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Development of a High Efficiency Thermoelectric Unicouple for Power Generation Applications

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Abstract

To achieve high thermal-to-electric energy conversion efficiency, it is desirable to operate thermoelectric generator devices over large temperature gradients and also to maximize the performance of the thermoelectric materials used to build the devices. However, no single thermoelectric material is suitable for use over a very wide range of temperatures (~300-1000K). It is therefore necessary to use different materials in each temperature range where they possess optimum performance. This can be achieved in two ways: 1) multistage thermoelectric generators where each stage operates over a fixed temperature difference and is electrically insulated but thermally in contact with the other stages 2) segmented generators where the p- and n-legs are formed of different segments joined in series. The concept of integrating new thermoelectric materials developed at the Jet Propulsion Laboratory into a segmented thermoelectric unicouple has been introduced in earlier publications. This new unicouple is expected to operate over a 300-973 K temperature difference and will use novel segmented legs based on a combination of state-of-the-art thermoelectric materials and novel p-type Zn_4Sb_3, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys. A conversion efficiency of about 15% is predicted for this new unicouple. We present in this paper the latest experimental results from the fabrication of this unicouple, including bonding studies between the different segments of the p-legs, n-legs, and p-leg to n-leg interconnect. Thermal and electrical tests of the unicouple are in progress and are briefly described.

Introduction

Although applications of thermoelectric power generation have been somewhat limited, primarily because of its relatively low efficiency, there has recently been renewed interest mostly due to emerging energy saving and environmental issues. A number of new potential applications have been cited in the literature [1], ranging from recovering waste heat from various industrial heat-generating processes, to using waste heat generated by vehicle exhaust to replace or supplement the alternator and thus decrease fuel consumption [2]. To achieve high efficiency, it is desirable to operate thermoelectric generator devices over large temperature differences and also to maximize the thermoelectric performance of the materials used to build the devices. One way to improve the efficiency is by segmenting the n- and p-legs of the unicouple into several segments made of different materials to increase the average thermoelectric figure of merit of the legs and operate the unicouple over a relatively large temperature gradient. Examples of this segmentation have recently appeared in the literature [3,4]. In these studies, the thermoelectric materials under investigation are state-of-the-art Bi_2Te_3, $FeSi_2$, PbTe, and Si-Ge alloys. We have recently proposed a new version of a segmented thermoelectric generator utilizing advanced thermoelectric materials with superior thermoelectric figures of merit [5,6,7,8]. The concept is briefly described in this paper and the results of the unicouple thermoelectric efficiency optimization are reported. Some details of the unicouple fabrication are presented are discussed as well as the initial thermal and electrical tests.

Unicouple Concept and Efficiency Optimization

The segmented unicouple under development at the Jet Propulsion Laboratory (JPL) incorporates a combination of state-of-the-art thermoelectric materials and novel p-type Zn_4Sb_3, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys developed at JPL [5,6]. The unicouple is illustrated in Figure 1. In a segmented generator as depicted in Figure 1, each section has the same current and heat flow as the other segments in the same leg. Thus in order to maintain the desired temperature profile (i.e. keeping the interface temperatures at their desired level) the geometry of the legs must be optimized. Specifically, the relative lengths of each segment in a leg must be adjusted, primarily due to differences in thermal conductivity, to achieve the desired temperature gradient across each material. The ratio of the cross sectional area between the n-type and p-type legs must also be optimized to account for any difference in electrical and thermal conductivity of the two legs.

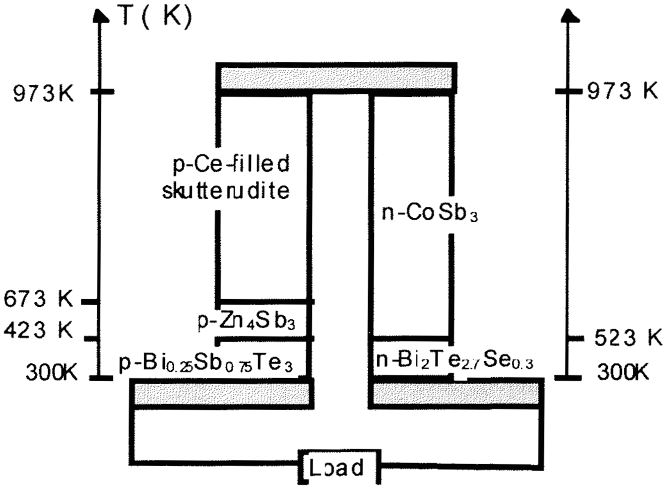

Figure 1. Illustration of the advanced unicouple incorporating new high performance thermoelectric materials. The relative lengths of each segment are drawn to scale. The calculated thermoelectric efficiency is 15%.

An approximate solution of the final geometry using the above considerations is straightforward, but does not include smaller contributions such as the Peltier and Thompson effects. A semianalytical approach to the problem is given by Swanson et al. [9] that includes smaller effects such as the Peltier and Thompson contributions and contact resistance in order to optimize and calculate the expected properties of the device. For each segment, the thermoelectric properties are averaged for the temperature range it is used. At each junction (cold, hot, or interface between two segments), the relative lengths of the segments are adjusted to ensure heat energy balance at the interface. Without any contact resistance between segments, the efficiency is not affected by the overall length of the device; only the relative length of each segment needs to be optimized. The total resistance and power output, however, does depend on the overall length and cross sectional area of the device. The calculated optimized thermoelectric efficiency is about 15% [7,8] with the hot junction at 973K and the cold junction near room temperature. The optimal geometry is illustrated in Figure 1.

High contact resistance between the thermoelectric segments can dramatically reduce the efficiency of a generator. Calculations show that a low contact resistance, less than about 20 $\mu\Omega cm^2$, is required to keep the efficiency from being significantly degraded by the contact resistance. This requirement is typical for Si-Ge-based thermoelectric generators developed in the past and can be achieved with careful consideration of the contacting method and material as we will describe in the following section.

Bonding Studies

To fabricate the unicouple, one needs to develop bonding techniques and materials to connect the various segments together as well as to the interconnects. In order to maximize the efficiency of the device, the bonds must have electrical contact resistance lower than 20 $\mu\Omega cm^2$. In addition, the bonds must be mechanically stable at the temperature of operation and also act as a barrier diffusion to prevent any potential diffusion across the junction of the two materials to be bonded which would potentially deteriorate the thermoelectric properties of these materials. All bonding tests were conducted by hot-pressing fine powder of two materials to be connected with a thin metal interface layer (25 to 50 µm) in a form of a foil between them. A mechanically stable and low contact resistance bond can be formed only if some reaction between the two materials and the foil occurs. The interface region created should also have a thermal expansion coefficient similar or intermediate to the materials to be bonded. The pressing was conducted in a graphite die with graphite punches in an Ar atmosphere. After pressing, a small strip of the samples was polished along the pressing axis to reveal the microstructure of the junction which was investigated by both optical microscopy and electron microprobe analysis. In addition, the electrical contact resistance was measured by a four probe technique up to the predicted optimum temperature of operation. One voltage probe is located at one end of the sample while the second probe can move along the sample. The variations of the electrical contact resistance is therefore recorded as a function of the distance of the moving probe to the fixed probe. Several brazing/contacting materials were investigated for each junction and under various pressing conditions (i.e. temperature and pressure) to obtain optimum material density and bond quality.

The best results obtained to date are shown in Figures 3 through 7. For the interconnect on the hot side, Nb metal was used successfully connected to $CoSb_3$ and $CeFe_4Sb_{12}$ using a $Cu_{28}Ag_{72}$ alloy as brazing material. Nb was originally selected because of the close match between its thermal expansion coefficient and those of the skutterudite materials (7.52 x 10^{-6}/K vs. ~ 8 x 10^{-6}/K for the skutterudites). Microstructure and microprobe analysis showed that the bonds were of good quality and that Cu and Ag diffusion in the skutterudite samples was confined within the ~ 50 µm layer next to the Nb disk. The electrical contact resistance was measured up to the maximum projected temperature of operation (700°C) and was found to be less than 20 $\mu\Omega cm^2$. Pd was successfully used as an interface material between Zn_4Sb_3 and $Bi_{0.25}Sb_{0.75}Te_3$, between $CoSb_3$ and $Bi_2Te_{2.7}Se_{0.3}$, and between Zn_4Sb_3 and $CeFe_4Sb_{12}$. The results of electrical contact resistance measurements are shown in Figures 5 and 6. They show that the contact resistance was minimal and below the 20 $\mu\Omega cm^2$ threshold. In addition, microprobe analysis showed that Pd provides a good diffusion barrier.

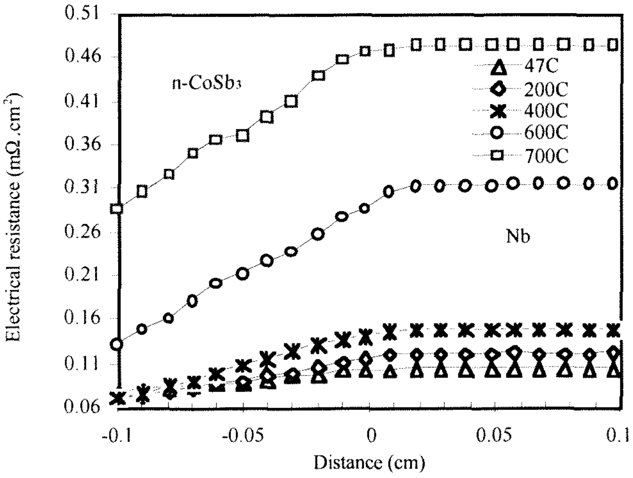

Figure 3. Electrical contact resistance as a function of distance for a n-$CoSb_3$/Nb junction using a $Cu_{28}Ag_{72}$ alloy interface. The origin corresponds to the interface position.

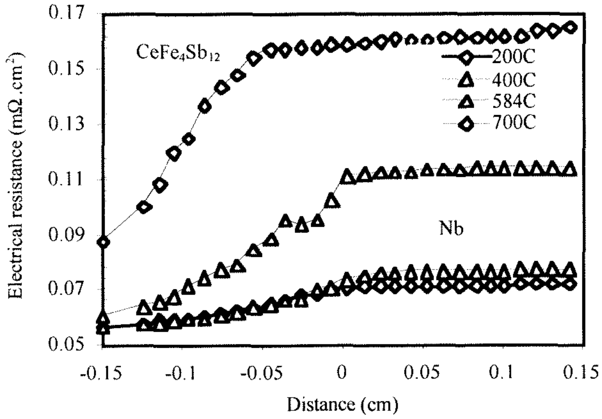

Figure 4. Electrical contact resistance as a function of distance

for a p-$CeFe_4Sb_{12}$/Nb junction using a $Cu_{28}Ag_{72}$ alloy interface. The origin corresponds to the interface position.

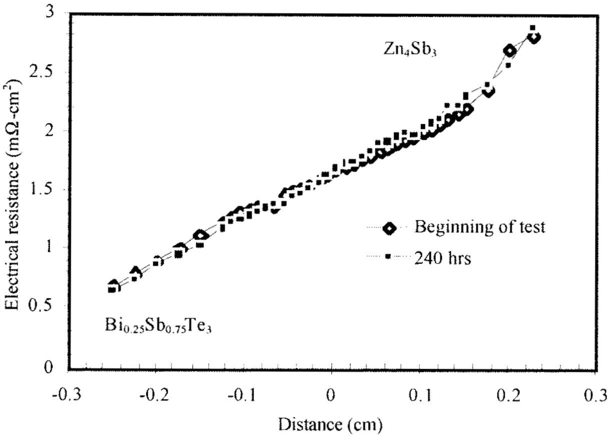

Figure 5. Electrical contact resistance as a function of distance for a p-Zn_4Sb_3/p-$Bi_{0.25}Sb_{0.75}Te_3$ junction using a Pd interface. The origin corresponds to the interface position. The test was conducted at 150°C.

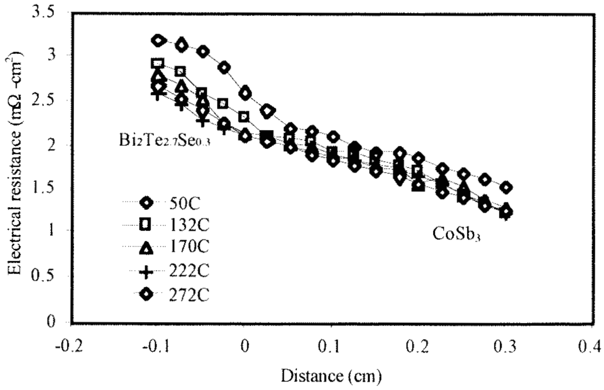

Figure 6. Electrical contact resistance as a function of distance for a n-$CoSb_3$/n-$Bi_2Te_{2.7}Se_{0.3}$ junction using a Pd interface. The origin corresponds to the interface position.

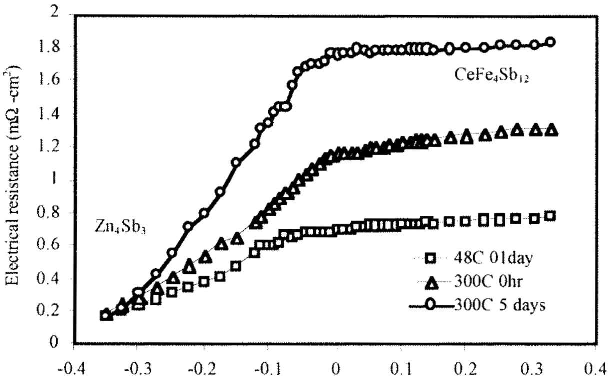

Figure 7. Electrical contact resistance as a function of distance for a p-$CeFe_4Sb_{12}$/p-Zn_4Sb_3 junction using a Pd interface. The origin corresponds to the interface position.

Unicouple Fabrication and Testing

The first step to build a unicouple was to fabricate the n- and p-legs made out of the various thermoelectric materials. This was accomplished by hot-pressing each entire individual leg at once and using fine powder of each material. Pd foils were introduced between the various segments. The hot-pressing was conducted in graphite dies, under Ar atmosphere and a temperature of 500°C. This temperature was found to result in an experimental density of about 95% or greater of the theoretical density for all thermoelectric materials utilized. Separate testing on each individual material also show that no dissociation occurs when the hot-pressing was conducted at 500°C. Examples of the legs fabricated using this technique are shown in Figure 8.

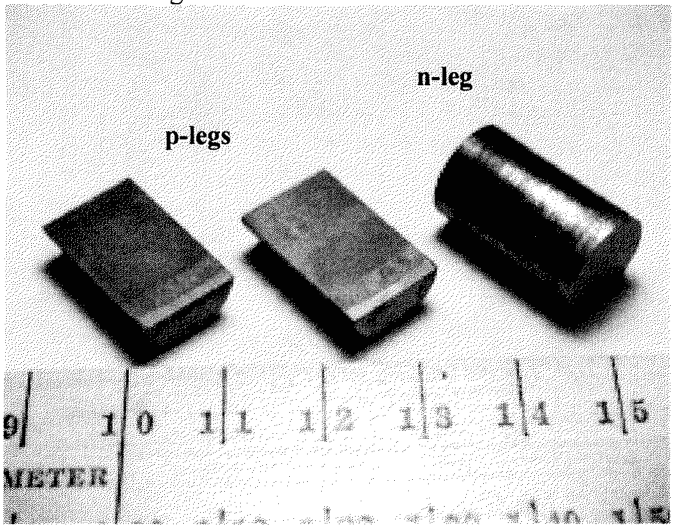

Figure 8. Photograph showing : 1) a p-leg composed of three segments and cut in half ; 2) an entire n-leg composed of two segments.

The second step was to connect the n- and p-legs to a "cold-shoe". We used a copper plated alumna plate as a "cold shoe". The alumina plate was about 1.5 mm thick and plated with a 100 μm thick Cu layer on both sides. A small Cu strip was first etched off on one side in the center of the plate to electrically insulate the legs. Ni was then electroplated on both Cu and the lower segments of the legs, i.e. Bi_2Te_3-based materials. Ni is standard diffusion barrier used to prevent Cu diffusion into Bi_2Te_3-based materials around room temperature. The legs were then soldered to Cu using a Bi-Sn solder.

Finally, a custom made heater was connected to the top surface of the legs using a Cu-Ag brazing alloy. This heater is shown in Figure 9. The heater is made out of Nb and a Ta heating element electrically insulated from the Nb block. Temperatures in excess of 700°C can be achieved with this heater. To test its thermal and electrical efficiency, the unicouple has been instrumented with various thermocouples. Two of them were placed directly under the n- and p-legs to measure the cold side temperature. Two thermocouples were placed on both side of the lower portion of the Nb block. The purpose of these thermocouple is twofold : 1) measure the hot-side temperature ; 2) determine the heat flux going into the legs. Difficulties in accurately determining the efficiency of a thermoelectric unicouple are sometime associated with an exact measurement of the power input. In our design, this issue has been somewhat reduced by brazing the heater directly onto the legs, thus providing a better thermal contact, and also measuring the power input using thermocouples located close to the legs. In addition, a thermal shield made out of Mo is being designed and will be placed around thermocouple during the testing to minimize heat losses due to radiation.

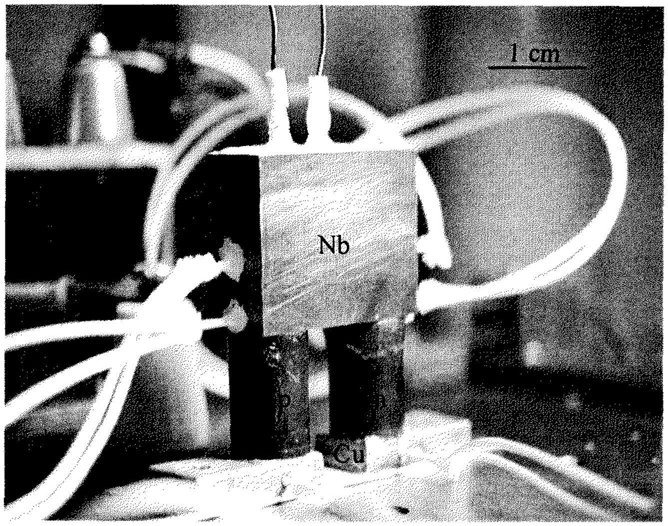

Figure 9. Photograph of a unicouple. The top Nb heater is brazed tot he n- and p- segmented legs. The legs are soldered to the Cu "cold-shoe" using a Bi-Sn solder. See text for fabrication details.

Conclusion

A new segmented thermoelectric unicouple is currently being developed with a predicted efficiency of about 15%. A number of materials were identified for connecting the various segments of the unicouple together. The resulting junctions were found to be of good mechanical stability and to possess low electrical contact resistance. Limited diffusion was also observed which is essential to prevent any degradation of the thermoelectric properties of the various segments. A unicouple has been fabricated and instrumented for thermal and electrical test which are in progress.

Acknowledgments

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