Development of thermoelectric generating cascade modules using silicide and Bi-Te

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Abstract

Bi-Te and siliside modules as well as BiTe/Silicide cascade-type module were successfully fabricated and characterized. Bi-Te modules using specially developed materials achieved a conversion efficiency η of more than 7.5% at $T_h = 280$ °C and $T_c = 30$ °C . Silicide modules consist of p-$MnSi_{1.73}$ and n-Mg_2Si, both were prepared using Spark Plasma Sintering technique. η of more than 6.5% at T_h = 550 ℃ with T_c = 30 ℃ has been obtained repeatedly.

In a first approach to realize a cascade-type module, the two modules were satcked while the thermal and electrical design was carefully optimized to adjust the interface temperature T_m between the two modules at 280 °C . It was found that η of more than 10% can be successfully achieved by this approach at the Research Division of Komatsu.

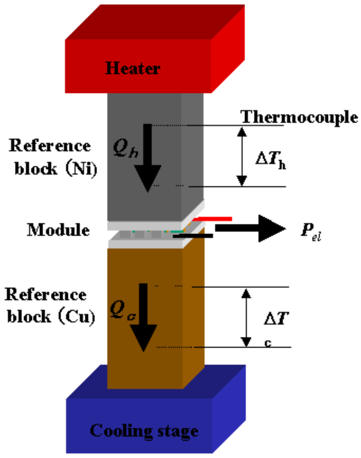

Figure 2: Conventional Generating Testing Fascility for thermoelectric generating module.

1 Introduction

A joint effort of several Japanese research groups supported by NEDO[1] to further develope thermoelectric generators in the medium temperature range up to 580 °C is aiming to achieve more than 12 % conversion efficiency η until March 2005 and the feasibility of η up to 15% shall be evaluated by March 2007 [1].

To reach this aim, the cascade-type modules using Bi-Te and silicide semiconductors as illustrated in Fig. 1 are developed . Research and investigation on materials and module designing as well as characterization technique are being carried out at the Research Devision of Komatsu Ltd.

The project emphasizes to realize actual generator modules. Broad investigations on the durability and endurance of the modules regarding thermal stability and thermally induced stress are included. This project is considered to have great impact on the industrial application and commercial availability of thermoelectric modules.

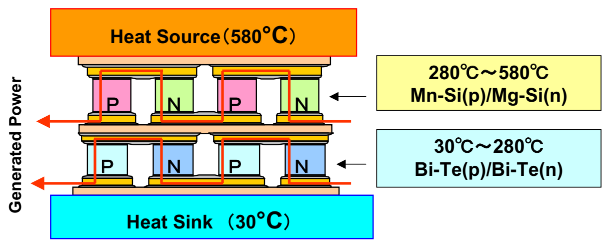

Figure 1: The concept of cascade-type module using Bi-Te and silicide modules.

Bi-Te alloys are well-known thermoelectric materials, especially for cooling modules. As generator materials, Bi-Te still owns the reliable and superior performance with Z-value of 3.0 $\times 10^{-3}$ K^{-1} in the room temoerature region regardless among recent novel materilas such as Skuterdites and Clathlate. Furhtermore, Research Division at Komatsu and its subsidiary named Komatsu Electronics (KELK), which has already involved in the thermoelectric industry for longer than 40 years, possess good knowledge and know-how concering Bi-Te module fabrication as well as materials production.

For silicide semiconductors such as Fe-Si, Cr-Si, Mn-Si and Mg-Si, the environmental advantages seemed to be the deciding factor rather than the thermoelectric performance [2][3]. However, after the publications [4][5][6] a hope to use p-type $MnSi_{1.73}$ and n-type Mg_2Si as potential generator materials became a real one. This is why both of them were used for this project.

Cascading or stacking is the conventional method to expand the temperature region and to improve the performance for thermoelectric modules. Though segmenting also has similar possibility, the cascading has priority against segmenting in terms of joinning and current matching.

So far, Komatsu is going to employ soldering to form the bridge electrode for Bi-Te module, whereas the silicide module will be constructed with metallic electrode by the thermal spray technique. The cascade-type module is finally stacked with Bi-Te and silicide modules with putting the insulating AlN plate

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in-between.

The reliable efficiency charaterization of the module has a great importance in particular regarding the ambitious aims of the NEDO project. As an independent institute AIST in Tukuba, Japan is working to standarize the module characterization technique. Their principle of the module characterization is of to measure the input thermal energy and output power as shown in Fig.2. The conversion efficiency η can be defined as (1)

$$\eta = \frac{P_{el}}{Q_h} = \frac{P_{el}}{Q_c + P_{el}} \quad (1)$$

where P_{el} is output power and Q_h and Q_c are heat flow on hot side and cold side, respectively.

Regarding the great difficulties with radiation heat losses that this method is prone to, the heat flow measurement on the cold side is considered as more reliable. However, the agreement between η deduced from the second (hot side) and third term (cold side) of eq.(1) tends to be very good and therefore use $\frac{P_{el}}{Q_c+P_{el}}$ in this paper.

Komatsu additionally set up a characterization equipment, which employs an absolute method with a shielded heater structure as shown in Fig.3. It enables to characterize the module efficiency without comparison to a reference. Further details can be found at [7].

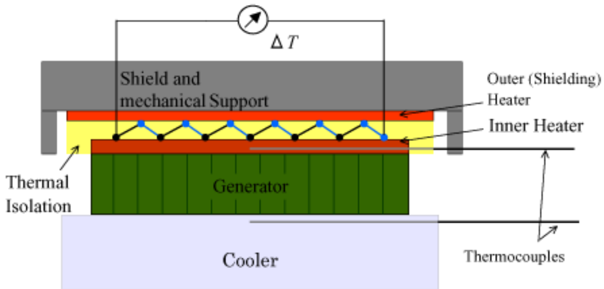

Figure 3: Generation Testing Fascility using the double heater structure [7].

2 Bi-Te modules

2.1 Bi-Te materials

For generating purpose the Bi-Te materials has to be optimised to have better performance in the higher temperature range compared with cooling application. A higher carrier concentration and a wider energy gap are the two major requirements. Tuning of doping species and their amount and adjustment of composition have been done based on the knowledge and experience for the cooling materials [8]. The materials are prepared by the modified sintering technique [9].

2.2 Module fabrication and characterization

The p- and n-type ingots obtained as mentioned above were sliced into the thick plates. They were plated by Ni layer with a few micrometers thickness and subsequently diced into blocks with several milimeters cube. Using the high temperature solder the Ni-plated Cu electrodes were connected and typically 7 or 8-pairs of p-n elements were aligned as shown in Fig.4. The top and bottom sides of the module were carefully leveled by polishing and finally the lead wires were connected using PbSn solder.

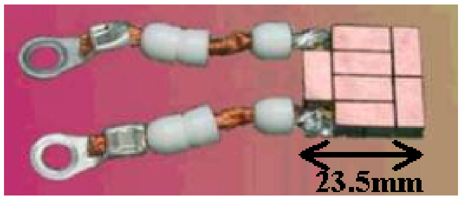

Figure 4: The typical Bi-Te module consisting of 7 p-n pairs.

The module characterization was performed using the equipment as shown in Fig. 2. Fig. 5 is conversion efficiency η as a function of hot side temperature T_h. More than 7.5% of η could be achieved at $T_h = 280$ and $T_c = 30$ °C . The module performance was also investigated by the equipment shown in Fig. 3. η-values from the two equipments were in excellent agreement within a few percent [7].

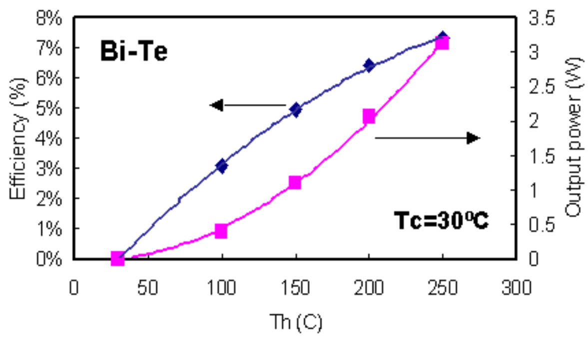

Figure 5: Generating performance of the Bi-Te module.

3 Silicide module

3.1 p-type Mn-Si

The weighed amount of $MnSi_{1.73}$ with proper amount of dopant materials such as Mo, Al and Ge were melted in a induction furnace [10][11]. Subsequently, the obtained ingot was crushed and pulverized into fine powder withparticle size ofless than 38 μm. The sintered compact was prepared by means of Spark Plasma Sintering (SPS).

3.2 n-type Mg-Si

The initial ingot of $Mg_2Si_{0.4}Sn_{0.6}$ doped with certain amount of Sb was obtained in the same way like for Mn-Si [12] and the sintered specimens were prepared using SPS technique as well. Subsequently, an annealing step was carried out in order to obtain $Mg_2Si_{0.4}Sn_{0.6}$ target compound homogeneously.

3.3 Module fabrication and characterization

There are 3 major strategies of module fabrication. Namely, these are 1) soldering (or brazing), 2) thermal spray and 3) mechanical contacting. Bi-Te generating modules by ALTEC in Uklane belongs to Category 1) [13]. Hi-Z provides Bi-Te modules in category 2) [14]. The NASAs' space crafts such as Cassini and Voyger use category 3) modules [15]. Generally speaking, Category 1) has good performance and poor endurance and category 3) is the other way around. Category 2) is a compromise between them. Then, thermal spray technique was employed to form the metallic electrodes such as Al and Cu. A masking ceramic plate is put at each end of the module which has two functions: firstly is to fix the position of each leg during thermal spray process and secondly to reinforce the mechanical stability of the module. Typically, the module has size of 23.5 $\times$ 23.5 mm and several milimeters in length and consisits of 7 pairs of p-n junctions as shown in Fig. 6.

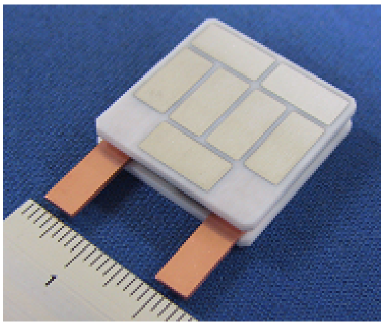

Figure 6: Typical silicide module consisiting 7 pairs of Mg-Si/Mn-Si.

Fig. 7 shows the efficiency η as a function of T_h. At the same time η-values expected from materials properties are also plotted. Actually η of 6.4% at T_h = 550 °C and T_c = 30 °C was obtained, whereas 7.5 % is expected. Insufficient contact performance both thermally and electrically is main reason for this discrepancy.

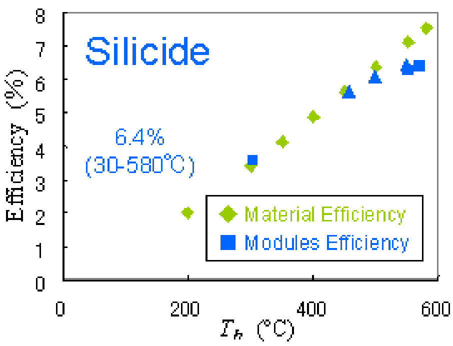

Figure 7: $\eta - T_h$ plot for the silicide module.

4 Cascade-type module

The cascade-type module was constructed by stacking Bi-Te and silicide modules with putting an AlN plate in-between for electrical isolation as shown in Fig. 8.

The output power from each module was measured separately and the load resistance was varied independently for each module as illustrated in Fig. 9. The heat flux was calculated from temperature drop in the reference block made from Cu or Ni positioned in a thermal series connection with the module. η for cascade-type deduced by (2) was employed.

$$\eta = \frac{P_h + P_c}{Q_c + P_h + P_c} \quad (2)$$

Figure 8: A cascade-type module consisting of Bi-Te and silicide module.

where P_h and P_c are output power from silicide and Bi-Te module, respectively and Q_c is heat flow on cold side.

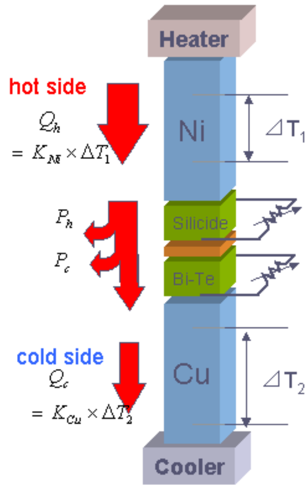

Figure 9: The characterization set-up for cascade-type module.

Fig. 10 shows the initial result of the cascade-type module as a function of hot side temperature T_h. Better than 10% of η could be achieved actually under the T_h =550 °C and T_c =30 °C . η is several percent lower than the expected, indicating that still electrical and thermal interface resistance especially for the silicide module significantly degrade the potential performance. However, the developement of the fabrication technique as well as materials improvement can surely contribute to progress of the module performance resulting that 12% or even 15% of η might be reachable.

Fig. 11 is η as function of the electrical current I_h and I_c flowing through silicide and Bi-Te module respectively at T_H = 550 °C and T_c = 30 °C . The current for each module depend on the connected electrical load resistance. At maximum value of η, totally output power and heatflow were $P_h + P_c$ = 6.0W and Q_c = 54W , respectively

5 Thermal stress in module

Terrestrial apllication needs heat cycling, which brings the repeated thermal stress and resulting material fatigue becomes a severe problems. Fig. 12 displays the distribution of thermal stress σ_Z and magnified deformation for the 7-pairs Bi-Te module with Cu electrodes. It was deduced by the FEM analysis under the condition of T_h=280 °C and T_c=30 °C . It is obvious that the tensile stress localize at the interface of hot side electorde and Bi-Te materials, which might be the major origin of the fatigue damage. For instance, Cu-based composite

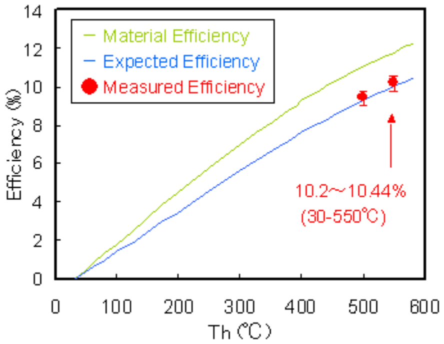

Figure 10: $\eta - T_h$ plot for cascade-type module.

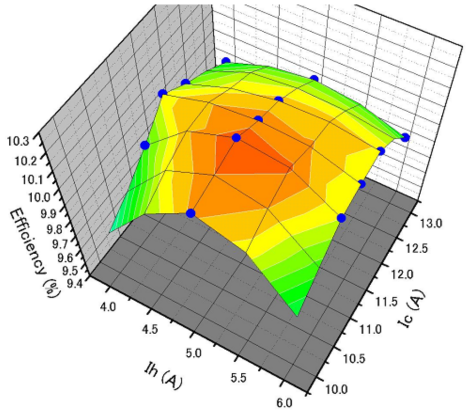

Figure 11: $\eta - I_h - I_c$ plot for cascade-type module at T_h = 550 °C .

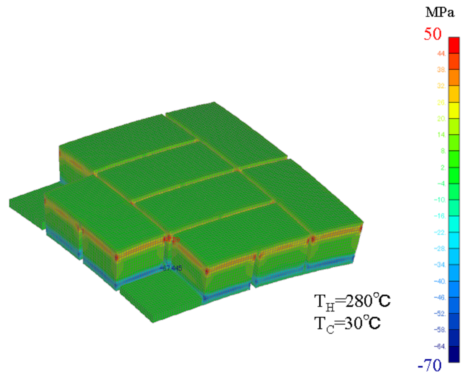

Figure 12: Thermal stress σ_Z for Bi-Te module during operation.

dispersed with cupper oxicide will be very useful to release the thermal stress.

6 Conclusion

1. Better than 7.5% of η can be achieved for Bi-Te module at T_h =280 °C and T_c =30 °C .
2. 6.5% of η can be achieved for silicide module at T_h =550 °C and T_c =30 °C .
3. Totally more than 10% of η can be successfully achieved for cascade module at T_h =550 °C and T_c =30 °C .

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