DEVELOPMENT OF HIGH EFFICIENCY THERMOELECTRIC GENERATORS USING ADVANCED THERMOELECTRIC MATERIALS

Thierry Caillat, Jean-Pierre Fleurial and Alex Borshchevsky
Jet Propulsion Laboratory/California Institute of Technology
Pasadena, CA 91109
(818) 354-0407

Abstract

Despite their relatively low efficiency, thermoelectric generators are used in a limited number of industrial applications where they are preferred to other energy conversion devices because of their high reliability, low maintenance and long life, in particular when considering harsh environments. New more efficient thermoelectric materials and devices are needed to expand the range of application of thermoelectric generators. Several new terrestrial applications requiring higher efficiency generators have been recently described in the literature. Heat sources for these applications range from low grade waste heat at 325-350K up to 850 to 1100K for heat recovery from processing plants of combustible solid waste. Commercial thermoelectric generators are usually built using Bi_2Te_3- or PbTe-based alloys depending on the maximum hot side temperature. A new approach consisting of using new high performance thermoelectric materials developed at the Jet Propulsion Laboratory (JPL) and operating the generator over a larger temperature difference is presented. By using 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. The maximum thermoelectric materials efficiency will be about 20?’0 for the optimum generator configuration. Various issues related to the fabrication of new segmented legs, including bonding and temperature stability tests, will be briefly discussed.

INTRODUCTION

The growing interest for thermoelectric power generation is mostly due to emerging energy saving and environmental issues. A number of new potential applications have been cited in the literature ranging from recovering waste heat from various industrial heat-generating processes to waste heat generated by vehicle exhaust to replace or supplement the alternator and thus decrease fuel consumption (Morelli 1997). For some of these applications, the efficiency as wett as the cost of the thermoelectric generators are critical. To achieve high 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 temperature (-3 OO-1OOOK). 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 rue formed of different segments joined in series. A number of studies on segmented thermoelectric generators using state-of-the-art thermoelectric materials have recently appeared in the literature (Schilz et al., 1997). The materials under investigation are mostly Bi_2Te_3-based materials, $FeSi_2$ and PbTe-based alloys. We have recently proposed a new version of a segmented thermoelectric generator utilizing advanced thermoelectric materials with superior thermoelectric figures of merit (Fleurial et al., 1997a; Fleurial et al., 1997b). The benefits of using these new materials are reviewed in this paper as well as the issues involved for the construction of this generator. Preliminary results for optimizing the geometry of the thermoelectric materials and the efficiency of the generator are also presented.

NEW SEGMENTED GENERATOR

The concepts of integrating new thermoelectric materials developed at the Jet Propulsion Laboratory (JPL) into segmented thermoelectric generators have been presented in details in earlier publications (Fleurial et al., 1997a, Fleurial et al., 1997b). The schematic of the first generation of the advanced generator is presented in Fig 1. The benefits of using these advanced thermoelectric materials are twofold: 1) the generator can be operated over a larger temperature drop compared to those using only state-o f-the-art Bi_2Te_3 and PbTe-based alloys (300-845 K versus 300-975K) 2) the average thermoelectric figure of merit, ZT, is larger. As a result, the calculated thermoelectric efficiency is higher for these generators and is 15.9% for the version depicted *in* Figure 1. It could be as high as 19.2% for the version utilizing a second generation of improved thermoelectric materials currently being developed at JPL (Fleurial et al., 1997a). This represents a significant increase in efficiency when compared to Bi_2Te_3 and PbTe-based segmented generators with an efficiency of about 12 % when *operating* between 300 and 845K.

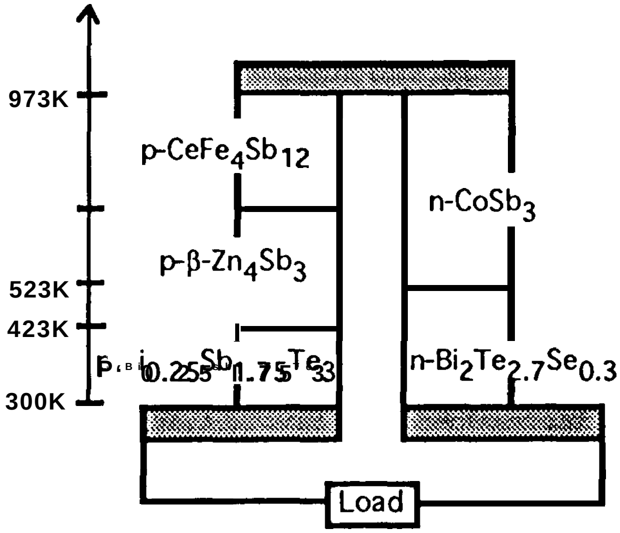

FIGURE 1. schematic of a segmented thermoelectric generator using improved thermoelectric material developed at JPL.

JPL is currently pursuing the development of the segmented generator shown in Figure 1. Ideally, the materials used in the different segments of the p- and -n legs should have similar thermophysical and mechanical properties to *ensure* reliable operation over a large temperature difference. In particular, they should have similar thermal conductivity and thermal expansion coefficient values. We have measured some of these properties and found that there is a reasonably good match between the properties of the different materials (Fleurial et al., 1997a). One additional requirement for the materials used in the different segments is their temperature stability. We are currently investigating the temperature stability of the thermoelectric materials used in the first version of the generator (see Figure 1). Experiments have been designed where samples are subjected to anneals over long period of time in various atmospheres and their thermoelectric properties and other physical and chemical properties such as weight and composition are monitored. In addition, the behavior of each material will be tested when subjected to a temperature gradient. The p- and n-legs are built by joining the different segments and all joints should have low electrical contact resistance as well as a good temperate stability. Joining the different segments can be achieved by directly bonding the different materials or using contacting layers which can be used to correct for any thermal expansion mismatch for example. A number of these tests are currently in progress.

OPTIMAL SEGMENT LENGTHS

A schematic segmented thermoelectric generator is shown in Figure 2 and is composed of *m p-type* and o n-type materials. The hot and cold junction are denoted by T_H and Tc, respectively. The optimization of the efficiency of this type of generator has been previously studied (Swanson et al., 1961). The thermal efficiency is defined as the quotient of the electrical power output *(P)* to the heat rate supplied at the hot junction. The optimization of the geometry of the legs involves primarily fine tuning the cross-section and length of the different segments. Given the average thermoelectric properties (Seebeck coefficient, electrical resistivity, and thermal conductivity) over the temperature range of operation for each segment of the n- and p-legs, one can calculate their optimum cross section, length as well as the optimum current and efficiency (Swanson et al., 1961). The lengths of the segments can be calculated using the following equations:

$$\frac{\lambda_{p_i}\Delta T_{p_i}}{l_{p_i}} = \frac{\lambda_{p_{i+1}}\Delta T_{p_{i+1}}}{l_{p_{i+1}}} \qquad (1)$$

$$\frac{\lambda_{n_i}\Delta T'_{p_i}}{l_{n_i}} = \frac{\lambda_{n_{i+1}}\Delta T'_{n_{i+1}}}{l_{n_{i+1}}} \qquad (2)$$

$$L = \sum_{i=1}^{m} l_{p_i} = \sum_{j=1}^{o} l_{n_j} \quad , \qquad (3)$$

where λ is the thermal conductivity, 1 is the length of each segment, AT is the temperature drop across each segment, and L is the total length of the legs.

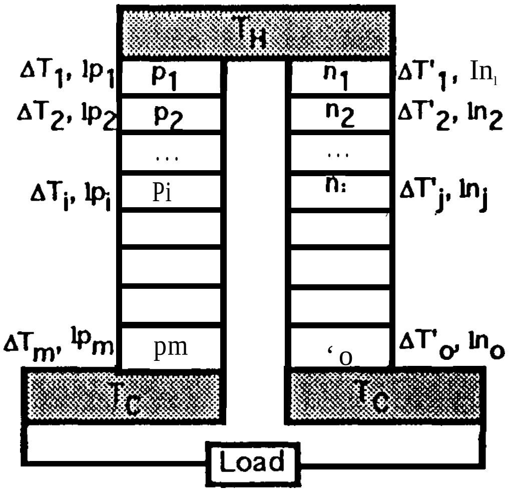

FIGURE 2. *Schematic* of a segmented thermoelectric generator

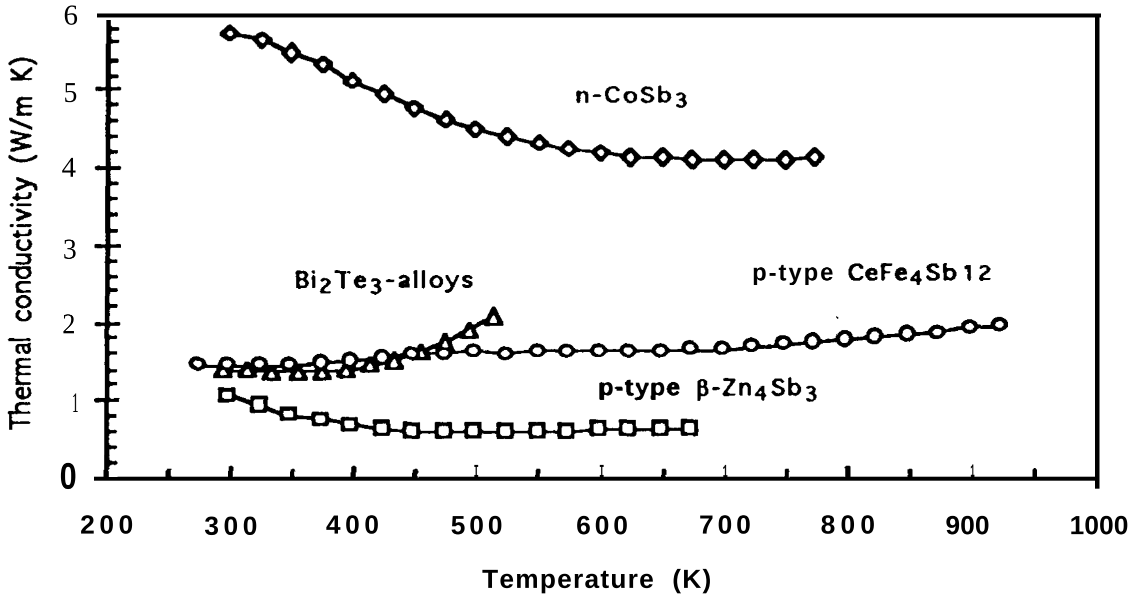

FIGURE 3. Thermal conductivity versus temperature for several state-of-the-art and advanced thermoelectric materials. N- and p-type Bi_2Te_3 based alloys have similar thermal conductivity and only the values for p-type rue shown for clarity.

Equations 1,2, and 3 were used to calculate the segment lengths in the case of the segmented generator depicted in Figure 1. For the calculations, we have used the average thermal conductivity reported in Figure 3 and a value of 10 cm for L. The results are shown in Figure 4. Because of the thermal conductivity values of n-type $CoSb_3$ is larger than those for the other materials used, the n-type $CoSb_3$-is quite long. Further estimations are in progress to calculate the optimal cress section of each leg, current and efficiency.

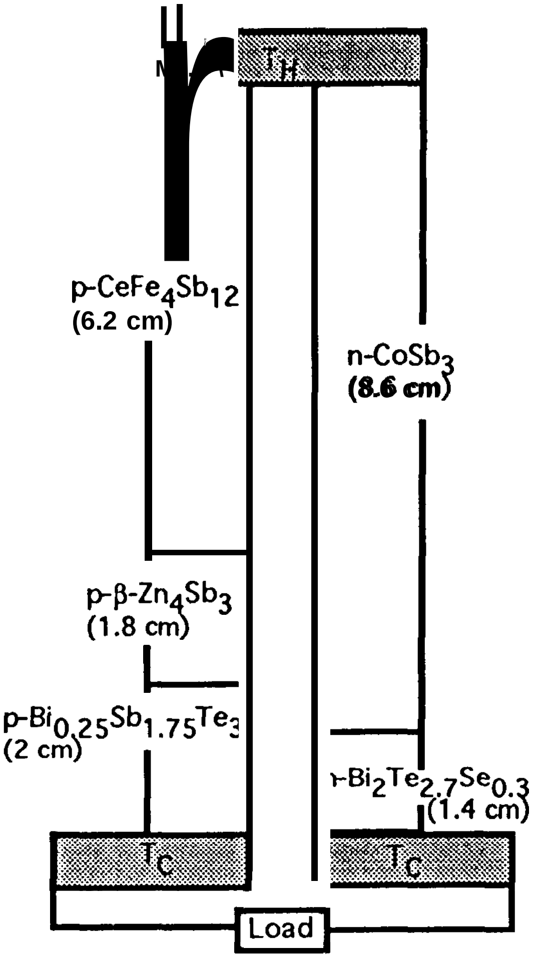

FIGURE 4. Schematic of an advanced thermoelectric generator operating between 300 and 975K illustrating the optimal segment length for each material use for the n-and p-legs.

Improved thermoelectric generators could be used in a variety of applications. Thermoelectric generators operating on natural gas, propane or diesel were built and used Bi_2Te_3 or PbTe alloys depending on the maximum hot side temperature (up to 873K) (Naughton, 1995). Despite their relatively low efficiency, these devices are used in various industrial applications because of their high reliability, low maintenance and long life, in particular when considering harsh environments. The most common applications are for cathodic protection, data acquisition and telecommunications. More recently, there has been a growing interest for waste heat recovery power generation using various heat sources such as the combustion of solid waste, geothermal energy, power plants, and *other* industrial heat-generating processes. There is currently an important effort in Japan to develop large scale waste heat recovery thermoelectric generators using state-of-the-art materials (Kajikawa et al., 1994). But perhaps the automobile industry is the market with the most potential (Morelli 1997). Because of the need for cleaner, more efficient cars, car manufacture worldwide are interested in using the waste heat generated by the vehicle exhaust to replace or supplement the alternator. According to some car manufacturers, the available temperature range would be from 350 to 800K, which would be match by the new segmented generators.

CONCLUSION

New highly efficient segmented thermoelectric generators using advanced thermoelectric materials are currently being developed In the optimal version, the thermoelectric efficiency is about 20 % for a generator operating between 300 and 975K. Various issues to be resolved to build these generators including joining of the different segments, studies of the temperature stability of the thermoelectric materials, and optimal geometry were presented and are currently being investigated. These high performance thermoelectric generators could be incorporated in a variety of applications, in particular those making use of waste heat recovery.

Acknowledgments

This work was carried out at the Jet Propulsion Laboratory/California Institute of Technology, under contract with the National Aeronautics and Space Administration.

References

Fleurial, J. -P., A. Borshchevsky, and T. Caillat (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, 1:293-298.

Fleurial, J. -P., A. Borshchevsky, T. Caillat, and R. Ewell (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, 2:1080-1085.

Kajikawa, T., M. Ito, E. Shibuya, and N. Hirayama (1994) "Conceptual Design of Thermoelectric Power Generation System Utilizing heat of Combustible Sotid Waste", in ***Proceedings of the 12th International Conference on Thermoelectrics,*** ed. K. Matsuura, Institute of Electrical Engineers of Japan, 1:491.

Morelli, D. (1997) "Advanced Thermoelectric Materials and Systems for Automotive Applications in the Next Millennium", in ***Proceedings of Materials Research Society,*** T. Tritt, M. G. Kanatzidis, H. B. Lyon, Jr., and G. D. Mahan, eds, Symposium Proceedings Vol. 478, 297-307.

Naughton, A. G. (1995) "Commercially Available Generators,", in ***CRC Handbook of Thermoelectrics,*** ed. M. Rowe, CRC Press, 459.

Schilz, J., L. Helmers, Y.S. Yang, Y. Noda, and M. Niino (1997) "Bismuth-Telluride/Iron-Disilicide Segmented Thermoelectric Elements: Patterning, Preparation and Properties", to be published ***in Proceedings of the XVI International Conference on Thermoelectrics,*** held August 26-29, 1997 in Dresden, Germany.

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