Progress in the Development of High-Efficiency Segmented Thermoelectric Generators

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Abstract. The integration of new more efficient thermoelectric materials developed at the Jet Propulsion Laboratory into a new high-performance segmented thermoelectric generator has been reported earlier. Progress in the development of this new segmented thermoelectric generator is reported in this paper. This generator would operate over a large temperature difference (300-973 K) and uses novel segmented legs based on a combination of state-of-the-art thermoelectric materials and p-type $Zn_{4-x}Cd_xSb_3$ alloys, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys. An increase in the thermoelectric materials conversion efficiency of about 60% is expected compared to Bi_2Te_3- and PbTe-based generators. A computer program was written to optimize the thermal efficiency of the device. The optimal geometry, power output, efficiency and other properties of the generator were calculated and are presented. In addition, results of bonding studies between Zn_4Sb_3 and $Bi_{0.4}Sb_{1.6}Te_3$ are reported and discussed.

INTRODUCTION

To achieve high thermoelectric energy conversion efficiency, it is desirable to operate thermoelectric generator devices over large temperature ranges and also to maximize the thermoelectric performance of the materials used to build the devices. However, no single thermoelectric material is suitable for use over a very wide range of temperatures (~300-1000 K). 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 concepts of integrating new thermoelectric materials developed at the Jet Propulsion Laboratory (JPL) into a segmented thermoelectric generator have been presented in detail in earlier publications (Fleurial et al., 1997a; Fleurial et al., 1997b). This new generator conceptually operates over a large temperature difference (300-973 K) and uses novel segmented legs based on a combination of state-of-the-art thermoelectric materials and p-type $Zn_{4-x}Cd_xSb_3$ alloys, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys. An increase in the thermoelectric materials conversion efficiency of about 60% is expected compared to Bi_2Te_3- and PbTe-based generators. In order to maximize the thermal efficiency of the segmented generator, it is necessary to optimize the geometry of the different segments because of their different thermoelectric properties. A computer program was written to calculate the optimal characteristics for the generator, including geometry of the legs, power output, and efficiency. The model is briefly described in this paper and applied to the new segmented generator. To build such a segmented generator requires ~~to develop~~ techniques and materials to bond the different segments between themselves as well as to interconnects for the top and bottom segments. The bonds should have low electrical contact resistance and possess good mechanical strength and temperature stability. Some results of bonding studies are also presented and discussed in this paper. These high-performance thermoelectric generators could be incorporated in a variety of applications, in particular those making use of waste heat recovery.

OPTIMIZATION OF SEGMENTED GENERATOR

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.

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. 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 (Swanson, 1961). 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. The paper provides an algorithm to rapidly converge to the optimum geometry. 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. For the following calculations, 1 cm total length and 1 cm^2 cross sectional area for the p-leg is assumed. Experimental thermoelectric properties listed in Table 1 were used for the calculation. The n-type bismuth telluride was assumed to have similar properties as the p-type bismuth telluride. The calculated optimized characteristics of the device are listed in Table 2, and the optimal geometry is illustrated in Figure 1.

TABLE 1. Average experimental thermoelectric values and optimized relative length for each segment

Material	Electrical Resistivity (mΩcm)	Seebeck (μV/K)	Thermal Conductivity (mW/cmK)	Relative length
p-Ce filled Skutterudite	0.88	186	29.0	0.740
p-Zn_4Sb_3	2.60	175	6.5	0.126
p-$(Bi/Sb)_2Te_3$	1.02	196	13.8	0.134
n-$CoSb_3$	1.42	-243	39.7	0.854
n-$Bi_2(Te/Se)_3$	1.29	-195	15.6	0.146

TABLE 2. Optimum design parameters for segmented generator

Overall length (mm)	10
Area of p-leg (cross section) (mm^2)	10
Area of n-leg (cross section) (mm^2)	83.8
Device resistance (mΩ)	2.79
Load resistance (mΩ)	4.31
Current (A)	39.1
Power (W)	6.58
Efficiency (%)	15.06

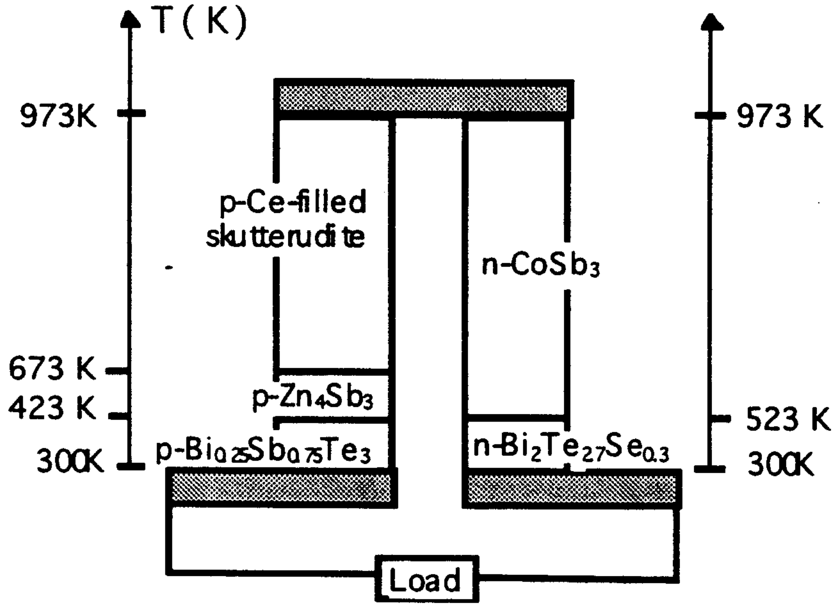

FIGURE 1. Optimized segmented generator having 15% efficiency with the relative lengths of each segment drawn to scale.

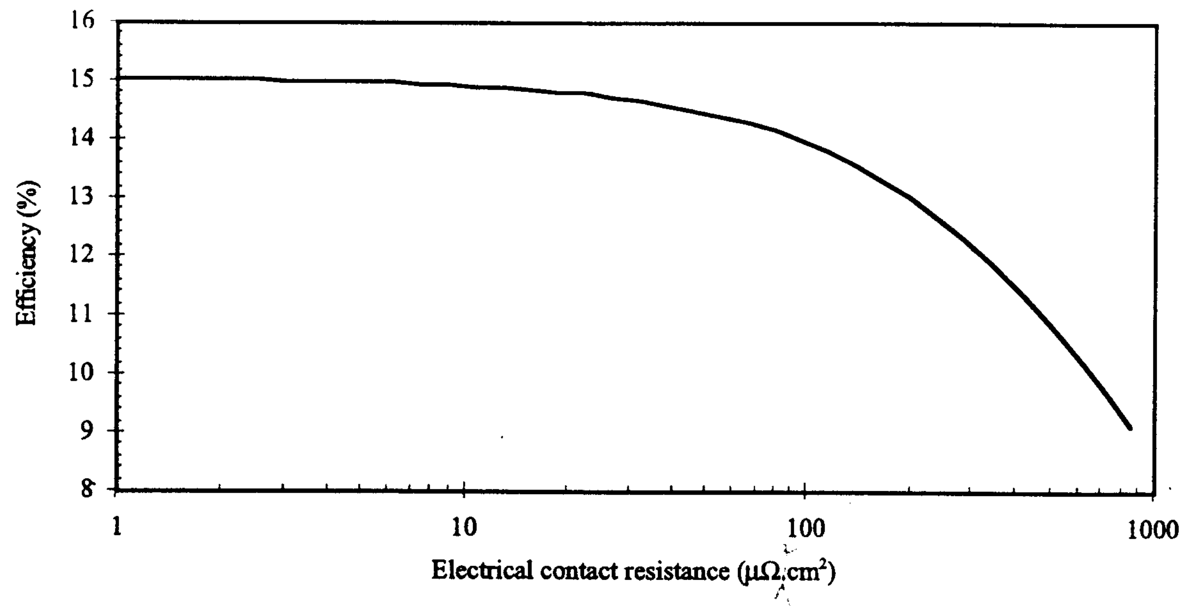

FIGURE 2. Power conversion efficiency as a function of the contact resistance between segments in the segmented generator.

High contact resistance between the thermoelectric segments can dramatically reduce the efficiency of a generator. In the following calculations, the same contact resistance was used for each of the three junctions between thermoelectric segments. In this calculation, a larger overall length will decrease the effect of contact resistivity. A length of 1 cm was used since the exact length for the prototype generator has not yet been determined. As shown by the calculation (Figure 2), low contact resistivity, less than about 20μΩcm², 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

In a segmented generator, the various segments are bonded together. In order to maximize the efficiency of the device, the bonds must have electrical contact resistance lower than 20 μΩcm². 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. Several attempts were made to bond the two lower segments of the p-leg: Zn_4Sb_3 and $Bi_{0.4}Sb_{1.6}Te_3$. All tests were conducted by hot-pressing fine powder of each material with or without a thin metal interface layer (~100 μm) in form of a foil. The pressing was conducted in a graphite die with graphite punches, in Ar, and at a temperature of 623K. 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 microprobe analysis. In addition, the electrical contact resistance was measured by a four-probe technique. One voltage probe is located at one end of the sample while the second probe can move along the sample. The variation of the electrical contact resistance is therefore recorded as a function of the distance of the moving probe to the fixed probe.

A first attempt to directly bond the Zn_4Sb_3 and $Bi_{0.4}Sb_{1.6}Te_3$ materials showed that no chemical reaction occurred between the two and the samples were not bonded. Ni, Ta, Pd, and $Pd_{70}Ag_{30}$ foils were then tried as contacting layers. In the case of Ni, the sample had almost no electrical contact resistance at room temperature but a crack developed in the center of the joint when heated up to 423K for a few hours. In addition, microprobe analysis showed a significant diffusion across the junction from both materials. The electrical contact resistance across the junction of the sample with Ta was found to be about 200 μΩcm². A small crack was revealed by investigating the microstructure of the junction. No interdiffusion was however found between the two thermoelectric materials after 7 days at 423K which suggests that Ta is a good diffusion barrier.

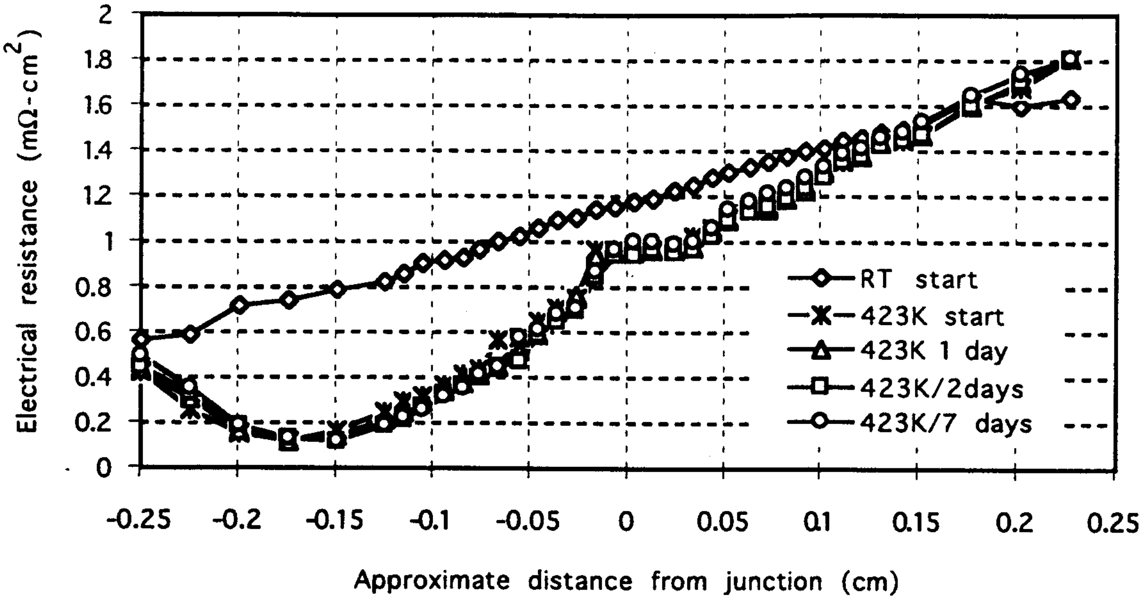

FIGURE 3. Electrical resistance as a function of the distance for a Zn_4Sb_3/Pd/$Bi_{0.4}Sb_{1.6}Te_3$ sample.

Figure 3 shows the electrical contact resistance of the two samples bonded with a Pd foil in between them. At room temperature no electrical contact resistance is observed, but when the sample was heated up to 423K, a crack developed in the joint, as seen in Figure 3. The contact resistance is about 200 $\mu\Omega cm^2$. Microprobe analysis showed that no interdiffusion occurred between the two thermoelectric materials. Figure 4 shows the electrical contact resistance of the two samples bonded with a $Pd_{70}Ag_{30}$ interface.

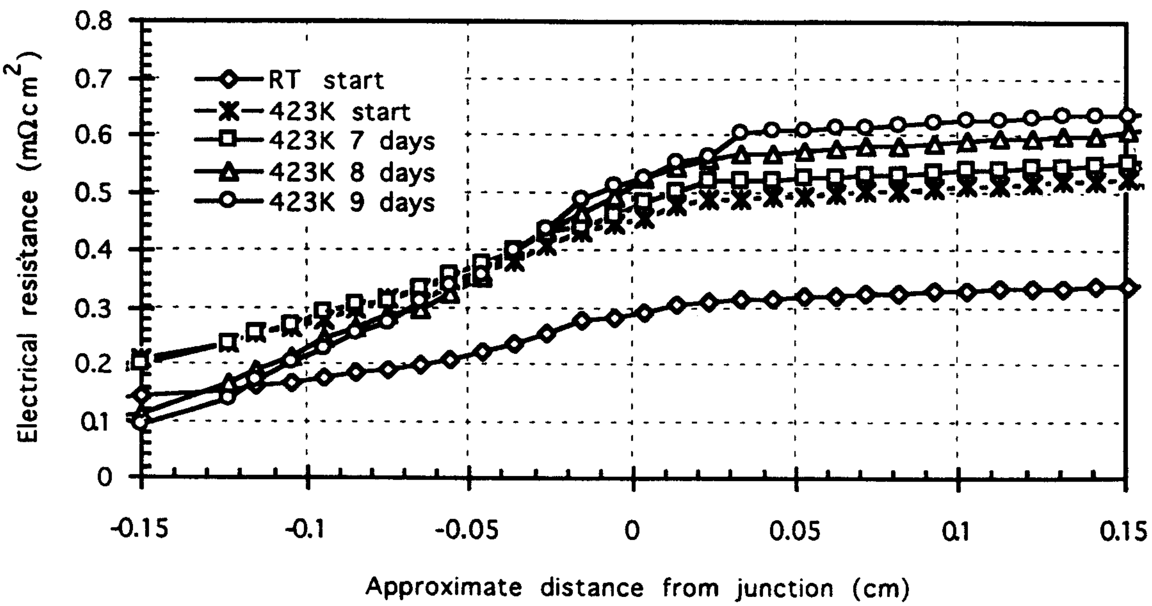

FIGURE 4. Electrical contact resistance as a function of the distance for a Zn_4Sb_3/ $Pd_{70}Ag_{30}$/$Bi_{0.4}Sb_{1.6}Te_3$ sample.

There is no contact resistance between the two samples at room temperature after hot-pressing. Even after 9 days at 423K, the measurements show that there is no contact resistance. Microprobe analysis showed that no diffusion across the junction could be detected after the 9 day anneal. The $Pd_{70}Ag_{30}$ alloy seems therefore to be a promising candidate to bond these two materials. Further testing as a function of time is however needed to determine the quality of the bond over extended period of times. When selecting a material to be used as a contacting layer for two samples to be bonded together, it is important to select a material with a coefficient of thermal expansion (CTE) close to those of the materials to be bonded. The $Pd_{70}Ag_{30}$ alloy has a CTE of 15, while the CTE is 16 and 19 for $Bi_{0.4}Sb_{1.6}Te_3$ and Zn_4Sb_3, respectively. The CTE for Ni, Ta, and Pd is 13.3, 6.5, 11.6, respectively. The $Pd_{70}Ag_{30}$ alloy has the closest CTE to the materials to bond and the best results were obtained with this material.

CONCLUSION

New highly efficient segmented thermoelectric generators using advanced thermoelectric materials are currently being developed. A computer program was written to calculate the optimum characteristics of the device to maximize its thermal efficiency. In the version presented in this paper, the efficiency would be of about 15%. Bonding studies have also been conducted to find a contacting material to bond the Zn_4Sb_3 and $Bi_{0.4}Sb_{1.6}Te_3$ materials. $Pd_{70}Ag_{30}$ alloy was identified as a promising material based on the low contact resistance bond obtained as well as the absence of any diffusion across the junction at a temperature of 423K. Further experiments are in progress to identify suitable materials to bond the other segments of the legs. These high-performance thermoelectric generators could be incorporated in a variety of applications, in particular those making use of waste heat recovery.

ACKNOWLEDGMENTS

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REFERENCES

Fleurial, J.-P., Borshchevsky, A., and Caillat, T. (1997a) "New Thermoelectric Materials and Devices for Terrestrial Power Generators," in *Proceedings of the 1st Conference on Synergistic Power and Propulsion Systems Technology*, M. S. El-Genk editor, American Institute of Physics, New York, AIP Conf. Proc. No. 387, 1, p.p.293-298.

Fleurial, J.-P., Borshchevsky, A., Caillat, T., and Ewell, R. (1997b) "New Materials and Devices for Thermoelectric Applications," in *Proceedings of the 32nd Intersociety Energy conversion Engineering Conference*, American Institute of Chemical Engineers, New York, 2, p.p.1080-1085.

Swanson, B.W., Somers, E.V., and Heike, R.R. "Optimization of a Sandwiched Thermoelectric Device," Journal of Heat Transfer, p.p.77-82 (1961).