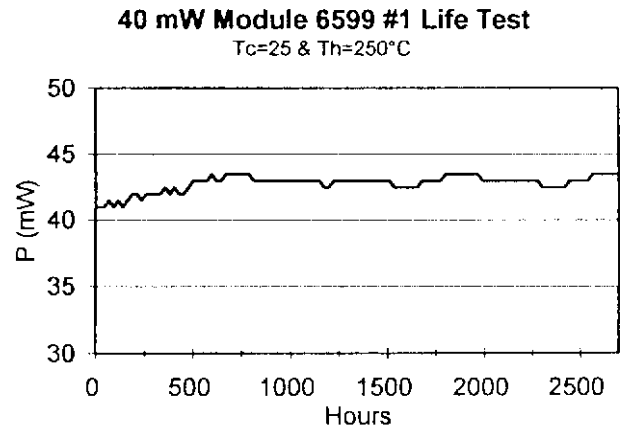


Fig. 9: Power data is not normalized. Small power variations are due to fluctuations in cooling water temperature on the cold side.

Conclusions and Summary

- High voltage milliWatt modules have been developed that have exhibited long lifetimes out to 90,000 hours.
- The modules being developed for DOE have an 18 x 18 array of 0.015 square legs and 0.9" long the highest packing density of any module yet fabricated by Hi-Z and deliver 40mW at 5 Volts at beginning of life (Fig. 9).
- For DARPA however, the module is composed of a 16 x 16 array of 0.023" square legs that is only 0.070" long. This module delivers 800 mW at 5V.
- Quantum-well materials are being developed and when ready will be implemented to produce higher voltage and higher efficiency mW modules.

References

1. Sharples, W.R., George, and J.E. Thompson, "The Sintering of Bismuth Telluride," Proceeding Physical Society London (1959) p.768.

Acknowledgement

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